Identification and Reduction of Errors in Thermoluminescent Dosimetry Systems

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A thesis submitted to the Department of Physics, University of Surrey, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

September, 1975.
Sources of error in a thermoluminescent dosimetry (TLD) system based on LiF/PTFE dosemeters are identified, and means described for reducing them by appropriate design of instrumentation and dosemeters, and suitable calibration and other operational techniques. A theory of thermoluminescent dose measurement has been developed, with special reference to the use of semi-transparent dosemeters for the measurement of penetrating and non-penetrating radiations. Studies of the thermoluminescence of lithium fluoride prepared with various activators are described, and the thermoluminescence mechanism in LiF:Mg,Ti is discussed. The major component in the system is a new readout instrument which has been designed to accept a wide variety of dosemeter configurations, and which employs several novel techniques to minimise errors during the readout of dosemeters. The light measurement system utilises variable negative feedback both to set the sensitivity to a desired level and to automatically maintain that level against system drifts. A heating cycle control system has been developed which employs a unique thermocouple cold junction compensation circuit to ensure reproducible readout cycle temperature. Different dosemeter forms, criteria for comparing them, and the particular characteristics of phosphor/PTFE dosemeters are described. Sources of sensitivity and background variations in LiF/PTFE dosemeters have been investigated, enabling the design of the dosemeters and operational techniques for precise measurements with them at both radiological protection and radiotherapy dose levels to be optimised. The dependence of the sensitivity of LiF/PTFE discs on thickness and optical transmission is explained in terms of the theory previously developed for semi-transparent dosemeters. An 80°C pre-irradiation anneal has been shown to be essential for precise measurements with LiF/PTFE dosemeters, due to the characteristics of the glow curve structure of the fine LiF powder used in their manufacture. The limiting factor in low dose measurements with LiF/PTFE discs is a background signal believed to be due to oxygen adsorbed too deeply in the PTFE surface to be removed by nitrogen flow. A number of recommendations for future work are given.

Summary

Sources of error in a thermoluminescent dosimetry (TLD) system based on LiF/PTFE dosemeters are identified, and means described for reducing them by appropriate design of instrumentation and dosemeters, and suitable calibration and other operational techniques. A theory of thermoluminescent dose measurement has been developed, with special reference to the use of semi-transparent dosemeters for the measurement of penetrating and non-penetrating radiations. Studies of the thermoluminescence of lithium fluoride prepared with various activators are described, and the thermoluminescence mechanism in LiF:Mg,Ti is discussed. The major component in the system is a new readout instrument which has been designed to accept a wide variety of dosemeter configurations, and which employs several novel techniques to minimise errors during the readout of dosemeters. The light measurement system utilises variable negative feedback both to set the sensitivity to a desired level and to automatically maintain that level against system drifts. A heating cycle control system has been developed which employs a unique thermocouple cold junction compensation circuit to ensure reproducible readout cycle temperature. Different dosemeter forms, criteria for comparing them, and the particular characteristics of phosphor/PTFE dosemeters are described. Sources of sensitivity and background variations in LiF/PTFE dosemeters have been investigated, enabling the design of the dosemeters and operational techniques for precise measurements with them at both radiological protection and radiotherapy dose levels to be optimised. The dependence of the sensitivity of LiF/PTFE discs on thickness and optical transmission is explained in terms of the theory previously developed for semi-transparent dosemeters. An 80°C pre-irradiation anneal has been shown to be essential for precise measurements with LiF/PTFE dosemeters, due to the characteristics of the glow curve structure of the fine LiF powder used in their manufacture. The limiting factor in low dose measurements with LiF/PTFE discs is a background signal believed to be due to oxygen adsorbed too deeply in the PTFE surface to be removed by nitrogen flow. A number of recommendations for future work are given.
Acknowledgments

I wish to thank Mr. D. A. Pitman, whose financial support made this research possible; Dr. W. B. Gilboy, for advice, discussions, and suggestions throughout the course of this research, and for reading and commenting on the draft manuscript; Messrs. R. M. Sheppard, J. A. P. Brabants, M. E. Davies, J. R. Marshall, and J. Pettifer, for much of the electronic design of the Toledo reader, and construction of the electronics on the prototype; Messrs. J. C. Stewart, R. J. Doyle, and D. Benham, for experimental assistance and much of the design and construction of the dosimeter irradiators and other accessories; Mrs. J. Howard, for her excellent typing of both the draft and the final manuscript; and finally my wife, Hilary, for assistance with the references and for encouragement, understanding, and moral support.
I dedicate this work to my sons, Cameron and Alexei.
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CHAPTER 1. SELECTION OF RESEARCH PROGRAMME

This thesis reports the results of a collaborative venture between the Department of Physics, University of Surrey, and D. A. Pitman Ltd., Weybridge, Surrey. A major part of the product range of D. A. Pitman Ltd. consists of instrumentation for health physics and nuclear medicine and their interest in thermoluminescence dosimetry dates from 1964, soon after the firm was founded. At the outset the terms of reference were fairly wide, and were basically to research into various aspects of thermoluminescence dosimetry (TLD) with the aim of directing the knowledge thereby obtained to commercial ends.

This first chapter briefly summarizes the development of TLD in 1969, in order to define the most promising areas for future research. The research programme which emerged is described in detail in the following chapters and was carried out between October 1968 and September 1974.

1.1. Thermoluminescence dosimetry

When a thermoluminescent phosphor is exposed to ionising radiation while at a sufficiently low temperature, many of the freed electrons or holes become trapped at lattice imperfections. They may remain trapped for long periods of time when stored at that (or a lower) temperature. As the temperature is raised the probability of escape is increased and the electrons (or holes) are released from the traps, subsequently returning to stable energy states, often with the emission of light.

In thermoluminescent dosimetry the dosemeters, which consist of thermoluminescent phosphors in suitable forms, are first irradiated, generally at or about ambient temperature, and at a convenient later time are heated in a readout instrument which is usually situated outside the radiation field. A TLD reader basically consists of means for heating a thermoluminescent dosemeter and means for measuring a constant fraction of the energy emitted by the dosemeter in the form of light as it is heated. The light emitted by the dosemeter is related to the integrated radiation dose it has received, and unknown doses can be accurately measured by comparing the amount of light from dosemeters which have received unknown doses with the amount of light emitted by the same or similar dosemeters which have received a known radiation dose.

1.2. Determination of experimental programme

On studying the existing and potential market, it became evident that few TLD installations were operating satisfactorily. Problems with instrumentation, dosemeters, and operational techniques were in many
instances taking up more time than could justifiably be spared; this was particularly so in radiotherapy units, and often the reaction was to suspend TLD operations. Few systems were being used to solve dosimetry problems, and general knowledge of the difficulties being experienced was restricting market growth.

It was thus decided to start a research programme aimed at improving TLD techniques rather than to use existing TLD techniques for researching into dosimetry problems; this would also fit in better with the commercial aspects. The first step was to ascertain the applications in which TLD would make a useful contribution to radiation dosimetry and to determine the particular advantages and limitations of TLD compared with other radiation dosimetry systems. The areas of possible improvement to make TLD into a more attractive dosimetry system would then be decided on, and the research programme defined.

1.3. Applications of radiation dosimetry

The main applications of integrating dosemeters are summarised in Table 1.1. The first impression is of the wide dose-range, spanning fifteen decades. It was clear from an initial study of the literature that TLD was most suitable for measurements of \(10^4\) rads and less, though doses of up to about \(10^6\) rads could be measured, with some difficulty. The market for TLD is thus basically in radiological protection and radiotherapy applications, although some areas of radiobiology can also be covered.

Table 1.1. Applications for integrating dosemeters

<table>
<thead>
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<th>Dose range (rad)</th>
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<td>(10^{-3} - 10^3)</td>
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</table>

1. Radiological protection
   (a) Routine personnel monitoring
   (b) Diagnostic radiology
   (c) Environmental monitoring

2. Radiotherapy
   \(10^2 - 10^4\)

3. Radiobiology
   \(10^2 - 10^6\)

4. Radiation chemistry
   \(10^3 - 10^8\)

5. Nuclear reactors
   \(10^6 - 10^{12}\)

1.4. Criteria for comparing dosimetry systems

The main practical characteristics which must be considered when choosing a dosimetry system are briefly summarized in this section, prior to a comparison of available dosimetry systems.
1.4.1. Integrated dose or dose-rate measurement

Some dosimetry systems are capable of both types of measurement, whereas others only measure integrated dose directly, and dose-rate has to be inferred indirectly.

1.4.2. Sensitivity to various radiations

A dosemeter does not generally respond in the same way to all types of radiation. The ability to distinguish between different types of radiation e.g. between gamma rays and neutrons, or between low and high energy gamma rays, is thus sometimes either a requirement or an advantage. A detailed dose spectrometry is not normally required in routine personnel monitoring, but if a high dose is received in a mixed radiation field it is helpful in evaluating the incident to know the approximate type of radiation that caused the high dose.

1.4.3. Dose or dose-rate range

A linear relationship between dosemeter response and dose or dose-rate makes for operational simplicity. However, correction factors can be used in regions of non-linear response to extend the range.

1.4.4. Accuracy and precision

The accuracy required varies with the application. For example, in radiotherapy measurements an accuracy of ± 2% is desirable, since success or failure in many treatments is believed to be critically dependent on the dose (Herring and Compton, 1971). In radiological protection this requirement is less stringent, and ± 20% is generally considered adequate.

Most practical dosimetry systems are secondary and have to be calibrated against absolute standards in a known radiation field. This introduces some systematic error, generally of the order of 1%.

In comparing radiation dosimetry systems, it is important to distinguish between the precision of repeated measurements with a single dosemeter and the precision of measurements with a batch of dosemeters of nominally the same sensitivity.

1.4.5. Matching the dosemeter to the medium

To give an accurate dose estimation, the dosemeter should respond to radiation in the same manner as the medium in which the dose is to be measured. In radiological protection, the term 'tissue equivalent' is used to describe a dosemeter that responds to radiation in a similar manner as tissue.
A true match would be achieved only if the two materials had (a) the same absorption coefficient for the primary radiation and (b) the same atomic stopping power for the secondary particles. This latter criterion is generally less critically dependent on atomic number than is the primary absorption coefficient. For neutrons, the neutron interactions would have to be similar. The introduction of the dosemeter should disturb the radiation field as little as possible, and the dosemeter should be positioned such that build-up effects or attenuation are taken into account in order to match the region of interest in the medium.

1.4.6. Size and mobility of dosemeter

The dosemeter generally averages the dose over its active volume, thus for most accurate results the radiation field strength should not change significantly throughout the volume of the dosemeter. This alone often determines the size of the dosemeter. The film badge is the only dosimetry method easily able to provide information on dose gradients throughout the dosemeter. Size is also a consideration when the dosemeter has to be used in not easily accessible places, e.g. in vivo. Different sizes and shapes of dosemeters may be required to suit particular applications; for example, extremely thin dosemeters may be required for beta dose measurements and skin dosimetry.

1.4.7. Time scale in which measurement is required

In some methods, exposure of the dosemeter to the radiation field must be followed by processing of the dosemeter by complementary instrumentation e.g. film must be developed and interpreted. It is not always practicable or economic to have the readout instrumentation at the site of the measurements. In routine personal monitoring where the time factor is not critical dosemeters are often posted to centralised readout services. The actual evaluation or readout time is usually relatively short. The accuracy of the reading may be affected by the time interval between exposure and evaluation, since the stored dose information may vary with time.

1.4.8. Effect of environment on dosemeter and dosemeter reading

Dosemeters and dosemeter readings may be affected by factors such as temperature, pressure, humidity, light, dust, shock, vibration, chemical attack, radioactive or chemical contamination, or electrostatic or electromagnetic fields.

1.4.9. Permanence of dose record

In film dosimetry the developed film provides a permanent dose record,
capable of reinterpretation if necessary. In most other systems, either the method of readout destroys the reading or it is not feasible to preserve the reading for any length of time. In such cases confidence has to be placed in instrument reliability and in the manual or automatic method of recording doses.

1.4.10. Costs

The true cost of a dosimetry system cannot be measured in terms of capital cost alone. Running costs must be taken into account, and these will depend on such factors as dosemeter throughput, lifetime and reusability, and convenience of use. In recent years the growing complexity of the working environment has led to increasing emphasis being placed on the need for instrumentation which is simple to set up and use, thereby reducing operating time. So far as TLD is concerned, running costs have previously been high due to instrument and dosemeter problems consuming an inordinately high percentage of user time.

1.5. Comparison of available dosimetry systems

The available dosimetry systems are listed in Table 1.2. Their theory and practice have in most cases been frequently reported, but references are given for some of the newer or rarer solid-state techniques. Four of the systems listed, namely TLD, RPL, ionisation chambers and film, are frequently used in radiological protection and/or clinical radiotherapy, and are compared in detail in Table 1.4. The favourable characteristics of TLD are summarized in Table 1.3. It should be noted that the figures quoted for dose range and precision are only typical, and that extended dose ranges and improved precision have been reported on occasion.

1.6. Characteristics of TLD

The advantages and limitations of TLD are discussed in this section.

1.6.1. Advantages of TLD

It can be seen from Tables 1.3 and 1.4 that, overall, TLD offers several significant advantages over other systems, especially in the fields of radiological protection and clinical radiotherapy. Considering first radiological protection, the wide dose range, approximate tissue equivalence, reusability, long term retention of stored dose in all terrestrial climates, and the availability of dosemeters in a number of configurations to suit special applications (e.g. beta and extremity dosimetry) have made TLD the most likely successor to the film badge as the most widely used personnel dosemeter. In clinical radiotherapy, the same advantages have led to increasing use of TLD to complement
1. Calorimetry
2. Chemical dosimetry
3. Ionisation chambers
4. Proportional and G-M counters
5. Scintillation counters
6. Semiconductor counters
7. Photographic methods
8. Solid state integrating dosemeter systems
   (a) Radiothermoluminescence (RTL)
   (b) Thermally stimulated exo-electron emission (TSEE)
   (c) Radiation induced thermally activated current (RITAC); also known as thermally stimulated conductivity (TSC) (Harper and Thomas, 1973; Harper et al., 1974; Moran and Cameron, 1974) or as thermo-current dosimetry (TCD).
   (d) Radiophotoluminescence (RPL)
   (e) Lyoluminescence; (also known as 'Aqualuminescence') (Arnihar et al., 1970; Atari and Ettinger, 1974; Ettinger and Atari, 1974)
   (f) Radiation induced thermally activated depolarization (RITAD) (Podgorsak et al., 1973)
   (g) Optically stimulated luminescence (Antonov-Romanovsky et al., 1955)
   (h) Degradation of luminescence (Schulman et al., 1957)
   (i) Coloration

Table 1.3. Characteristics of TLD
1. Few limitations on the size of dosemeters, thus suitable for most applications in radiological protection and radiotherapy.
2. Can be used for the measurement of most types of radiation, with discrimination between the different types.
3. Wide dose range, and a linear response over the greater part.
4. Response independent of dose-rate over all ranges of practical interest.
5. Near tissue equivalent systems achievable.
6. Reasonable accuracy attainable.
7. Resistant to variations in temperature, pressure, and humidity, and therefore suitable for use in most terrestrial climates.
8. Long-term retention of stored dose.
9. Mechanically rugged dosemeters.
10. Rapid on-site evaluation, if required.
11. Reusable, therefore low cost per readout.
12. Coded dosemeters available, suitable for automatic readout and record-keeping.
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<th>RPL</th>
<th>Ionisation Chambers</th>
<th>Film</th>
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<td>Integrating</td>
<td>Integrating</td>
<td>Either or both</td>
<td>Integrating</td>
</tr>
<tr>
<td>2. Normal dose range (rads)</td>
<td>$10^{-5}$ - $10^{6}$</td>
<td>$10^{-2}$ - $10^{4}$</td>
<td>$10^{-5}$ - $10^{4}$</td>
<td>$10^{-2}$ - $10^{3}$</td>
</tr>
<tr>
<td>3. Linearity of response</td>
<td>Supralinearity possible</td>
<td>Linear</td>
<td>Linear</td>
<td>Nonlinear</td>
</tr>
<tr>
<td>5. Typical precision (coefficient of variation)</td>
<td>± 5%</td>
<td>± 5%</td>
<td>± 5%</td>
<td>± 10%</td>
</tr>
<tr>
<td>(a) Batch calibration</td>
<td>± 1%</td>
<td>± 1%</td>
<td>Not applicable</td>
<td>No</td>
</tr>
<tr>
<td>(b) Individual calibration</td>
<td>± 1%</td>
<td>± 1%</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>6. Approximate tissue equivalence</td>
<td>Yes</td>
<td>No</td>
<td>Yes (pulse ionisation chambers)</td>
<td>Limited</td>
</tr>
<tr>
<td>7. Dose-rate dependence</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
</tr>
<tr>
<td>8. Dose spectrometry</td>
<td>Difficult</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>9. Measurement of dose gradients across dosemeter</td>
<td>Low</td>
<td>Low</td>
<td>Not applicable</td>
<td>Moderate</td>
</tr>
<tr>
<td>10. Relative fading of stored dose</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>11. γ and X detected (within limits of photon energy dependence)</td>
<td>Can be very good</td>
<td>Possible</td>
<td>Possible</td>
<td>Possible</td>
</tr>
<tr>
<td>12. β dosimetry</td>
<td>Possible</td>
<td>Possible</td>
<td>Possible</td>
<td>Possible</td>
</tr>
<tr>
<td>13. Neutron dosimetry</td>
<td>Possible</td>
<td>Possible</td>
<td>Possible</td>
<td>Possible</td>
</tr>
<tr>
<td>14. Alpha dosimetry</td>
<td>Possible</td>
<td>Not reported</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>15. Relative size</td>
<td>Can be very small</td>
<td>Small</td>
<td>Moderae</td>
<td>Good</td>
</tr>
<tr>
<td>16. Mobility</td>
<td>V. Good</td>
<td>V. Good</td>
<td>Wide variety</td>
<td>Limited</td>
</tr>
<tr>
<td>17. Geometrical configurations available</td>
<td>Wide variety</td>
<td>Limited</td>
<td>Wide variety</td>
<td>Limited</td>
</tr>
<tr>
<td>18. Directional effects</td>
<td>Probably not</td>
<td>Probably not</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>19. Sensitivity to environmental conditions</td>
<td>Temperature, oxygen light, dust</td>
<td>Light, dust</td>
<td>Temperature, pressure, humidity, dust</td>
<td>Light, temperature, humidity, dust</td>
</tr>
<tr>
<td>20. Resistance to chemical attack</td>
<td>Can be very good</td>
<td>Can be good</td>
<td>Variable</td>
<td>Poor</td>
</tr>
<tr>
<td>21. Ruggedness</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
<td>Yes</td>
</tr>
<tr>
<td>22. Rapid evaluation</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes, but not generally on site</td>
</tr>
<tr>
<td>23. Permanent dose record</td>
<td>Indirect</td>
<td>Direct or indirect</td>
<td>Indirect</td>
<td>Direct or indirect</td>
</tr>
<tr>
<td>24. Reusability</td>
<td>Easy</td>
<td>Not easy</td>
<td>Easy</td>
<td>No</td>
</tr>
<tr>
<td>25. Measurement of cumulative doses</td>
<td>Not easy</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>26. Suitable for skin dosimetry</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>27. Suitable for extremity monitoring</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Not easy</td>
</tr>
<tr>
<td>28. Suitable for in vivo measurements</td>
<td>Yes</td>
<td>Yes</td>
<td>Difficult</td>
<td>No</td>
</tr>
<tr>
<td>29. Relative cost of dosemeter</td>
<td>Moderate</td>
<td>Moderate</td>
<td>High</td>
<td>Moderate</td>
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<td>30. Cost of reading device</td>
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<td>Low</td>
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<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>33. Skilled personnel required for evaluation</td>
<td>Not for routine work</td>
<td>Not for routine work</td>
<td>Sometimes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
ionisation chamber measurements, and new forms of treatment planning have become possible.

1.6.2. Inherent limitations of TLD

1. Accuracy: TLD is not an absolute dosimetry system so there is always some additional error introduced during the calibration in a standard radiation field.

2. Composition of dosemeter: The dosemeter material is invariably not the same as the medium in which the dose is to be measured, thus there will generally be errors due to the dosemeter and the medium responding differently to the various radiations.

3. State of dosemeter surface: Light generated within the dosemeter during the readout process has to pass through the dosemeter surface before a measurement can be made. The condition of the dosemeter surface is thus a critical factor in the accuracy and precision attainable, since any change in the surface, for instance discolouration or surface distortion, can alter light transmission or scattering and affect the amount of light reaching the detector. In addition, it has been found that contamination of, or gaseous adsorption onto the surface can give rise to non-radiation induced light signals which complicate the measurement of the radiation induced volume signal.

The dosemeter surface is often protected by sealing the dosemeter in a plastic container of shape and composition suitable for the application.

1.6.3. Practical limitations of TLD

The following comments relate to the 'state of the art' in practical TLD systems that generally pertains to the early 1970's.

1. Phosphors: The thermoluminescent phosphors in common use have complex trap distributions. This leads to difficulty in isolating the dosimetry peaks from unwanted peaks during the readout cycle, and thence to problems with fading and precision, since small variations in the heating cycle can critically affect the measured peaks.

2. Variations in the readout instrument: The instrumentation required for repeatable readout of dosemeters is complex and there are many opportunities for errors to be introduced.

3. Variations in the sensitivity of dosemeters from the same batch: Numbers of nominally identical dosemeters, made from the same batch of phosphor, do not necessarily have the same sensitivities due to variations in the manufacturing process. In some applications individual calibration
is required to improve precision to acceptable levels.

4. Variations in the sensitivity of a given dosemeter with re-use: The sensitivity of a dosemeter is affected by its thermal and radiation history and by its surface condition, and is therefore liable to change with re-use.

5. Variations in dosemeter background signals: The background signal is the signal from an unirradiated dosemeter. High and variable background signals can be caused by several effects, and their variations determine the lowest measurable dose.

6. Operational procedure: Detailed and careful operational procedures have to be followed to obtain accurate and precise results.

1.7. Research programme

From the foregoing it is evident that errors in application of TLD can arise from a variety of sources, including variations in the readout instrument, variations in the sensitivity and background of the dosemeters, and calibration errors. It was decided to investigate the various sources of error, in order to design a thermoluminescent dosimetry system in which these errors were minimised.

The relationship of the following chapters to this research programme is as follows. The physical basis of thermoluminescence is described in chapter 2. In chapter 3 a theory of thermoluminescent dose measurement is developed, to determine the various factors which govern the reading obtained from a dosemeter, and thence the sources of error involved. The theory is also applied to calibration techniques. Thermoluminescent phosphors are described in chapter 4. Phosphors were investigated with a view to producing materials with simplified glowpeak structures that more closely approximate to ideal thermoluminescent materials. One of the main aims of the research programme was to produce a readout instrument capable of handling a wide variety of dosemeters, but which contributed very little to the overall error. The development of this reader is described in chapters 5 and 6. Different forms of dosemeter and criteria for comparing them are discussed in chapter 7.

D. A. Pitman Ltd. have a particular commercial interest in phosphor/PTFE* dosemeters, and sources of sensitivity and background variations in these dosemeters are investigated in chapters 8 - 11. This has enabled the design of these dosemeters and operational techniques for precise measurements at both radiological protection and radiotherapy levels to be optimised.

* PTFE = polytetrafluoroethylene = Teflon (Trade name of Du Pont de Nemours Inc) = Fluon (Trade name of I.C.I. Ltd.)
The limitations of the present study, and recommendations for future work, are discussed in chapter 12. Generally, only photon and electron radiation fields have been considered, the coverage of neutron dosimetry being superficial. However, most of the results are also applicable to neutron dosimetry, and provide a good basis for any future studies on this subject.
This chapter is concerned with providing the basic knowledge necessary for a more complete understanding of the properties of thermoluminescent phosphors, as a prelude to the development of the thermoluminescent dosimetry system. The physical basis of thermoluminescence is described in section 2.1, and followed in section 2.2 by an introduction to the theory of thermoluminescence, in which some methods for obtaining information on thermoluminescent phosphors are outlined. The emphasis has been on the information obtainable from glow curves and integrated light sum measurements, since this is generally the only information readily available from a practical TLD system. Other means of obtaining information on thermoluminescent mechanisms, such as analysis of absorption or emission spectra, dielectric loss measurements, or the use of complementary solid-state effects, have either not been considered or only mentioned in passing. Some aspects of the theory are applied more specifically in later chapters, for example, in discussions on the thermoluminescent mechanism in LiF (chapter 4), and in thermal quenching in LiF/PTFE discs (chapter 9).

2.1. Description of thermoluminescence

2.1.1. Imperfections in crystals (Quéré, 1967; Schulman, 1967; Kittel, 1968)

A crystal is an agglomerate of atoms (or molecules) characterised by a 3-fold periodicity. To describe completely a crystal one has to define the positions of atoms (or molecules) inside a unit cell, built on 3 vectors \( \mathbf{a}_i \) (i = 1, 2, 3) of arbitrary origin. All the atoms of the crystal will be obtained from the atoms of the unit cell by all the translations \( t = \sum_i n_i \mathbf{a}_i \) .................................. (2.1)

where \( n_i \) represents all the positive and negative integers. Solids are generally classified through the type of chemical bonding between the atoms. Ionic crystals may be described by classical physics. One or more electrons is given by an electropositive atom to a nearby electronegative atom. The result is the existence of ions of opposite signs, each ion surrounded by ions of opposite sign, which results in a strong electrostatic attraction. The equilibrium distance between ions results from a balance between this attraction and the repulsion of internal electronic shells of the ions. NaCl is commonly cited as an example of a simple ionic crystal.

Covalent bonding is a quantum mechanical effect which describes the decrease of energy of electrons shared by several atoms. For example, in
the case of diamond (or Ge or Si) 4 electrons of one atom are shared with its four nearest neighbours, each of which shares 4 electrons. The perfect periodicity implied by (2.1) is impossible, since the atoms are never at rest. An atom at rest would contradict the Heisenberg Uncertainty Principle since one would then know simultaneously its position and its velocity \( v (v = 0) \). Thermal vibrations make it impossible to obey (2.1). We can specify an equilibrium (average) position which we call the atomic site. The distance \( \Delta a \) between the atom and the site is such that \( \frac{\Delta a}{a} \) is small \( (a \) is the average nearest neighbour distance) and reaches a maximum of about 1/10 near the melting point. Another obvious limitation to (2.1) is the finite crystal size. Crystals are limited by free surfaces and these free surfaces are the first and most unavoidable type of crystal defect. A crystal defined by (2.1) is termed an ideal crystal. A crystal in which only the thermal vibrations disturb the periodicity is called a perfect crystal. A crystal which has at least free surfaces, and probably many other defects, is a real crystal.

Any deviation in a crystal from a perfect periodic lattice or structure is an imperfection or defect. Defects are classified according to their dimension. Point defects (zero dimension) are essentially concentrated in one, or very few, atomic volumes, and include:

a) Vacancies: a vacancy (Schottky defect) is the defect obtained if one atom is extracted from its site and not replaced.
b) Self-interstitial: an atom \( A \) inserted in a crystal \( A \) in a site not belonging to the perfect crystal. This is known as a Frenkel defect.
c) Chemical impurities: an atom \( B \) in a crystal \( A \). This atom \( B \) may have taken the place of an atom \( A \) (substitutional impurity) or may be inserted in the crystal site in an additional site not belonging to the perfect crystal (interstitial impurity).

Dislocations (one dimension) are lines along which stresses are concentrated in the crystal. Surface defects (two dimensional) include free surfaces, grain boundaries, and stacking faults. Volume defects (three dimensional) include precipitates, i.e., clusters of \( B \) atoms in a matrix \( A \) and vacancy (or interstitial) clusters, which are agglomerates of point defects. The distinction between point and volume defects is not always very clear; for instance, when vacancies group together to become a cluster, one deals successively with divacancies, trivacancies, etc. Clusters of a few (<5) point defects are still called point defects.
Figure 2.1. Imperfections in alkali halides

(a) Ideal crystal

+ - + - +
- + - - +
+ - + - +
- + - + -
+ - + - +

(b) Schottky defects

+ - + - +
- [ ] - - +
+ - - - +
- + - [ ] -
+ - + - +

(c) Frenkel defect
(& associated Schottky defect)

+ - + - +
- + - - +
+ - [ ] - -
- + - [ ] -
+ - + - +

(d) Frenkel defect
(& associated Schottky defect)

+ - + - +
- + - - +
+ - [ ] - -
- + - [ ] -
+ - + - +

+ Alkali ion
- Halide ion

[ ] Alkali ion vacancy
[ ] Halide ion vacancy

[ ] Interstitial alkali ion
[ ] Interstitial halide ion
Imperfections in the alkali halides are particularly suitable for illustrating the concepts involved in luminescence dosimetry. The structure of these salts consists of two interpenetrating cubic lattices of alkali ions and halide ions, and is represented schematically in figure 2.1, together with illustrations of some structural imperfections. The ideal crystal is shown in figure 2.1 (a). Schottky, i.e. occasional positive and negative ions missing at random, are illustrated in figure 2.1 (b). In a pure crystal the number of positive ion vacancies must equal the number of negative ion vacancies to ensure electrical neutrality. Frenkel defects are illustrated in figures 2.1 (c) and (d). Alkali ions or halide ions have been displaced from normal lattice positions into interstitial positions, leaving behind corresponding vacancies (Schottky defects).

2.1.2. Effect of radiation on imperfect crystals (Schulmann, 1967; Kittel, 1968)

The existence of imperfections in crystals has important consequences when the crystal is exposed to ionizing radiation. For example, negative ion vacancies are regions of localised positive charge, because the negative ion which normally occupies the site is missing and the positive charges of the surrounding ions are not fully neutralized. If an electron is made free in the crystal by the action of ionizing radiation and wanders near the negative ion vacancy, it is attracted by a Coulomb force to the localised positive charge and can be 'trapped' in the vacancy. The system (or 'centre') comprising an electron trapped at a negative ion vacancy roughly resembles a hydrogen atom, in which an electron is bound by the positive charge of a proton. Like a hydrogen atom, the electron–vacancy system also has discrete allowed energy levels, and it can make transitions between pairs of these levels by absorption or emission of the proper quantum of energy. The absorption of a light photon of the proper frequency can raise the electron from the ground state of the system to one of its higher excited states, and a sufficiently energetic photon can even expel it from its vacancy 'trap' altogether. The possibility of selective absorption of light makes the crystal coloured when viewed in white light and the imperfections which give rise to these absorptions are therefore called 'colour centres'. The particular centre consisting of an electron trapped at a negative-ion vacancy is termed an 'F' centre, and is illustrated schematically in figure 2.2 (a).

Similarly, a positive ion vacancy represents a region of localised negative charge. When ionising radiation strips an electron from one of the normal lattice ions, the deficiency of electronic charge (or 'hole') can migrate through the crystal and can be attracted and bound coulombically. The
Figure 2.2. Possible Colour Centres in Alkali Halides

(a) F-centre

(b) V-centre

(c) $V_k$-centre

(d) H-centre

$\circ$ electron $\bullet$ hole

Figure 2.3.

Effect of a divalent positive ion impurity in an alkali halide
antimorph to the 'F' centre would be a hole trapped near a positive ion vacancy. This is illustrated in figure 2.2 (b), but is physically unrealisable. However, other types of hole centre are possible. For example, the \( V_{K} \) centre illustrated in figure 2.2 (c) is formed when a hole is trapped by a pair of negative ions. The stable condition resembles a negative halogen molecular-ion. Interstitial halide ions also represent regions of localised excess negative charge. A hole trapped at an interstitial halide ion is known as an 'H' centre, and is illustrated in figure 2.2 (d). Other more complex hole centres have been proposed, such as the \( V_{1} \) centre, in which a neutral halogen molecule occupies the site of a halogen ion, i.e. in effect a two-hole trap. Ionising radiation can also produce vacancies and interstitials in structurally perfect regions of the crystals, in addition to liberating free electronic charges, which are attracted to electron and hole traps as described above.

2.1.3. Effect of doping with impurities (Schulman, 1967; Kittel, 1968)

The concentration of electron and hole traps can be influenced by doping with impurities. For example, figure 2.3 shows how a divalent positive-ion impurity, substituting for an alkali ion in an alkali halide, can affect the concentration of vacancies. In order to compensate for the excess positive charge of the impurity an alkali ion must be omitted from the structure, i.e. each substitutional divalent impurity ion creates a positive-ion vacancy. The concentration of negative-ion vacancies is correspondingly decreased since at a finite temperature the equilibrium condition of a crystal is the state of minimum free energy, which limits the total allowable number of lattice vacancies. Furthermore since the divalent cation impurity is a local positive charge and the cation vacancy is a local negative charge, the two attract each other and can form 'complexes', as shown in figure 2.3. The vacancy-impurity complex is in fact a dipole. The concentration and nature of electron and hole traps is thus profoundly affected by the impurity, since in addition to the changes it makes in the numbers and relative proportions of positive and negative ion vacancies, the divalent impurity cation is itself a possible electron trap by virtue of its excess positive charge.

The trapping properties of thermoluminescent LiF are known to be connected with the presence of Mg\(^{2+}\) as an activator; the vacancy-impurity dipoles can form higher complexes by clustering together, e.g. two dipoles may meet to form a 'dimer', three to form a 'trimer' and so on.
2.1.4. Luminescent processes (Schulman, 1967)

Luminescence can be defined, for the present purpose, as the emission of light that is not attributable to incandescence. The term 'light' is generally assigned to electromagnetic radiation in the visible region of the spectrum, but in dosimetry applications may also include ultra-violet or infra-red light. The features common to all forms of luminescence are (a) the occurrence of some process whereby an atom, molecule, or 'centre' (an aggregate of atoms or defects in a crystal) is excited to a higher energy state and (b) its radiative de-excitation to the ground state, e.g., via the emission of a photon of appropriate energy, after a lapse of some period of time.

The distinction between various types of luminescence was originally based on the time dependence of emission. 'Fluorescence' was luminescence which persisted only as long as the excitation was continued; 'phosphorescence' was the luminescence observable after removal of the exciting source. Schulman (1967) has suggested that a more meaningful distinction may be based on the temperature-dependence of the luminescence decay time. The decay time of fluorescence is essentially independent of temperature, being determined by the probability of the transition from an excited energy level $E_c$ to the ground state $E_0$ (see figure 2.4 (a)). The term 'phosphorescence' is most properly applied when the luminescence decay time depends on the temperature. Referring to figure 2.4 (b), this situation can arise when the atom, molecule, or centre is somehow excited (e.g., by ionising radiation) from a ground state $E_0$ to a metastable energy level $E_m$, from which it cannot return to the ground level with emission of a photon, i.e., the transition $E_m \rightarrow E_0$ is completely or largely forbidden by the selection rules. However, let us suppose that a higher excited level, $E_c$, exists to which the system can be raised by absorption of the energy $(E_c - E_m)$, and that the radiative transition $E_c \rightarrow E_0$ is an allowed one. If the energy $(E_c - E_m)$ can be provided by thermal means at room temperature, e.g., by absorption of phonons from the lattice in the case of a crystalline system, a continuing luminescence emission (phosphorescence) can be observed even after the excitation source is removed. This emission will continue with diminishing intensity until there are no longer any centres in the metastable state. If the system is raised to a higher temperature the transition $E_m \rightarrow E_c$ will occur at an increased rate; consequently the phosphorescence will be brighter and the decay time will be shorter due to the faster depopulation of the metastable state via the path

$$(E_m + \text{heat}) \rightarrow E_c \rightarrow (E_0 + \text{photon}).$$
Figure 2.4. Luminescent processes

(a) Fluorescence

(b) Phosphorescence

Figure 2.5. Thermoluminescent processes

(a) Irradiation

Conduction band

Ionising radiation

Valence band

(a) Trapping at defects (b) Radiative (Fluorescence) or non-radiative recombination (c) Radioluminescence

(b) Heating

(a) Retrapping at defects (b) Radiative or non-radiative recombination (c) Thermoluminescence

- Electron → Electron trap  
- Electron-activated luminescence centre → Electron transitions

- Hole ← Hole trap  
- Hole-activated luminescence centre
Thermoluminescence, i.e. temperature-stimulated light emission following removal of excitation, is merely a case of phosphorescence observed under conditions of steadily increasing temperature. In the usual thermoluminescence experiment the system is irradiated at a temperature at which the phosphorescent intensity is low (long decay time), and later heated through a temperature range where the phosphorescence is bright (very short decay time), until a temperature is reached at which all the centres have been thermally excited out of their metastable levels and the luminescence completely disappears. (The energy \( E_c - E_m \) can sometimes be provided by light absorption, e.g. infra-red light. In this case the phenomenon is called 'optically stimulated luminescence').

Luminescent materials are commonly referred to as 'phosphors', whether or not they exhibit phosphorescence. Efficient thermoluminescent phosphors have high concentrations of electron or hole traps, provided by structural defects and impurities (or 'activators') as discussed in the preceding sections.

In figure 2.5 thermoluminescence is illustrated schematically in terms of the properties of defects in crystalline insulators. Energy states in the crystal are represented with energy increasing upwards along the ordinate. The irradiation process is shown in figure 2.5 (a). Irradiation produces free electrons and holes. The electrons are then free to travel through the solid in the conduction band for a short time. They may be ultimately either (a) trapped at defects, i.e. the metastable energy state \( E_m \), or (b) fall back into the valence band and recombine either radiatively (fluorescence) or non-radiatively with holes, or (c) be captured at luminescent centres already activated by holes as a result of the irradiation, and de-activate the centre with the emission of light. This last process, 'radioluminescence', is the basis of scintillation counting and can be used for dose-rate measurements. Similarly, holes can move freely through the valence band before being trapped at defects, or recombining radiatively or non-radiatively with electrons, or recombining radiatively at electron activated luminescent centres.

The effect of the subsequent heating process is illustrated in figure 2.5 (b). The electrons trapped at the metastable energy states are given sufficient thermal energy to escape from the traps into the conduction band again, where they are free to travel and have three possible fates, as before. They may either be retrapped at defects, or fall back into the valence band and recombine radiatively or non-radiatively with holes, or recombine...
radiatively at a hole-activated luminescent centre. The light emitted by the last process is the 'thermoluminescence'. Similarly, holes can be thermally liberated from their traps, and migrate via the valence band, from whence they may either be retrapped at defects, or recombine radiatively or non-radiatively with electrons, or recombine radiatively at an electron-activated luminescent centre, also producing thermoluminescence.

Direct radiative recombination of electrons and holes with a transition across the bandgap gives rise to radiation which has a quantum energy greater or equal to the energy gap, and consequently self-absorption occurs with high probability. Since some direct transitions are non-radiative, there is very little chance of light emission from this process in crystals of practical dimensions.

2.1.6. Thermoluminescence measurements (Fowler and Attix, 1966)

It has been shown above that when a thermoluminescent phosphor is exposed to ionising radiation while at a sufficiently low temperature, many of the freed electrons or holes become trapped at lattice imperfections. They may remain trapped for long periods of time when stored at that (or a lower) temperature. As the temperature is raised the probability of escape is increased and the electrons (or holes) are released from the traps, subsequently returning to stable energy states, often with the emission of light. Figure 2.6 illustrates the type of apparatus generally used in thermoluminescence measurements. The phosphor or dosimeter is placed on a heater pan or tray, which may be heated by a variety of means. The pan temperature is measured by a thermocouple in close thermal contact. The light emitted by the hot phosphor may pass through one or more optical filters before being detected by a photomultiplier (PM) tube. The output current from the PM tube is proportional to the light input, and may, for example be further amplified and fed to an integrator or converted into pulses and fed to a scaler.

If the light intensity is plotted as a function of temperature (or a related function such as time) by a suitably connected chart recorder, the resulting graph is called a glowcurve. Typical glowcurves exhibit one or more maxima as traps of various energy 'depths' are emptied. The relative amplitudes of the peaks indicate approximately the relative populations of trapped charge carriers in the several trap species (provided the heating rate is constant throughout the glowcurve). Faster heating rates result in peaks of greater amplitude, and with the maxima shifted to higher temperatures. Glowcurves of several phosphors in common use are shown in figure 2.7.
Figure 2.6. Schematic of TLD Reader

![Schematic of TLD Reader](image)

Figure 2.7. Typical glow curves from some phosphors

Notes: (a) assuming a linear heating rate of about 5°C/sec.
(b) glow curve structure may vary considerably, depending on the manufacturing method.
Either the total light emitted during part or all of the glowcurve, or the height of one or more of the peaks, may serve as a measure of the absorbed dose in the phosphor. When the peak height is used, the heating cycle must be sufficiently reproducible to avoid causing peak height fluctuations. After the traps have been emptied by heating at a high enough temperature for a sufficient length of time, and the phosphor has subsequently cooled, it is normally returned to its original condition and is ready to register another exposure to radiation.

2.2. Thermoluminescence analysis (Curie, 1963; Townsend & Kelly, 1973)

2.2.1. Phosphorescence

We first consider the phosphorescence process, since thermoluminescence is merely a case of phosphorescence observed under conditions of steadily increasing temperature. The thermal activation energy \( E \) required to liberate a trapped charge carrier is known as the trap depth, the energy being received by phonon interaction with the surroundings. The situation is illustrated in figure 2.8 for one kind of electron trap, \( E \) being the depth of the trap below the conduction band. Although only electron traps will be referred to in the following analysis, it will be evident that a similar treatment could be applied to hole traps.

The probability \( p \) per unit time that a trapped electron will escape is of the form

\[
p = s \exp\left(-\frac{E}{kT}\right)
\]

where \( E \) is the trap depth (generally expressed in eV)

\( k \) is Boltzmann's constant

\( T \) is the absolute temperature

and \( s \) is a factor having the dimensions of frequency, and related to (but generally much less than) the frequency of atomic vibrations in the solid; it is often referred to as the 'frequency factor'.

\( \tau = p^{-1} = \) the mean life time of the trapped charges.

One of the first steps in the analysis of a phosphorescent process is to determine the different trap depths. This can be achieved by analysis of decay curves or glowcurves, as shown below.

2.2.2. Kinetics of phosphorescence

The term 'first-order kinetics' is used to describe the situation in which no retrapping occurs. This is generally a valid assumption if the concentration of traps is small compared with the concentration of luminescent centres. It will also be assumed that no direct transitions take place from the defects to the luminescent centres.
Figure 2.8.
Energy level diagram for thermoluminescence from single type of electron trap

![Energy level diagram]

Figure 2.9.
The effect of retrapping on the glow curve from a single type of trap
(concentration of traps comparable to or greater than the concentration of luminescent centres)

![Glow curve diagram]

Figure 2.10.
Emission spectra of some phosphors

![Emission spectra graph]
If \( n \) is the number of trapped electrons in the sample, which is maintained at a constant temperature \( T \), then \( n \) decreases with time \( t \) as:
\[
\frac{dn}{dt} = -pn
\]
\[
\therefore n = n_0 \exp(-pt)
\]
where \( n_0 \) is the number of trapped electrons at time \( t = 0 \).
Let \( n_c \) be the number of conduction band electrons. If the life-time of electrons in the conduction band is very much less than the life-time of electrons in traps, then
\[
\frac{dn}{dt} = \frac{dn}{dt} + \frac{dn}{dt}
\]
Let \( I(t) \) = the phosphorescence intensity, i.e. the number of photons emitted per unit time at time \( t \). If a constant proportion of the electrons in the conduction band lead to luminescent transitions, then
\[
I(t) = \alpha \frac{dn}{dt} \exp(-pt)
\]
\[
\therefore I(t) = \kappa n_0 \exp(-t) \exp(-pt)
\]
If a distribution of trap depths is present, \( n_0 \) \( d\tau \) being the number filled initially with life-times between \( \tau \) and \( \tau + d\tau \), then
\[
I(t) = \int n_0 \exp(-t) d\tau
\]
The term 'second-order kinetics' is used to describe situations in which retrapping does take place, for example, where the number of traps is comparable to, or more than, the number of luminescent centres. Then, it can be shown (Curie, 1963) that
\[
\frac{dn}{dt} = -pn + An_c(n - n)
\]
where \( A \) is the electron capture cross-section of the trap multiplied by the thermal velocity of the electrons.
For the case of equal probability of retrapping or a luminescent transition,
\[
\frac{dn}{dt} = -\frac{n^2}{n_0 \tau}
\]
and
\[
I(t) = A(n + n_c)n_c
\]
The practical effects of the order of kinetics are described in section 2.2.9.

2.2.3. Glowcurves

The method of glow curves was first proposed by Urbach (1930) but first achieved extensive use due to Randall and Wilkins (1945). The method is as follows:

(i) The phosphor is first excited by exposure to radiation at a
temperature $T_0$ low enough for the traps to be investigated, i.e. such that significant numbers of trapped charge carriers are not released during irradiation.

(2) The phosphor is then heated at a constant rate of temperature rise and the traps begin to empty as the temperature increases. The resulting thermoluminescence increases with temperature and if there is only one trap depth reaches a maximum at a characteristic 'peak temperature', and then decreases to zero as the traps are all emptied. If the trap distribution consists of traps of various depths, these each give rise to a separate peak in the glow curves.

2.2.4. Simple glow curve theory of Randall and Wilkins

The theory assumes first-order kinetics, and a single trap depth. The rate determining process for the luminescence is the rate of escape of the electron from the trap. Following sections 2.2.1. and 2.2.2.:

$$I(t) = - \alpha \frac{dn}{dt} = \kappa n p = \kappa n s \exp\left(\frac{-E}{kT}\right)$$

If the phosphor is heated at a constant rate $\beta = \frac{dT}{dt}$

$$- \frac{dn}{dt} = - \beta \frac{dn}{dt} = n s \exp\left(\frac{-E}{kT}\right)$$

$$n = n_0 \exp\left(\int_0^t - \frac{\beta}{E} \exp\left(\frac{-E}{kT}\right) dt\right)$$

and

$$I(t) = \kappa n_0 s \exp\left(\frac{-E}{kT}\right) \exp\left(\int_t^\infty - \frac{\beta}{E} \exp\left(\frac{-E}{kT}\right) dt\right)$$

Numerical integration allows this expression to be evaluated and yields a bell-shaped curve (see figure 2.9) with a maximum intensity at a characteristic temperature T*.

The integrated light sum S is given by

$$S = \int_0^\infty I dt = \int_0^\infty - \alpha \frac{dn}{dt} dt = \int_{n_0}^{n} - \alpha dn = \kappa n_0$$

Thus S is proportional to the initial number of trapped charges and is independent of the readout cycle, as long as $\alpha$ remains constant. If the number of trapped charges is proportional to the radiation dose, as is the case in many practical situations, then the light sum is proportional to the radiation dose. This inherent linearity is an important property of this method of dosimetry.

2.2.5. Phosphor analysis by means of decay curves

For simplicity, only first-order kinetics will be considered. Information on the trap distribution of a phosphor can be obtained by maintaining the phosphor at a convenient temperature T and observing the decay in I(t).
Use is made of the formula

\[ I(t) = \alpha \frac{n_0}{\tau} \exp\left(-\frac{t}{\tau}\right) \]

However, this method is only suitable for phosphors with a measurable light output, at the storage temperature, over the length of time necessary to obtain significant information. The decay is exponential for a single trap, and must be followed over several half-lives, hence a high initial intensity is required.

An alternative method, more suitable for many phosphors, is to store the irradiated phosphor for varying times (t) over a range of temperatures (T), and to obtain the light sums, \( S_t \), remaining after the corresponding times by thermoluminescence methods, i.e. after storage the phosphor is warmed to a temperature sufficient to rapidly remove all the charge carriers from the traps. To obtain the trap depths and frequency factors the experimental decay curves are broken down into a series of exponential terms, i.e.

\[ S_t = \sum n_{0 \tau}(\tau) \exp\left(-\frac{t}{\tau}\right) \Delta \tau \]

The method is illustrated by the analysis of a single trap. Let the initial light sum be \( S_o \). For first-order kinetics,

\[ S_o = \alpha n_0 \]

\[ S_t = \alpha n_0 \exp(-pt) \]

\[ = \alpha n_0 \exp(-st \exp\left(-\frac{E}{kT}\right)) \]

\[ \therefore \ln \frac{S_t}{S_o} = -st \exp\left(-\frac{E}{kT}\right) \]

\[ \therefore \ln(S_t/S_o) = -st \exp\left(-\frac{E}{kT}\right) \]

A graph of \( \ln(S_t/S_o) \) vs t is plotted for each set of data obtained at a storage temperature T. For a single trap, these graphs should be straight lines of gradient \( m = -s \exp\left(-\frac{E}{kT}\right) \)

\[ m = -\exp\left(-\frac{E}{kT}\right) \]

\[ \therefore \ln(-m) = \ln s - \frac{E}{kT} \]

Therefore a plot of \( -m \) against \( 1/T \) yields a straight line of slope \( -E/kT \), and intercept \( \ln s \) on the ordinate axis. Hence \( E \) and \( s \) are obtained. Note that the heating rate during the thermoluminescence readouts should be the same for all samples, to avoid variations due to thermal quenching effects (see section 2.2.8).

This method is only suitable with phosphors in which the trap distribution is stable at the storage temperatures. For example, in thermoluminescent LiF the trap distribution is often not stable and
great care has to be taken to avoid erroneous results (Townsend, 1971).

2.2.6. Phosphor analysis by means of glow curves

These methods are less precise than analysis of isothermal decay curves, but are more convenient and rapid. The complete form of a thermoluminescent curve can be found by numerical integration of eqn. (2.3), but this is not generally feasible. A relationship between \( E \) and \( T^* \) can be found by setting \( \frac{dI}{dT} = 0 \), as follows,

\[
I(t) = \alpha_n s \exp\left(-\frac{E}{kT}\right) \exp\left(\int_{T^*}^{T} -\frac{s}{\epsilon} \exp\left(-\frac{E}{kT}\right) dT\right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.3)
\]

Differentiating eqn. (2.3) wrt \( T \),

\[
\frac{dI(t)}{dT} = E \alpha_n s \exp\left(-\frac{E}{kT}\right) \exp\left(\int_{T^*}^{T} -\frac{s}{\epsilon} \exp\left(-\frac{E}{kT}\right) dT\right) + \alpha_n s \exp\left(-\frac{E}{kT}\right) -\frac{s}{\epsilon} \exp\left(-\frac{E}{kT}\right) \exp\left(\int_{T^*}^{T} -\frac{s}{\epsilon} \exp\left(-\frac{E}{kT}\right) dT\right)
\]

\[= 0 \text{ for maximum } T, \text{ i.e. } T^*.
\]

Rearranging and cancelling,

\[
\frac{E}{k(T^*)^2} = s \exp\left(-\frac{E}{kT^*}\right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.7)
\]

From eqn. (2.7) it can be seen that \( T^* \) moves to higher temperatures as \( E \) or \( \theta \) increase, or as \( s \) decreases. Note that in practice the observed glow peak temperature is also affected by instrumentation factors, such as the closeness of the thermal contact between the thermocouple and the phosphor, and thermal radiation losses from the phosphor. These tend to increase the apparent glow peak temperature.

The relation between \( E \) and \( T^* \) is thus defined by the parameter \( \theta = \frac{\theta}{s} \).

Curie and Curie (1955) solved this equation by numerical methods to an accuracy of better than 1% ;

\[
T^* = cE + T', \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2.8)
\]

where \( c \) and \( T' \) are functions of \( \theta \), and are tabulated in the above reference.

In practice eqn. (2.8) is not very useful for determining trap depths, since \( s \) is not generally known accurately enough. Its main use is in the determination of \( T^* \) when \( E \) and \( s \) are already known, e.g. from isothermal decay curves. The value of \( T^* \) calculated in this way can be usefully compared with the experimentally observed value of \( T^* \), to give an estimate of the thermal lag during the readout process.

\( E \) can be determined without the need to know \( s \), if two different heating
rates, $\beta_1$ and $\beta_2$, are used. The same trap depth then results in two different values of $T^*_x$, i.e., $T^*_1$ and $T^*_2$. If $\beta_1 > \beta_2$, then $T^*_1 > T^*_2$.

From eqn.(2.7), eliminating $s$:

$$
E \left( \frac{1}{T_2^*} - \frac{1}{T_1^*} \right) = \ln \left( \frac{\beta_1}{\beta_2} \frac{\sigma_1^2}{\sigma_2^2} \right)
$$

from which $E$ can be obtained. To find $s$, the above value for $E$ is substituted back into eqn.(2.7). The accuracy of the above procedure is limited by instrumental factors, i.e. the difficulty of knowing the exact temperature of the phosphor at any time.

2.2.7 Calculation of fading rates

If $E$ and $s$ are known for a single trap in a phosphor, it is possible to calculate fading curves for storage at any temperature $T$. These can be compared with experimentally observed fading. Discrepancies between the curves may for example, be indicative of the presence of a distribution of traps instead of a single trap. From eqn.(2.2) the trap half-life, $t_{1/2}$, is given by

$$
t_{1/2} = \frac{0.693}{s} \exp \left( \frac{E}{kT} \right)
$$

2.2.8 Thermal quenching

In section 2.2.2, it was assumed that a constant proportion $\alpha$ of the electrons which transiently occupy the conduction band lead to luminescent transitions. $\alpha$ is less than unity because excitation of lattice vibrations occurs in competition with the photon emission. If $P_r$ is the probability of luminescence emission and $P_{nr}$ the probability of a non-radiative transition, then $\alpha$ is given by

$$
\alpha = \frac{P_r}{P_r + P_{nr}}
$$

It is generally assumed that $P_r$ is independent of temperature. However, it has been experimentally observed that, for many phosphors, $P_{nr}$ rises rapidly with temperature, leading to a decrease in luminescence efficiency with increasing temperature, often referred to as 'thermal quenching'. One practical consequence of this effect, important in dosimetry applications, is that the light sum, $S$, will be dependent on the heating rate, $\beta$.

At lower heating rates more of the light will be released at lower temperatures, when the luminescence efficiency is higher. Conversely, the light sum will be reduced as the heating rate increases. The observed glow peaks are also affected, thermal quenching causing them to shift to
lower temperatures. Thermal quenching effects in several thermoluminescent phosphors have been investigated by Gorbics et al (1969).

2.2.9. Effect on glow curves of second-order kinetics

The effect on glow curves of second-order kinetics is best shown by considering a specific case. Assuming an equal probability of retrapping or a luminescent transition, for a single trap depth the intensity is given by

\[ I(t) = \omega n_0 s \exp\left(\frac{-E}{kT}\right) \left[ 1 + \int_{0}^{t} \frac{s \exp\left(-\frac{E}{kT}\right)}{S} \, dt \right]^{2} \]

From this eqn, \( T^* \) is given by

\[ \frac{6}{2} \frac{E}{kT^*^{2}} \left[ 1 + \int_{0}^{T^*} s \exp\left(-\frac{E}{kT}\right) \, dt \right] = s \exp\left(-\frac{E}{kT^*}\right) \]

which differs from eqn. (2.7) by the factor

\[ \frac{1}{2} \left[ 1 + \int_{T^*}^{T} s \exp\left(-\frac{E}{kT}\right) \, dt \right] = \frac{n_0}{2n^*} \]

where \( n^* \) is the number of electrons left in traps at \( T^* \). This difference is not large; \( T^* \) is increased by the order of 1%. The main difference from first-order kinetics is that a greater fraction of the light is produced at temperatures above the peak temperature because the retrapping effectively delays the release of the electrons. This is illustrated in figure 2.9, which compares the glow curves from a single type of trap, assuming either 1st order or 2nd order kinetics.

These glow curves apply when the concentration of traps is comparable to or greater than the concentration of luminescent centres. As the concentration of luminescent centres relative to the concentration of traps is increased, the probability of retrapping decreases, and the curve for 2nd order kinetics moves closer to the curve for 1st order kinetics. When the concentration of luminescent centres is very much greater than the concentration of traps, the 2nd order curve is practically indistinguishable from the 1st order curve.

2.2.10. Temperature independence of \( s \), the frequency factor

In the preceding analyses, it has been assumed that \( s \) is independent of temperature. Keating (1961) has considered changes in the shape of the glow curve for various functions \( s(T) \).

2.2.11. Emission spectra and luminescent centres

Any study of glow curves is, of course, dependent on the spectral response of the light detector, which should ideally be uniform over the range of wavelengths of interest. To be sure of obtaining all possible information,
the detector should be capable of detecting photons ranging in energy from near zero to the difference in energy between the conduction and valence bands. This is not generally feasible, and it must always be borne in mind that glow curves are probably being distorted by the detector response. The emission spectra of some phosphors in common use are shown in figure 2.10. The spectral responses of several different types of photocathode used in photomultiplier tubes are shown in figure 6.3.

The electron or hole-activated luminescent centres illustrated in figure 2.5 are believed to exist in phosphors such as LiF. Radiation releases electrons and holes which may be trapped at a variety of crystal defects. However, equal numbers of electrons and holes must be trapped to avoid a build-up of one sign of charge carrier. For example, in a particular phosphor electrons may be trapped at one type of defect and holes at another, deeper trap. If the phosphor is subsequently heated to a temperature such that the electrons are released but the holes remain trapped, electrons may migrate via the conduction band to encounter hole traps, where the electrons and holes annihilate with the emission of light. In such a case the distinction between 'traps' and 'luminescent centres' is simply the difference between shallow and deeper traps containing opposite charge carriers. It is interesting to note that luminescent centres are generally assumed to be stable with time, but this need not be so. In figure 2.5, electron and hole-activated luminescent centres are depicted as traps, but are positioned somewhat deeper than normal traps to indicate their greater stability.

Other types of luminescent centre may exist. For example, some types of defect may accept a charge (with the emission of light) and then be complete, so they cease to act as luminescent centres. It is generally assumed, in the analysis of thermoluminescent mechanisms, that released charge carriers of the same sign will produce the same luminescent spectrum, whatever the depth of trap, as long as the process is phosphorescence. A totally different spectrum will occur for a glow peak which results from direct charge transfer between a pair of associated centres, if no interaction with the conduction or valence bands takes place.
CHAPTER 3. THEORY OF THERMOLUMINESCENT DOSE MEASUREMENT

In this chapter the theory of thermoluminescent dose measurement is developed, in order to determine firstly the factors which govern the reading obtained from a dosemeter, and thence the various sources of error involved. The theory is extended to investigate the response of semi-transparent dosemeters to penetrating and non-penetrating radiations, to complement the work on LiF/PTFE discs described in later chapters. The theory is also applied to calibration techniques.

3.1. Identification of variables

3.1.1. Relating the light output from the dosemeter to the dose and dose distribution throughout the dosemeter

The quantity of light $L(\lambda)$, due to an absorbed dose, detected and measured during the heating cycle will be proportional to :-

(a) $D_0$, the absorbed dose. Whether this is the peak or mean dose will depend on the method of evaluating $k_1$ (see below).

(b) $P(\lambda)$, the light generated in the dosemeter per unit absorbed dose. The emission spectra of all phosphors in common use are fairly broad (see figure 2.10), and thus the relative quantum efficiency of the detector should preferably be uniform (and at least stable) over the spectral region of interest. $P(\lambda)$ is a very complex function; it is the sum of contributions from different traps and depends on :

(i) The mean phosphor sensitivity (i.e. the mean light output per unit absorbed dose) throughout the dosemeter, the mass of phosphor, and in some cases on the percentage loading of phosphor in the dosemeter and the uniformity of the mix with other (generally inert) materials.

(ii) The mean absorbed dose. Non-linearity of light output vs absorbed dose occurs in many TL phosphors. This non-linearity has also been shown to be LET dependent.

(iii) The thermal and radiation history.

(iv) The time interval between irradiation and readout.

(v) The heating rate during readout (Gorbics et al, 1969). The light output often decreases at high heating rates due to thermal quenching.

(c) A geometrical - optical factor $k_1$, summarising the effects of dosemeter shape and transparency, the distribution of dose throughout the dosemeter, and the effective geometrical efficiency of light collection. $k_1$ is a function of :

(i) $\nu$, the mass absorption coefficient of the radiation.
(ii) $A(\lambda)$, the absorption coefficient of the dosemeter for the light generated within the dosemeter.

(iii) $G$, the geometrical efficiency of light collection.

(iv) $r$, the effective tray reflectivity (see section 3.2).

(v) the orientation of the dosemeter in the readout instrument (see section 3.2).

(d) A factor $k_2$, the fraction of the total light sum measured. This will be a function of the heating cycle used, and the interval over which the light is measured.

The light $L(\lambda)$ reaching the PM tube photocathode (or optical filter arrangement associated with the photocathode) due to an absorbed dose, and measured, is thus given by

$$L(\lambda) = P(\lambda) k_1 k_2 D_0$$ \hspace{1cm} (3.1.)

The total light measured $L' = L(\lambda) + B(\lambda)$, where $B(\lambda)$ is the light due to an unirradiated dosemeter. In many applications the signal $L(\lambda)$ is large compared with the background $B(\lambda)$. However in low dose applications $B(\lambda)$ can be a limiting factor, and the contributions to $B(\lambda)$ are considered in detail in Chapter 10. $B(\lambda)$ is assumed to be negligible throughout the remainder of this chapter.

### 3.1.2. Relating the readout instrument display reading to the light output from the dosemeter

The light from the dosemeter may be modified by optical filters with a transmission characteristic, $F(\lambda)$, before it reaches the PM tube photocathode. The photons reaching the photocathode are converted to electrons in a manner determined by the quantum efficiency, $Q(\lambda)$, of the PM tube. This electrical signal is amplified within the PM tube by the gain, $M$. Thus the output charge from the PM tube due to a light signal, $L(\lambda)$, reaching the photocathode or associated filter is:

$$\int_0^\infty L(\lambda) F(\lambda) Q(\lambda) M \, d\lambda \text{ coulombs}$$

This signal may still not be powerful enough to drive a display and is often further amplified, usually by a DC amplifier or a high sensitivity charge-to-pulse convertor (CTPC). Taking the latter case as an example, let the conversion characteristic of the CTPC be $C$ counts per coulomb. The display reading, $R$, is then equal to

$$C \int_0^\infty L(\lambda) F(\lambda) Q(\lambda) M \, d\lambda \text{ counts}$$
Substituting for $L(\lambda)$ from eqn. 3.1, this becomes

$$R = k_1 k_2 D \frac{C}{A} \int_{\infty}^{\infty} L(\lambda) F(\lambda) Q(\lambda) \lambda d\lambda \text{ counts} \quad \ldots \ldots \ldots \ldots (3.2)$$

In practice, the sensitivity of the light measurement system is often checked by means of a reference light source of intensity $U(\lambda)$. When exposed to the PM tube this will produce a signal of, say, $f_0$ counts per second at a certain sensitivity setting. On the same sensitivity setting the reading $R'$ from the dosemeter will be

$$R' = \frac{\int_{0}^{\infty} L(\lambda) F(\lambda) Q(\lambda) d\lambda}{\int_{0}^{\infty} U(\lambda) F(\lambda) Q(\lambda) d\lambda} \quad \ldots \ldots \ldots \ldots (3.3)$$

### 3.2. Determination of $k_1$, for thin dosemeters of uniform cross-sectional area

$k_1$ can be evaluated for thin dosemeters of uniform cross-sectional area irradiated by a collimated beam incident normally on one surface of the dosemeter. This example approximates the situation in radiological protection, where such dosemeters (e.g. LiF/PTFE discs) are often used, either taped to a finger or in a badge under appropriate filters for measuring skin and whole body dose.

The description 'thin' implies that the geometrical efficiencies of light collection from thin cross-sectional layers of the dosemeter do not vary significantly throughout the dosemeter thickness (i.e. the dosemeter thickness is small compared with the dosemeter to photocathode distance).

#### 3.2.1. Dose distribution through dosemeter

Referring to figure 3.1, it is assumed that the dosemeter is matched to the surrounding media, that secondary electron equilibrium has been reached, and that the source is sufficiently far away to minimise inverse square law effects. Let $D_0$ be the peak dose deposited at surface 1, and $T$ be the dosemeter thickness. The dose distribution through the dosemeter is illustrated in figure 3.1 (b), and is of the form

$$D_t = D_0 \exp(-\nu t) \quad \ldots \ldots \ldots \ldots (3.4)$$

where $\nu$ is the mass energy absorption coefficient,

$t$ is the distance from surface 1 (in mg cm$^{-2}$),

and $D_t$ is the dose deposited at a distance $t$ from surface 1.

#### 3.2.2. Reflectivity of dosemeter tray

During readout, some of the light collected will be due to reflection from the dosemeter heating tray. Let the tray reflectivity be $r'$. In a
Figure 3.1. Idealised irradiation conditions

(a) Irradiation conditions

Collimated radiation

Surface 1

Surface 2

(b) Dose distribution

Distance from surface 1

Figure 3.2.

Side view of readout arrangement, showing light paths from dosemeter to photocathode (surface 1 nearest photocathode)
practical system the solid angle subtended by the tray surface to the PM tube photocathode will be slightly less than the average solid angle \( \Theta \) subtended by the dosemeter. Additionally, there may be some light scattering at the dosemeter/tray interface, thus we can define an effective tray reflectivity \( r \), where \( r < r' \), to compensate for these effects, but \( r \) will be dependent on the type of dosemeter as well as the type of tray.

3.2.3. **Self-attenuation of light output by the dosemeter**

The light generated within the dosemeter will be attenuated in its path to the PM tube by absorption and scattering effects within the dosemeter. The attenuation is of the form

\[
I_t = I_o \exp\left(-\alpha(X) t\right) \quad \text{(3.5)}
\]

where \( I_o \) is the intensity of the light at point 0,

\( I_t \) is the intensity at a distance \( t \) from 0,

and \( \alpha(X) \) is the coefficient of attenuation by the dosemeter of its internally generated light. Assume this is uniform throughout the dosemeter.

Referring to figure 3.2, light from the phosphor point volume 0 in a very thin phosphor layer \( dt \), situated at a depth \( t \) from surface 1, is emitted equally in all directions. All light from the grain 0 which reaches the PM tube is emitted either:

- (a) into the solid angle \( \text{BOG} \); all light except that emitted in the direction \( \text{OA} \) traverses a distance through the dosemeter greater than \( t \).
- (b) into the solid angle \( \text{DOF} \), reaching the PM tube after specular reflection at the dosemeter/tray interface; similarly, most of the light traverses a distance through the dosemeter greater than \( (2T - t) \).
- (c) in other directions, reaching the PM tube after scattering within the dosemeter. This contribution can reasonably be assumed to be negligible for practical dosemeter dimensions.

Figure 3.3 shows in greater detail the path of the light rays from 0 which eventually strike a general point \( H \) on the PM tube photocathode. The rays \( \text{OB} \) and \( \text{DE} \) are approximately parallel if the thickness of the dosemeter is very much less than the distance from the dosemeter to the PM tube. The angles \( \alpha' \) shown may differ from angles \( \alpha \) due to refraction at the dosemeter/air interface.

- (a) The distance travelled through the dosemeter by the light ray \( \text{OB} = \frac{t}{\cos \alpha} = m_1 t \), where \( m_1 \) is a constant
Figure 3.3. Side view of dosemeter, showing light paths from 0 to H.

To point H on PM tube photocathode

Figure 3.4. Readout arrangements

(a) PM tube

(b) PM tube
The distance travelled through the dosemeter by the light ray
\[ \text{O}_{DE} = \text{OD} + \text{DE} = \left( \frac{T-t}{\cos \alpha} \right) + \frac{T}{\cos \alpha} = m_1(2T-t) \]

Similarly, the distance travelled through the dosemeter by rays from 0 which strike the photocathode at some other point \( H' \) is given by (a) \( m_2t \) and (b) \( m_2(2T-t) \), where \( m_2 \) is a constant.

This argument can be extended to any ray which originates from any other phosphor point volume in the layer \( dt \) and eventually strikes the photocathode, and can similarly be applied to other phosphor layers. Averaging over all phosphor point volumes, and all points on the photocathode, the average distance travelled through the dosemeter by all rays originating in it and striking the photocathode is given by (a) \( m_1t \) and (b) \( m_2(2T-t) \), where \( m_1 \) is a constant.

For light emitted in the direction of the PM tube :-
Average distance = \( k_3t \)

For light emitted in the direction of the tray :-
Average distance = \( k_3(2T-t) \)

where \( k_3 \) is a constant whose value is determined by the form of the dosemeter and the geometry of light collection. It is given by
\[ k_3 = \sum_{n} \frac{m_n}{m} \]

where \( m_n \) is a constant for the \( n \)th ray. \( k_3 \) will be independent of \( t \) as long as the thickness of the dosemeter is very much less than the distance from the dosemeter to the PM tube, i.e. if the angle \( \alpha \) is essentially independent of \( t \).

### 3.2.4 Combined effects of dose distribution, attenuation of light output, and tray reflectivity, during readout

Let a thin dosemeter of thickness \( T \) be irradiated as in figure 3.1.(a) ; surface 1 is closest to the radiation source.

1. **Readout with surface 1 closest to the PM tube**

   The readout configuration is shown in figure 3.4 (a)

   \[ L(\lambda) = P(\lambda) k_1 k_2 D_0 \]

   The light \( dL(\lambda) \) reaching the detector from a thin layer \( dt \), at a distance \( t \) behind surface 1, is given by

   \[ dL(\lambda) = P(\lambda) k_2 D_0 e^{-\lambda t} \left[ G e^{-A(\lambda)k_3 t} + G r e^{-A(\lambda)k_3 (2T-t)} \right] dt \]

   (i.e. light generated in \( dt \) reaching detector directly + light reaching detector after reflection at tray).

   \( G \) is assumed to be constant over all points in the dosemeter. It
can be shown (e.g. Karzmark et al, 1965; see also section 6.1) that variations in $G$ will be of the order of 1% for a typical reader and dosimeter (thin disc) arrangement.

Putting $b = A(A)k_3$, and simplifying,

$$dL(\lambda) = \frac{P(\lambda)k_2D_0 G}{T} \left[ \exp\left\{-(\nu+b)t\right\} + r \exp\left\{-2bt\right\} \exp\left\{-(\nu-b)t\right\} \right] dt$$

:: Total light output $L(\lambda)$ is given by

$$L(\lambda) = \frac{P(\lambda)k_2D_0 G}{T} \int_0^T \left[ \exp\left\{-(\nu+b)t\right\} + r \exp\left\{-2bt\right\} \exp\left\{-(\nu-b)t\right\} \right] dt$$

:: Comparing with equation 3.1,

$$k_1 = \frac{G}{T} \left[ - \exp\left\{-(\nu+b)t\right\} - r \exp\left\{-2bt\right\} \exp\left\{-(\nu-b)t\right\} \right]$$

$$= \frac{G}{T} \left[ 1 - \exp\left\{-(\nu+b)t\right\} + r \exp\left\{-2bt\right\} \left(1 - \exp\left\{-(\nu-b)t\right\}\right) \right] \quad \ldots (3.6)$$

The above equation simplifies as $b \to 0$ (i.e. $A(\lambda) \to 0$), or as $\nu \to 0$.

(a) $\nu \to 0$

$$k_1 = \frac{G}{T} \left[ \left(1 - \exp\left\{-bt\right\}\right) - r \exp\left\{-2bt\right\} \left(1 - \exp\left\{-bt\right\}\right) \right]$$

$$= \frac{G}{T} \left(1 - \exp\left\{-bt\right\}\right) \left(1 + r \exp\left\{-bt\right\}\right) \quad \ldots (3.7)$$

(b) $b \to 0$ (i.e. $A(\lambda) \to 0$)

$$k_1 = \frac{G}{T} \left[ \left(1 - \exp\left\{-vt\right\}\right) + r \left(1 - \exp\left\{-vt\right\}\right) \right]$$

$$= \frac{G}{T} \left(1 + r\right) \left(1 - \exp\left\{-vt\right\}\right) \quad \ldots (3.8)$$

(c) $\nu \to 0$, $b \to 0$

$$k_1 = G(1 + r), \quad \ldots (3.9)$$

since $\left(1 - \exp\left\{-vt\right\}\right) \to 0$ as $\nu \to 0$.

(ii) Readout with surface 2 closest to the PM tube

The readout configuration is shown in figure 3.4.(b).

$$dL(\lambda) = \frac{P(\lambda)k_2D_o}{T} \exp\left\{-vt\right\} \left[ G \exp\left\{-b(T-t)\right\} + Gr \exp\left\{-bt\right\} \exp\left\{-bt\right\} \right] dt$$

(i.e. light generated in $dt$ reaching detector directly + light reaching detector after reflection at tray).

$$dL(\lambda) = \frac{P(\lambda)k_2D_o}{T} G \exp\left\{-bt\right\} \left[ \exp\left\{-(\nu+b)t\right\} + r \exp\left\{-(\nu+b)t\right\} \right] dt$$
This equation simplifies as $b \to 0$ or as $v \to 0$, resulting in equations identical to equations (3.7), (3.8) and (3.9), for similar conditions.

3.2.5. Dependence of light output from dosemeter on the orientation of the dosemeter in the tray

With the notation of figure 3.1.(a), it can be seen by comparing equations (3.6) and (3.10) that, if $v$ and $b \neq 0$, then the light output from the dosemeter during readout will differ according to whether surface 1 or 2 is nearest the PM tube.

Let the light reaching the detector when surface 1 is nearest the detector be $L_1$. Let the light reaching the detector when surface 2 is nearest the detector be $L_2$. Then, from equations (3.6) and (3.10),

$$\frac{L_2}{L_1} = \exp \left\{ \frac{-bf}{T} \right\} \left[ \frac{(v+b)\left(1 - \exp\left\{-\frac{(v-b)T}{v+b}\right\}\right) + r(v-b)\left(1 - \exp\left\{-\frac{(v+b)T}{v+b}\right\}\right)}{(v-b)\left(1 - \exp\left\{-\frac{(v+b)T}{v+b}\right\}\right) + r(v+b)\exp\left\{-\frac{2bf}{T}\right\} \left(1 - \exp\left\{-\frac{(v-b)T}{v+b}\right\}\right)} \right]$$

\hspace{10cm} \ldots \ldots \ldots (3.11)

Note that $\frac{L_2}{L_1} \to 1$ as $b \to 0$ or as $v \to 0$.

In practice this dependence on dosemeter orientation is important for the case of semi-transparent dosemeters irradiated with radiation having a significantly high mass absorption coefficient, e.g. beta particles. A similar dependence on dosemeter orientation can arise due to causes other than attenuation of the radiation by the dosemeter, i.e. in any situation where there has been an appreciable dose gradient across a semi-transparent dosemeter. However, the above equations have been derived assuming an exponential fall in dose across the thickness of the dosemeter, and do not necessarily apply to other situations. Transparent dosemeters are not affected by dosemeter orientation.

The applications of equation (3.11) are discussed further in Chapter 11.

3.2.6. Effective light transmission of semi-transparent dosemeters

It is helpful in the design of semi-transparent dosemeters to be able to make use of the preceding equations to predict the response to radiations of various mass absorption coefficients. This necessitates a knowledge of $b = A(\lambda)k_3$ for the readout instrument. A simple method of measuring this is illustrated in figure 3.5. A thin solid-state light source, having an emission spectrum similar to that of the dosemeter, is placed on the dosemeter tray, and a reading, $R_1$, taken. The dosemeter is then placed on top of the light source, and another reading, $R_2$, taken. If necessary,
optical coupling compound can be used between the light source and the
disc to minimise light scattering. The effective transmission, $t_m$, is
deﬁned as the ratio of the second over the ﬁrst reading. It can be
seen from the argument in section 3.2.3, that if the distance from the
dosemeter to the photocathode is very much greater than the thicknesses
of the disc and light source, then $t_m$ is given by:

$$t_m = \frac{R_2}{R_1} = \exp\{-A(\lambda)k_3T\} = \exp\{-bf\},$$

from which $b$, the 'effective coefficient of attenuation' by the dosemeter
of its internally generated light, can be found.

This method of measuring the effective transmission was utilised in
experiments with LiF/PTFE discs (Chapter 8). The usefulness of $t_m$ in
predicting the response of semi-transparent dosemeters to non-penetrating
radiations is discussed in Chapter 11.

3.3. Some calibration techniques and problems

3.3.1. Calibration of dosemeters in a known photon field

When calibrating the sensitivity of dosemeters it is usual to irradiate
them in a known radiation field of photons of about 1 MeV energy. $^{60}$Co is
generally used, since it has the convenience of a 'clean' photon energy
spectrum and a reasonably long half-life, and is readily available at a
comparatively low cost. Some calibration errors are inevitable in
relating the photon field to an absolute standard, but an uncertainty of
not more than $1\%$ is attainable. The photon field is usually calibrated in
rads in air.

Dose should be deposited uniformly throughout the dosemeter to simplify
interpretation of results. This requirement is especially important for
semi-transparent dosemeters, due to the orientation effect. Non-uniformity
of dose can be caused by absence of charged particle equilibrium, or by
attenuation or inverse-square law effects. With $^{60}$Co, attenuation through
the dosemeter is generally negligible, i.e. $\nu \rightarrow 0$.

3.3.2. Charged particle equilibrium

Charged particle equilibrium can be approximately attained throughout the
dosemeter as illustrated in figure 3.6. A sufﬁciently thick slab of
medium or dosemeter equivalent material is interposed, close to the
dosemeter, between the dosemeter and the radiation source. The exact
choice of material will depend on how well the dosemeter is matched to the
medium of interest. The slab performs two functions, which may be
summarised as the attainment of approximate secondary equilibrium within
the dosemeter by removal of 'build-up' and 'build-down' effects.
Figure 3.5. Measurement of effective light transmission ($t_m$) of a dosemeter

Figure 3.6. Approximate attainment of charged particle equilibrium

Figure 3.7. Inverse-square law effects
The well-known 'build-up' effect (e.g. Boag, 1966) is associated with irradiation by a photon beam. The thickness of air intervening between the radiation source and the dosemeter is often much too small, or the beam too narrow, to allow the equilibrium electron field to be attained in air. The ionisation density in an unshielded dosemeter builds up from a low value at the surface nearest the radiation source to a maximum value (which may or may not be reached in the dosemeter, depending on its thickness) at which secondary electron build-up is balanced by the absorption and inverse-square decrease of the primary beam. The build-up material placed in front of the dosemeter should be of such a thickness that the maximum ionisation density is reached at about the front surface of the dosemeter. The optimum thickness of build-up material will vary with photon energy and atomic number. For a tissue-equivalent material and $^{60}$Co, it is about 4mm.

In the not so well-known 'build-down' effect, a decrease in dose is observed when build-up material is placed in front of the dosemeter. This is due to removal from the beam of electrons of appreciably higher energy or intensity than those generated within the build-up material. For example, higher energy electrons may be generated in materials used in the construction of the radioactive source.

3.3.3. Dose gradients due to inverse-square law effects

With reference to figure 3.7, a thin disc dosemeter of thickness $T$ and radius $R$ is being irradiated by a point source placed at a distance $r$ from the nearest surface (surface 1) of the disc. It is assumed that only inverse-square law effects are operating. The highest dose ($D_1$) is to a point $A$ at the centre of surface 1. The lowest dose ($D_2$) is to points such as $B$ on the rim of surface 2.

A useful criterion for uniform irradiation throughout the dosemeter is if the ratio $D_2/D_1$ is greater than or equal to a certain fraction $x$,

\[
\frac{D_2}{D_1} \geq x
\]

i.e. if $D_2 \geq x$, where $x$ is somewhat less than unity.

\[
D_1 \propto \frac{1}{r^2} \quad \text{and} \quad D_2 \propto \frac{1}{(r + T)^2 + R^2}
\]

\[\therefore \text{The above criterion becomes:} \]

\[
\frac{r^2}{(r + T)^2 + R^2} \geq x
\]

from which \[r^2 \geq \frac{x}{1-x} \cdot (R^2 + 2rT)\] \[.........(3.12)\]
As a practical example, put $R = 5 \text{ mm}$, $T = 0.4 \text{ mm}$, and $x = 0.99$ (i.e., 1% variation in dose throughout the dosemeter). These are relevant dimensions for a LiF/PTFE disc, 12.7 mm in diameter $\times$ 0.4 mm thick, read out in the 'Toledo' TLD reader (there is a 10 mm aperture in the light measurement system). Substituting these values in equation 3.12, it is found that $r \gg 103.4 \text{ mm}$ to achieve less than 1% variation in dose throughout the dosemeter.

3.3.4. Underestimation of dose when $\nu$ is significant

Consider the usual situation, where a TLD system has been calibrated in a radiation field such that the dose gradient across the thickness of the dosemeter due to attenuation effects is negligible, i.e., $\nu \to 0$. This leads to errors when subsequently measuring radiation for which $\nu$ is appreciable, where there is a significant dose gradient across the thickness of the dosemeter due to attenuation of the radiation by the dosemeter. These errors can be assessed for thin dosemeters of uniform cross-sectional area by comparing the appropriate values obtained for $k_1$ in section 3.2.4.

Irradiation is as in figure 3.1.

For optically transparent dosemeters, i.e., $b \to 0$, the ratio $R_T = \frac{k_1(\nu \neq 0)}{k_1(\nu \to 0)}$ is given by:

$$R_T = 1 - \exp\left[-\frac{\nu T}{\nu T}\right] \quad \text{(3.13)} \quad \text{(cf equations 3.8 and 3.9)}$$

For semi-transparent dosemeters, i.e., $b \neq 0$, read out with surface 1 closest to the PM tube, the ratio $R_{ST1} = \frac{k_1(\nu \neq 0)}{k_1(\nu \to 0)}$ is given by:

$$R_{ST1} = b \left[ \frac{1 - \exp\left[-(\nu+b)T\right]}{\nu+b} + r \exp\left[-2bT\right] \frac{1 - \exp\left[-(\nu-b)T\right]}{\nu-b} \right] \left(1 - \exp[-bT]\right) (1 + r \exp[-bT])$$

$$\quad \text{(3.14)} \quad \text{(cf equations 3.6 and 3.7)}$$

For semi-transparent dosemeters read out with surface 2 closest to the PM tube:

$$R_{ST2} = \frac{1 - \exp\left[-(\nu-b)T\right]}{\nu-b} + r \exp(-bT)$$

$$\quad \frac{1 - \exp\left[-(\nu-b)T\right]}{\nu-b} \left(1 - \exp[-bT]\right) (1 + r \exp[-bT]) \quad \text{(3.15)} \quad \text{(cf equations 3.7 and 3.10)}$$

The practical effects of these results are illustrated in figure 3.8, in which the ratios are plotted for a dosemeter of thickness 50 mgcm$^{-2}$. In curve 1 the dosemeter is assumed to be transparent. Dosemeter orientation in the tray and tray reflectivity do not affect the ratio. In the other
Figure 3.8. Theoretical effect of dosemeter orientation and tray reflectivity on relative light output
(dosemeter thickness, $T_z = 50$ mg cm$^{-2}$)

(1) $t_m = 1$
(2) $t_m = 0.1$, $r = 0$, surface 1 nearest PM tube
(3) $t_m = 0.1$, $r = 0$, surface 2 nearest PM tube
(4) $t_m = 0.1$, $r = 1$, surface 1 nearest PM tube
(5) $t_m = 0.1$, $r = 1$, surface 2 nearest PM tube

Mass absorption coefficient, $\gamma$ (cm$^2$ g$^{-1}$)

$E_0$ (MeV), assuming media is tissue
curves the dosemeter is assumed to have an effective transmission $t_m$ of 0.1 during readout. The reading is then dependent both on dosemeter orientation in the tray and tray reflectivity. Considering first the case when $r = 0$, it can be seen that a semi-transparent dosemeter underestimates less than a transparent dosemeter of the same thickness when surface 1 is nearest the detector (curve 2), but underestimates more when surface 2 is nearest the detector (curve 3).

Next, to consider the effects of variations in tray reflectivity, corresponding curves are plotted for the above cases, with $r = 1$. It can be seen that when surface 1 is nearest the detector, an increase in tray reflectivity causes a greater underestimate (curve 4). However, if surface 2 is nearest the detector, an increase in tray reflectivity has the opposite effect (curve 5).

Thus, if the mass attenuation coefficient of the dosemeter for a given radiation is greater than that for the calibrating radiation, the dosemeter will always under-respond, but the degree of this effect varies subtly due to optical considerations. The values for $T$ and $t_m$ used in figure 3.8 were selected to illustrate the effect, rather than to simulate any particular practical situation. However, in chapter 11 the above results are applied to the design of LiF/PTFE discs for the measurement of surface doses.

3.3.5. Dose evaluation

TLD is a comparative technique and unknown doses are measured by comparing the dosemeter readings with the readings from the same or similar dosemeters irradiated to known doses. Dose evaluation could be achieved by first calibrating a group of dosemeters and subsequently re-using the same dosemeters for the measurement of unknown doses, but this method has two disadvantages; (a) no compensation is made for any change in sensitivity with re-use, and (b) there is no direct check on the stability of the readout instrument. Thus, dose evaluation is generally carried out by comparison with similar dosemeters irradiated to known doses at about the same time. Calibrated dosemeters are required to determine both sensitivity and background. 'Sensitivity calibration dosemeters' are irradiated to a known dose very much greater than the expected standard deviation of the background signal. 'Background calibration dosemeters' receive zero dose, apart from natural background radiation. A statistically significant fraction of an experimental group of dosemeters should be selected for calibration purposes. For example, for a group of 100 dosemeters, 10 sensitivity and 5 background calibration dosemeters would be adequate for most applications.

The doses received by operational dosemeters are evaluated simply by
comparison with the readings from the calibrated dosemeters. For ease of interpretation the reader can be adjusted to give a direct reading of dose in suitable units, but this should be regarded simply as an aid to the operator; precise measurements can only be obtained by comparison. Measurements can be obtained either by assigning the mean sensitivity of the group to all dosemeters in the group or, more accurately, by precalibrating the sensitivity of individual dosemeters. In the latter case it is assumed that the whole group will undergo similar thermal treatment, and that the relative sensitivities between dosemeters will be maintained after the precalibration dose and the following read cycle (including, if necessary, an anneal). Since background signals are relatively low in many applications, it is usual to determine a mean background signal and apply this to all dosemeters in the same experimental group, rather than to precalibrate the background signals of individual dosemeters. Even for low dose measurements, there is no substantial evidence that precision could be significantly improved by individual calibration of background signals, which are influenced by random events, such as chemiluminescence from a speck of dust.

Before an experiment, all dosemeters in an experimental group should receive a similar thermal treatment (readout and/or anneal), at about the same time, sufficient to standardise their sensitivity and background levels. Most accurate results will be obtained when the sensitivity calibration dosemeters are irradiated at about the same time as the operational dosemeters, thus minimising variations due to pre- and post-dose room temperature annealing. The readout instrument's parameters should not change by an unacceptable amount in the time interval between the readout of calibrated and operational dosemeters, thus calibrated dosemeters are generally read at fixed intervals during the readout of a sequence of operational dosemeters. Following the readout sequence, the readings from the calibrated dosemeters can be analysed to determine whether significant instrumental drift occurred during the readout sequence. If so, the readings from the operational dosemeters can be corrected accordingly. In practice the frequency with which calibrated dosemeters are read out will depend on the accuracy required, and the stability and reliability of the readout instrument.

In radiotherapy measurements, where the dose must be known to the highest possible accuracy, typically 1 sensitivity calibration dosemeter for 10 or less operational dosemeters is employed. Background calibration dosemeters are read out less often. In radiological protection applications, a much lower frequency of readout of calibrated dosemeters
can be tolerated.

Calibration techniques for obtaining precise measurements with LiF/PTFE dosemeters are described in section 9.6. The calibration procedures developed for use with the 'Toledo' Model 654 reader are described in Appendix 2.
CHAPTER 4. THERMOLUMINESCENT PHOSPHORS

Thermoluminescent phosphors are described in this chapter with particular reference to LiF:Mg,Ti, whose thermoluminescent mechanism is discussed in detail. LiF doped with various activators was investigated with a view to producing a phosphor with a simplified glow curve structure.

4.1. General properties of thermoluminescent phosphors

The following general properties of useful thermoluminescent phosphors are arrived at by combining basic theory with operational considerations.

4.1.1. Characteristics of pure materials suitable for potential development into thermoluminescent phosphors

Stability of chemical form is a mandatory requirement; materials should be resistant to chemical attack both from the atmosphere and also from a wide range of solvents, and their physical and chemical structure should not be significantly affected either by temperatures ranging from ambient to the readout and annealing temperatures, or by other environmental factors such as humidity, light, and pressure. For loose powder measurements it is advantageous if crystals of size 75 to 200 microns can readily be manufactured (see section 7.2). The colour of the crystal should be such that photons generated within the crystal volume during the thermoluminescence process reach the crystal surface without appreciable attenuation, i.e. there should be few absorption bands in the visible region of the electromagnetic spectrum. In its dosimetric form the material must be sufficiently non-toxic to allow routine handling with few precautions.

4.1.2. Sensitivity

The intrinsic efficiency of energy conversion, i.e. the light output per unit absorbed dose, will be determined by the concentrations and types of activators and defects present in the thermoluminescent phosphor. To obtain a high energy conversion efficiency, the phosphor should have a high concentration both of electron or hole traps and of luminescent centres, and a high efficiency of luminescence when the charge carriers are thermally released and recombine. The measurable dose range will be determined not only by phosphor sensitivity but also by other factors such as glow peak structure, emission spectra, and variations in background signal, which are discussed below.

4.1.3. Glow curve structure and stability of stored signal

For the greatest simplicity of operation and interpretation of readings the phosphor should have a simple trap distribution, with preferably a single
trap depth. The glow curve structure also affects the stability of the stored signal with respect to time and storage temperature. For long storage of trapped electrons or holes at normal working temperatures the trap depth \(E\) needs to be large, and the frequency factor \(s\) low. In some phosphors the glow curve structure is a function of thermal history, e.g. the structure can be altered in a temporary or permanent way by certain annealing procedures.

Most commonly used phosphors have the main glow peak temperature at about 200°C. If it is much higher, it becomes more difficult to discriminate against spurious and thermal radiation from the phosphor and the heating source; if it is much lower, fading of the stored signal becomes operationally significant. The temperature at which a glow peak appears is not fixed but varies with the heating rate roughly as predicted by the theory of Randall and Wilkins (1945). Figure 4.1 shows the extent of these variations for the major glow peaks of several thermoluminescent phosphors, as measured by Gorbics et al. (1969), using special care to control and measure the phosphor temperature. This fundamental dependence on heating rate, combined with the effect of poor thermal contact, which commonly occurs between the thermocouple and the phosphor, accounts for much of the variability of glow peak temperatures reported in the literature, and careful interpretation is required when comparing earlier results. The integrated light sum is also dependent on heating rate, due to the thermal quenching effect, which leads to a reduction in light output at fast heating rates (Gorbics et al., 1969).

In phosphors with complex trap structure, such as LiF:Mg,Ti, the stability of the stored signal with time is sometimes dependent not only on fading effects, but also on the migration and aggregation of traps at the storage temperature (Booth et al., 1972; Johnson, 1974). This latter phenomenon can counteract fading, and on occasion lead to an increase in stored signal with time.

Fading of stored signal can also be caused by exposure of the phosphor to light, especially if the light contains a strong ultra-violet (uv) component. The glow curve structure and stability of stored signal are sometimes functions of phosphor grain size (section 8.5).

4.1.4. Emission spectra

The emission spectrum should be such that it matches the detector, which is generally a photomultiplier tube with peak sensitivity in the blue region of the spectrum. Thermal radiation emitted by the hot phosphor and the heating source is situated in the red and near infra-red region,
Temperatures of the major glow peaks of several TL materials as a function of heating rate (Gorbics et al, 1969)

Figure 4.1.

Glow curve structure of LiF(TLD-100) and effect of 80°C anneal

(A) Fast cool from 400°C
(B) Fast cool from 400°C + 80°C for 16 hours.
hence the shorter the wavelength of the emission spectra the easier it is to discriminate against thermal radiation. Near ultra-violet, blue, or green emission is preferred; orange or red emissions are disadvantageous. Emissions in the ultra-violet region necessitate the use of a quartz window photomultiplier tube.

4.1.5. Response vs dose, dose-rate, and dose history

The response vs dose characteristic should be linear over as wide a dose range as possible. Many phosphors have a supralinear response above a certain dose level and various mechanisms have been proposed to explain this (Cameron et al., 1968; Claffy et al., 1968; Attix, 1974). For some phosphors there is an inverse relationship between the linear energy transfer (LET) of the radiation and the amount of supralinearity (Naylor, 1965; Wagner et al., 1966; Suntharalingam, 1967). At very high doses the response saturates as all the available traps are filled, or as radiation damage takes effect. Supralinearity is probably batch dependent, so for highest accuracy each batch of phosphor should be calibrated over the dose range in which it is to be used.

Exposure to high doses can cause sensitivity enhancement (often referred to as 'sensitization') and remove the supralinearity for subsequent doses (Zimmerman et al., 1964). The sensitivity enhancement may also show a LET dependence (Suntharalingam, 1967; Cameron et al., 1968). A feature of some thermoluminescent phosphors is their extremely low dose-rate dependence, up to at least $10^8$ rad/sec (Karzmark et al., 1964; Marrone & Attix, 1964; Goldstein, 1972).

4.1.6. Background signals

Variations in background signal, which is defined as the reading obtained when a zero-dose dosemeter is read out, limit the lowest measurable dose. Contributions to this signal from the phosphor are discussed below.

Thermal radiation from the hot phosphor and the heating source can be minimised by careful choice of heating cycle, and by using infra-red absorbing filters. As mentioned earlier, this is easier to achieve if the phosphor emission spectrum is at shorter wavelengths than that of orange light. Non-radiation induced signals can be caused both by a chemiluminescence reaction, e.g. light emitted during the oxidation of contaminants such as oil and dust, and by triboluminescence (shock and friction effects). These signals can often be considerably reduced by reading out dosemeters in an inert gas stream, i.e. by removing oxygen from the dosemeter's environment during the heating cycle (Aitken, 1963; McGall, 1963; Karzmark et al., 1964; Nash et al., 1965; Rhyner and Cameron,
Generally nitrogen or argon is used. The triboluminescence signal is greatest with loose powder, and can be considerably reduced by either forming or incorporating the phosphor into a solid matrix (Bjarngard and Jones, 1967).

Some phosphors respond to visible and ultra-violet (uv) radiation. There are two distinct mechanisms, which have been defined by Mason (1971) as the intrinsic and the induced responses. The thermoluminescence signal obtained by exposure of previously unirradiated phosphor to uv radiation is the intrinsic response. The induced response is dependent on the phosphor's dose and thermal history. Some phosphors store a fraction of their absorbed energy in deep traps which are not affected by the usual readout cycle. Irradiation with uv light can cause some of this absorbed energy to be transferred to shallower traps. Thus if a phosphor is first irradiated and read out such that the deep traps are not destroyed, and then exposed to uv light, a subsequent readout yields a light sum which is a function of dose and thermal history. The phenomenon can be used to check previous readouts, or utilized for a convenient uv dosimeter (Schayes et al, 1967; Linsley & Mason, 1971b; Sunta and Watanabe, 1974). The quantity and quality of the uv light has to be carefully controlled, since in a dosed dosimeter uv light can also cause fading. The induced response is sometimes referred to as photo-transferred or photo-stimulated thermoluminescence (PTTL or PSTL).

High background signals may thus occur when re-using, in daylight, phosphors which have previously been exposed to high radiation doses (but have not had the deep traps removed by an anneal) since daylight contains a uv component. Two other background signals due to deep traps may be noted. Firstly, luminescence from the lower tails of the glow peaks associated with deep traps and secondly, transference from deep traps to dosimetry traps by thermal activation and retrapping.

4.1.7. Photon energy dependence

The thermoluminescent phosphor should respond to radiation in the same manner as the medium in which the dose is to be measured. For photons this requirement is satisfied (macroscopically) if the ratio of the mass energy absorption coefficients of the phosphor and the medium does not vary with the photon energy. The requirement is approximately satisfied (over the energy range of general interest) if the phosphor and the medium have the same 'effective atomic number' (Maynard1937; Jayachandran, 1968), and comparison of effective atomic numbers is thus a simple and useful method of comparing the response to photons of different media. Much research has been devoted to the development of phosphors which are approximately
'tissue equivalent' i.e. in which the phosphor responds to radiation in a similar manner to tissue.

The effective atomic number of the pure starting material will of course be modified by the presence of activators. It is now usual to quote the response of the thermoluminescent material relative to air, to aid interpretation.

In practice the energy dependence may be modified by factors such as the presence of a matrix material and the grain size of the thermoluminescent material, sensitization, self-absorption, backscattering from, and absorption in, the body of the wearer and the degree of electronic equilibrium. For optimum accuracy in a particular TLD system, the energy response of the dosemeter should be determined experimentally. The factor to correct for the energy response of the dosemeter at a given energy can be obtained from the ratio between the response at the energy in question and that at some reference energy, which is commonly taken as that of $^{60}$Co gamma rays.

4.1.8. Response to different types of radiation

As mentioned above, the supralinearity and sensitization effects observed in some phosphors are a function of LET. It is often required to distinguish between beta radiation, low and high energy gamma rays and X-rays, and thermal neutrons. The distinction between beta particles and photons, and analysis of the energy spectrum of photons, can be achieved by the use of filters, or by using the differential response of several phosphors with differing effective atomic numbers. The response of some phosphors to neutrons can conveniently be varied without significantly altering their thermoluminescence characteristics by suitable adjustments to the isotopic composition of their component elements. In calculating the response of a phosphor to thermal neutrons, the thermal neutron capture cross-section of activators should also be taken into account.

4.1.9. Response to electrons and beta radiation

The thermoluminescence from a phosphor irradiated with electrons would be expected to be proportional to the energy absorbed, which is a function of stopping power. For low-energy electrons the response is dependent upon the thickness, shape, and optical transmission of the detector (see Chapter 11) and therefore changes significantly with the energy distribution. Above 1 MeV there is little change in response with energy for typical dosemeter dimensions.
4.1.10. Re-use of phosphors

Thermoluminescent materials are inherently re-usable. The previous dose information has to be erased to a level such that the residual signal does not interfere with subsequent dose measurements, and it is important that the sensitivity and glow curve structure should not be changed significantly by the method of erasure. However, the sensitivity and/or glow curve structure of many phosphors are functions of their dose and thermal history, and consequently operational procedures have to be carefully defined to obtain reproducible readings. These procedures may differ according to the phosphor, the application, and the form of dosemeter.

To obtain the desired stability, certain phosphors may require special thermal treatments prior to re-use i.e. pre-irradiation or post-irradiation anneals. The thermal treatment may be complicated by taking into consideration such additional factors as sensitization, a requirement for dose re-estimation, throughput, or the stability with temperature of any matrix material into which the phosphor may be incorporated. The thermal treatment may be carried out in a separate annealing oven, or incorporated into the heating cycle of the normal readout apparatus.

4.1.11. Other considerations

The phosphors in most common use are those for which the manufacturer has established a good reputation for batch reproducibility. Exact reproducibility of the desired characteristics from one batch of phosphor to the next is extremely difficult to obtain, since variations in activator concentration or type of a few parts per million can cause drastic changes. To some extent, batch reproducibility will depend on the ease of preparation of the phosphor. Some phosphors are currently available from more than one manufacturer, and their properties may vary considerably due to different manufacturing techniques.

Thermoluminescent phosphors cost between about £0.50 and £10 per gram (December, 1974), depending on their ease of preparation and their isotopic composition, the most expensive being those which contain elements which have been isotopically separated.

4.1.12. Characteristics of currently available thermoluminescent phosphors

A large number of thermoluminescent materials have been produced but only a few have sufficiently desirable characteristics to be useful for dosimetry purposes. The properties of the most useful phosphors are given in Table 4.1. Where most of the information on a phosphor has been obtained from a single reference, the reference is indicated beside the
### Table 4.1. Characteristics of some thermoluminescent phosphors

<table>
<thead>
<tr>
<th></th>
<th>LiF:Mg,Tl (1)</th>
<th>Li₂B₂O₅:Mn (1)</th>
<th>CaSO₄:Ti (2)</th>
<th>CaSO₄:Tb (1)</th>
<th>BeO (2)</th>
<th>CaF₂:Tb (4)</th>
<th>CaF₂:Mn (1)</th>
<th>CaF₂(natural) (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective atomic number</td>
<td>8.2</td>
<td>7.4</td>
<td>15.3</td>
<td>15.3</td>
<td>7.2</td>
<td>16.3</td>
<td>16.3</td>
<td>16.3</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>2.64</td>
<td>2.3</td>
<td>2.61</td>
<td>2.61</td>
<td>3.01</td>
<td>3.18</td>
<td>3.18</td>
<td>3.18</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>Good</td>
<td>Hygroscopic</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Very toxic in powder form</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Intrinsic efficiency %</td>
<td>0.039</td>
<td>0.073</td>
<td>1.1</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td>0.44</td>
</tr>
<tr>
<td>Practical sensitivity relative to LiF</td>
<td>1 0.02-0.5*</td>
<td>30 ~70</td>
<td>1.2</td>
<td>15-20</td>
<td>~3</td>
<td>~23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Useful dose range (rad)</td>
<td>10⁻³ - 10⁻⁵</td>
<td>10⁻² - 10⁻⁶</td>
<td>10⁻⁵ - 10⁻⁴</td>
<td>10⁻⁵ - 10⁻⁴</td>
<td>10⁻⁴ - 10⁻⁵</td>
<td>10⁻² - 10⁻⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photon energy response without added filter (0.03/1.25 MeV)</td>
<td>1.25</td>
<td>0.9</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Main glow peak temp(°C)</td>
<td>210</td>
<td>200</td>
<td>220</td>
<td>110</td>
<td>180</td>
<td>140</td>
<td>300</td>
<td>270</td>
</tr>
<tr>
<td>(at a heating rate of 100°C/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Typical range of linear dose-response (rad)</td>
<td>&lt; 300</td>
<td>&lt; 100**</td>
<td>&lt; 3 x 10³</td>
<td>&lt; 5 x 10³</td>
<td>&lt; 50</td>
<td>&lt; 600</td>
<td>&lt; 2 x 10⁵</td>
<td>&lt; 5 x 10³</td>
</tr>
<tr>
<td>Stability of dosimetry</td>
<td>~5% fading in 3 months(12)</td>
<td>~10% fading in 2 months</td>
<td>~1-2% fading per month</td>
<td>35% fading in 1 day</td>
<td>No fading in 2 months</td>
<td>25% fading in first month</td>
<td>~10% fading in first month</td>
<td>43% fading in 9 months</td>
</tr>
<tr>
<td>Emission spectrum peak(nm)</td>
<td>400</td>
<td>605</td>
<td>478 and 571</td>
<td>500</td>
<td>330</td>
<td>483 and 576</td>
<td>500</td>
<td>360</td>
</tr>
<tr>
<td>Response to thermal neutrons</td>
<td>Can be high or low depending on isotopic composition</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>LET dependance</td>
<td>Yes</td>
<td>Yes</td>
<td>Not known</td>
<td>Not known</td>
<td>Not known</td>
<td>Not known</td>
<td>Not known</td>
<td>Not known</td>
</tr>
<tr>
<td>Intrinsic response to uv light</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Not known</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Induced response to uv light</td>
<td>Yes</td>
<td>Not known</td>
<td>Not known</td>
<td>Not known</td>
<td>Yes</td>
<td>Not known</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Fading of stored signal when exposed to uv light</td>
<td>Yes</td>
<td>Not known</td>
<td>Yes</td>
<td>Not known</td>
<td>Not known</td>
<td>Yes</td>
<td>Not known</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Varies considerably according to detector response.

** Varies considerably with manufacturer.

References:
Currently there are three phosphors, lithium fluoride activated with magnesium and titanium (LiF:Mg,Ti), lithium tetraborate activated with manganese (Li$_2$B$_4$O$_7$:Mn), and calcium sulphate activated with dysprosium (CaSO$_4$:Dy) which possess significant advantages over other phosphors and taken together are well suited to cover the majority of applications. The dosimetry peaks in these phosphors are at about 200°C, and thus the stored signal is adequately stable with time.

LiF:Mg,Ti is approximately tissue equivalent, sensitive enough for dose measurements in the range 1 mrad to $10^4$ rads, and is readily available in isotopic forms of lithium which make it either sensitive or insensitive to thermal neutrons. For these reasons it is the phosphor most widely used in radiological protection and radiotherapy applications. Its main disadvantage is that it has a rather complex glow curve structure and for re-use requires well defined thermal treatment both during readout and in any subsequent anneal.

Li$_2$B$_4$O$_7$:Mn has an intrinsic efficiency of energy conversion comparable to LiF, and the advantages of a simpler glow curve structure and better tissue equivalence. Its disadvantages are that it has an orange-red emission spectrum, is affected by humidity, and is not readily available in a thermal neutron insensitive form due to the presence of both lithium and boron. Its main application to date has been in radiotherapy. However, with suitable readout equipment, doses of the order of a few millirad can be measured and Brunskill (1974) has recently prepared lithium borate in an isotopic form insensitive to thermal neutrons, so that in future more use may be made of lithium borate in radiological protection applications.

CaSO$_4$:Dy is approximately 30 times as sensitive as LiF, but is not tissue equivalent. It can be used to provide some degree of photon energy discrimination (often in conjunction with a tissue equivalent phosphor), or for low dose measurements where the contribution to the photon spectrum of photons of energy less than about 150 keV is minimal, e.g. environmental monitoring. It is also being used, with filtration to modify its photon energy response, in personal monitoring, but then has the disadvantage of reduced response to photons of energy less than about 20 keV. CaSO$_4$:Tm is a phosphor with similar properties to CaSO$_4$:Dy, and may vie with the latter in the above mentioned applications. Gorbics and Attix (1968) originally suggested utilizing the difference in photon energy response of LiF and CaF$_2$:Mn to determine the energy of unknown radiation. Rossiter (1974) has exploited this, using LiF and CaSO$_4$:Dy.
Many other phosphors have been investigated, and some are listed in Table 4.2, together with selected references. References on lithium borate and calcium sulphate are also included in this Table. LiF is likely to remain the most widely used phosphor for some years, and its characteristics are discussed in greater detail in the following sections.

4.2. Lithium fluoride

Lithium fluoride (LiF) is widely used in many applications because it combines several particularly advantageous characteristics. It is now available from several commercial sources but most of the earlier research into its properties was based on material obtained from the Harshaw Chemical Co. (TLD-100, TLD-600, and TLD-700) and this is the material described below, unless otherwise indicated. The main activators are believed to be magnesium and titanium. The re-use of LiF is a rather complex subject and is discussed separately in section 4.3.

4.2.1. Characteristics of pure lithium fluoride

LiF is a colourless material of density 2.64 g cm$^{-3}$ and effective atomic number 8.2. It is resistant to chemical attack from most substances, with the exception of hydrofluoric acid. It is slightly soluble in water (Weast, 1964). Chronic ingestion of aqueous solutions of thermoluminescent grade LiF can be fatal (Dettmer et al, 1968) and the implication is that ingestion of small amounts of LiF by humans may produce serious reactions. It is recommended that this material be handled with caution to avoid possible inhalation or prolonged direct contact with body surfaces, and for in vivo dosimetry the thermoluminescent phosphor should be totally encapsulated.

Large crystals of LiF can readily be grown by standard procedures. Recent work indicates that thermoluminescent LiF is slightly affected by humidity (Mason, 1974b).

4.2.2. Sensitivity

Thermoluminescent grade LiF has an intrinsic efficiency of energy conversion of about 0.04% (Lucke, 1970) and a blue-green emission spectrum. With suitable forms of dosemeter and readout equipment it is possible to measure doses down to about 1 mrad before background variations begin to dominate.

4.2.3. Glow curve structure

LiF has a complex glow curve structure. Kathuria et al (1974) have identified 12 peaks between room temperature and 400°C. Further glow peaks below room temperature have been investigated by Podgorsak et al (1971). For most dosimetric applications only the five peaks between room
<table>
<thead>
<tr>
<th>Phosphor</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$B$_4$O$_7$·Mn</td>
<td>Schulman et al, 1965</td>
</tr>
<tr>
<td></td>
<td>Christensen, 1967, 1968, 1970</td>
</tr>
<tr>
<td></td>
<td>Brunskill, 1968</td>
</tr>
<tr>
<td></td>
<td>Jayachandran, 1970</td>
</tr>
<tr>
<td></td>
<td>Brunskill and Langmead, 1970</td>
</tr>
<tr>
<td>CaSO$_4$·Dy</td>
<td>Yamashita et al, 1968</td>
</tr>
<tr>
<td></td>
<td>Webb, 1970</td>
</tr>
<tr>
<td></td>
<td>Schmidt et al, 1974</td>
</tr>
<tr>
<td></td>
<td>Nambi and Baput, 1974</td>
</tr>
<tr>
<td>CaSO$_4$·Mn</td>
<td>Bjarngard, 1963a, 1963b</td>
</tr>
<tr>
<td></td>
<td>Lippert and Mejdahl, 1965</td>
</tr>
<tr>
<td>CaF$_2$(natural)</td>
<td>Schayes et al, 1965, 1968</td>
</tr>
<tr>
<td></td>
<td>Brooke, 1967</td>
</tr>
<tr>
<td>CaF$_2$·Mn</td>
<td>Ginther and Kirk, 1957</td>
</tr>
<tr>
<td>CaF$_2$·Dy</td>
<td>Schulman et al, 1960a, 1960b</td>
</tr>
<tr>
<td>BeO</td>
<td>Binder et al, 1968</td>
</tr>
<tr>
<td></td>
<td>Tochilin and Goldstein, 1969</td>
</tr>
<tr>
<td></td>
<td>Scarpa, 1970</td>
</tr>
<tr>
<td></td>
<td>Scarpa et al, 1971</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>Lucas et al, 1974</td>
</tr>
<tr>
<td>ThO$_2$</td>
<td>Harvey, 1974</td>
</tr>
<tr>
<td>DNA</td>
<td>Dolecek and Appleby, 1974</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Rieke and Daniels, 1957</td>
</tr>
<tr>
<td></td>
<td>McDougall and Rudin, 1970</td>
</tr>
<tr>
<td>Various sulphates</td>
<td>Yamashita, 1974</td>
</tr>
<tr>
<td></td>
<td>Dixon and Ekstrand, 1974</td>
</tr>
<tr>
<td>Diamond</td>
<td>Boyle, 1663</td>
</tr>
<tr>
<td></td>
<td>Carter, 1975</td>
</tr>
</tbody>
</table>
temperature and about 210°C need be considered. These peaks are identified as peaks 1 – 5 (see figure 4.2), following a convention established by Cameron (1964). Johnson (1974) has since identified a new peak, between peaks 3 and 4, as peak 4b. Several peaks above peak 5 appear with high doses of low-LET radiation, or with somewhat lower doses of high-LET radiation such as neutrons. This, coupled with the fact that the response vs dose curves for these peaks are supralinear, suggests that the deep traps responsible for these peaks are being created by the radiation (Sunta et al, 1971; Mason et al, 1971b).

The glow curve structure of LiF, and in particular the ratio of the heights of peaks 2 and 5, is known to be affected by a number of variables, such as (i) the concentration and state of aggregation of Mg impurity, (ii) the concentration of Ti (Rossiter et al, 1971), (iii) the concentration of hydroxide ions (DeWerd et al, 1974), (iv) phosphor grain size (8.5), and (v) high previous radiation doses (Mayhugh and Fullerton, 1974).

Variations in isothermal annealing or rate of cooling from the readout or anneal temperature can cause large changes in glow curve structure (see section 4.3). The peak structure (peaks 1 – 5) of LiF (TLD-100) powder, grain size 75-200 microns, which has been annealed at 400°C and cooled moderately fast is shown in figure 4.2. Characteristics of the traps responsible for these peaks are given in Table 4.3 (Gayton et al, 1972). Variations in glow curve structure with grain size are discussed in section 8.5.

Routine dose measurements generally utilise the light output from peaks 5 and 4, which are the most sensitive and stable peaks, and are often referred to as the 'dosimetry peaks'.

Table 4.3.

Characteristics of some LiF(TLD-100) glow peaks (after Gayton et al, 1972)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Temperature°C</th>
<th>Trap depth eV</th>
<th>Frequency factor, s⁻¹</th>
<th>Half-life at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65</td>
<td>1.04</td>
<td>1.2 x 10¹²</td>
<td>~10 min</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>1.11</td>
<td>10¹² (1-15) x 10¹¹</td>
<td>~30 h</td>
</tr>
<tr>
<td>3</td>
<td>160</td>
<td>1.19 ± 0.5</td>
<td>(0.5-14) x 10¹¹</td>
<td>~3.4 mths</td>
</tr>
<tr>
<td>4</td>
<td>195</td>
<td>1.25 ± 0.6</td>
<td>~8.5 yrs</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>210</td>
<td></td>
<td>~80 yrs</td>
<td></td>
</tr>
</tbody>
</table>

* Heating rate, 100°C/min.
4.2.4. Stability of stored signal

Booth et al (1972) showed that the rather complex effects of storage on the TL signal in LiF were explained by the growth and decay of the various TL peaks due to trap migration and aggregation, in addition to the normal fading of TL peaks. The stored signal can be made sufficiently stable for routine measurements in several ways. One approach is to use isothermal annealing techniques to reshape the distribution of traps of different depths. Cameron et al (1964) found that a pre-irradiation anneal of 80°C for 16 hours practically eliminates the shallow traps responsible for peaks 2 and 3, thus considerably reducing fading effects (and also trap migration and aggregation). The modified glow curve is also shown in figure 4.2. The low temperature traps are reformed by the readout process, so that it is necessary to repeat the pre-irradiation anneal before re-using the phosphor. An alternative method is to use a post-irradiation anneal e.g. 100°C for 10 minutes. This does not restructure the traps but merely accelerates the fading of peaks 1, 2, and 3.

The post-irradiation anneal can conveniently be included in the heating cycle as a 'preheat' stage (see section 9.5). It is shown, in section 8.5, that the variation in stored signal with time is dependent on such factors as the concentrations of Mg and Ti activators, grain size, and the cooling rate from the readout or anneal temperature. Fading effects are greatly complicated if LiF is exposed to light containing a strong uv component, e.g. daylight over an extended period, since uv light causes fading of stored signal.

4.2.5. Emission spectrum

Several measurements of the emission spectrum have been made, and are in general agreement that the peak emission is at about 400 nm (figure 2.10). Harris and Jackson (1970) observed that the emission spectrum shifted to slightly shorter wavelengths for higher temperature glow peaks, and this was confirmed by DeWerd et al (1972). Pearson et al (1966) found no difference in the emission spectrum of sensitized and unsensitized LiF. Bloch (1968) reported that the emission spectrum tends towards longer wavelengths with increasing exposure, but this is in disagreement with the results of DeWerd et al (1972), Harris and Jackson (1968b), and Pearson et al (1966), who all found that the emission spectrum of LiF appears to be the same at both low and high exposures. Fairchild et al (1974) show that the principal emission centre for peaks 2 and 3 may be different from that for peaks 4 and 5. However, peaks 1 and 6 may be associated with more intrinsic effects, since their emission spectra are significantly different.
to the spectra from peaks 2 - 5 (Crittenden et al, 1974).

4.2.6. Response vs dose, dose-rate, dose history, and LET

The response vs dose curve is linear up to at least 100 rads, with supralinearity becoming well-defined above 500 rads. Saturation occurs at about $10^5$ rads. Supralinearity is batch dependent, being associated with the amount of Ti activator, which in practice is difficult to reproduce exactly (Rossiter et al, 1971). There is an inverse relationship between the LET of the radiation and the amount of supralinearity (Naylor, 1965; Wagner et al, 1966; Suntharalingam, 1967). Exposure to high doses can cause a sensitivity enhancement (Zimmermann and Cameron, 1964), which exhibits an LET dependence similar to the supralinearity (Suntharalingam, 1967; Cameron et al, 1968). The sensitivity enhancement can be retained by a suitable thermal treatment, and has several advantages for subsequent doses (section 4.3.5).

4.2.7. Background signals

Thermal radiation, chemiluminescence, and triboluminescence signals are obtained when reading LiF, but can be minimised as indicated in section 4.1.6. Nitrogen is the preferred inert gas (Nash et al, 1965). LiF is sensitive to uv light, having both intrinsic and induced responses (Mason, 1971; Sunta et al, 1974; Kathuria et al, 1974) which can also contribute to the background signal, but which can be minimised by encapsulation and by carrying out readouts in subdued lighting.

4.2.8. Photon energy dependence

The effective atomic number of LiF is 8.2, compared with 7.4 for muscle tissue and 7.6 for air. Consequently LiF will somewhat over-represent the tissue dose and the exposure dose at low photon energies. The theoretical photon energy dependence has been calculated by Johns (1965). Experimental results have been obtained for TLD-100 by Klick et al (1967) and Becker et al (1970). These are shown, together with the theoretical curve, in figure 4.3, as the response relative to the absorbed dose in air normalised to 1 MeV photons, for the energy range 10 keV - 10 MeV. The excellent agreement between the theoretical and experimental curves implies that the thermoluminescent response of LiF per rad in LiF is constant over this energy range.

Some investigators (Pinkerton et al, 1966; Crosby et al, 1966; Almond et al, 1970) have reported a decrease in sensitivity to high energy (~20 MeV) X-rays. Almond et al (1970) have attributed differences in experimental results to the configuration of the phosphor, rather than to any intrinsic
Figure 4.3.
Response of LiF relative to the absorbed dose in air normalised to 1 MeV photons

1. Johns, 1965
2. Klick et al, 1967

Figure 4.4.
Glow curves of 'Op tran' LiF

1. Op tran, 500 rad, at 20 mrad/hour
2. Op tran, 40 rad, at 1.5 rad/hour
3. TLD-700, 1.5 rad at 150 mrad/sec
effect. The photon energy response is also affected by sensitization (Mayhugh and Fullerton, 1974).

4.2.9. Response to electrons and beta particles

Kastner et al (1965) and Harvey and Townsend (1967) have shown that the thermoluminescence of LiF is directly proportional to the energy absorbed when irradiated with beta particles having end point energies ranging from 18 keV ($^3$H) to 2.2 MeV ($^{90}$Y). A decrease in sensitivity to high energy electrons when compared with $^{60}$Co has been reported by Pinkerton et al, 1966; Crosby et al, 1966; Binks, 1969; and Almond et al, 1970. The decrease is 6 - 10% for electron energies of 10 MeV to 35 MeV. Harvey and Townsend (1967) pointed out that in beta and electron dose measurements it is necessary to consider the geometrical conditions very carefully, and Almond et al (1970) have explained the sensitivity decrease in terms of the phosphor configuration and the general cavity theory (Burlin, 1966).

4.2.10. Response to neutrons

Lithium has the natural isotopic ratio 92.6% $^7$Li, 7.4% $^6$Li, and as such is incorporated into LiF (TLD-100). The thermal neutron cross-section of $^7$Li is negligible in comparison with the 945 barn cross-section for the exothermic $^6$Li (n,α)$^3$H reaction. The response of thermoluminescent lithium fluoride containing lithium in its natural isotopic ratio to 1 rem of thermal neutrons is about twenty times the response to 1 rad of gamma radiation. Thermoluminescent lithium fluoride can also be obtained in the isotopic forms $^7$LiF or $^6$LiF (TLD-700 or TLD-600 respectively, for the Harshaw product). $^7$LiF has a very low response to thermal neutrons and is frequently used to measure only the beta and gamma components in a mixed beta, gamma and neutron field.

The 2.06 MeV alpha-particle and the 2.72 MeV triton liberated by the (n,α) reaction have high average LET values of 160 and 120 keV/μm respectively, compared with 2 keV/μm for 1 MeV electrons. Wingate et al (1965) have shown that the response falls off with increasing LET for both alpha and proton irradiation. At the mean value appropriate to thermal neutrons, 140 keV/micron, the response is only 20% of that calculated from energy deposition considerations based on gamma calibration. This fall-off is thought to be due to two effects: recombination of charge carriers in the densely ionized track, and saturation of the available trapping centres in the vicinity of the particle tracks.

The fast neutron response is not dependent on isotopic composition as it is due primarily to recoiling Li and F nuclei. Wingate et al (1965) have
shown that the response of powder in equivalent gamma rads per fast neutron tissue rad is roughly proportional to neutron energy, ranging from 1% at 1 MeV to 10% at 10 MeV. The response to fast neutrons can be enhanced by surrounding the powder grains by a hydrogenous moderator, e.g. by suspending the LiF powder in ethyl alcohol.

In a known neutron energy spectrum, the total neutron dose in the energy range 0.5 eV to 10 MeV can be estimated by the albedo method, which utilizes the thermal neutron flux scattered out of the human body when exposed to fast and epi-thermal neutrons (Preston, 1968; Harvey et al, 1972). The feasibility of mixing TLD-100 and TLD-700 in the correct proportions to obtain rem equivalent TL dosemeters for mixed fields of thermal neutrons and $\gamma$-rays has been discussed by Attix (1970). Ayyanger et al (1974) have recently arrived at a suitable mixture for a mixed field consisting of thermal and intermediate energy neutrons (up to 10 keV) and $\gamma$-rays.

A characteristic of the glow peak structure of LiF exposed to neutrons is the growth of a peak at about 280°C. This peak is more sensitive to fast neutrons than it is to photon radiation on a rad for rad basis and Endres and Lucas (1974) have suggested that this may lead to the use of $^7$LiF for simultaneous measurement of dose due to photons and fast neutrons. Earlier, Buswood et al (1970) proposed using the ratio of the 210°C and 280°C peaks in TLD-100 to distinguish between photons and slow neutrons.

4.2.11. Supply

Originally the Harshaw Chemical Co. was the only source of supply of thermoluminescent LiF. Subsequently several other preparations have been described, and some of these are available commercially (Frank & Edelmann, 1966; Naba, 1971; Portal et al, 1971; Niewiadomski, 1971; Rossiter et al, 1971; Brunskill, 1974). However, supply of the different isotopic forms is more limited. To date (December, 1974) $^7$LiF and $^6$LiF are only obtainable from Harshaw (U.S.A.) or C.E.C. (France), though a U.K. source may soon be available (British Nuclear Fuels Ltd.).

4.3. Variations in sensitivity of LiF with re-use

4.3.1. Introduction

The sensitivity and glow curve structure of LiF dosemeters are dependent on such factors as radiation and thermal history. The thermal treatment given to a dosemeter before re-use should be optimised according to the application. Factors to be considered are:

(a) What residual signal can be tolerated (total erasure of previous
doses is not always necessary, or convenient)?

(b) If sensitization has occurred, due to high previous doses, should the phosphor be returned to its original sensitivity by a suitable thermal treatment, or should it be recalibrated?

(c) Will dose re-estimation by photo-transferred thermoluminescence be required?

(d) For solid forms of dosemeter, significant changes in surface condition can be caused by a high temperature anneal. Also, the stability of any matrix material into which the LiF is incorporated is clearly important.

(e) The cooling rate from the anneal or readout temperature.

(f) Will a low temperature (80°C) pre-irradiation anneal be required to optimise the stability of stored signal and precision, or would a short post-irradiation anneal (e.g. preheat) suffice?

(g) For very high doses, has irreversible radiation damage occurred?

(h) Workload and throughput.

Most of the following work concerns LiF manufactured by the Harshaw Chemical Co. i.e. TLD-100, TLD-600, or TLD-700, but some of the conclusions are probably valid for LiF from other manufacturing sources. This section is concerned with LiF dosemeters in general. The more specific case of the re-use of LiF/PTFE dosemeters is considered in sections 9.4 and 9.5.

4.3.2. High temperature post-readout (pre-irradiation) anneal

The primary purpose of the high temperature post-readout anneal is to reduce the residual dose remaining after the read zone, i.e. the portion of the overall heating cycle during which light is integrated, to a tolerable level. The read zone heating profile should be selected to optimise the overall accuracy in the application (Robertson and Gilboy, 1974) and in some applications the residual signal may be as much as 5% of the previous dose. In all cases where the residual signal is likely to interfere with the measurement of succeeding doses, it should be reduced further, prior to re-use of the dosemeter, by a high temperature anneal. A recommended working rule for radiological protection applications (EEC, 1974) is to use the high temperature anneal whenever the residual signal is more than 50% of the minimum detectable dose of the system (i.e. typically equivalent to ~5 mrad). In radiotherapy applications, the high temperature anneal is required whenever the residual signal is likely to interfere with the accuracy of measurement of subsequent doses, e.g. if a dose of 100 rad is to be measured, a residual signal of 1 rad will cause an error of 1%. With high dose measurements, a separate reason for the high temperature anneal is to remove sensitization effects. This is discussed in section 4.3.5.
Considerable research has been devoted to the study of variations in sensitivity and glow curve structure with (a) pre-irradiation annealing at different temperatures and for different times, and (b) different cooling rates from the readout or anneal temperature (Cameron et al., 1965; Cameron, 1967; Harris and Jackson, 1968; Carlsson, 1969; Jackson and Harris, 1970; Mason and Linsley, 1971b; Sunta et al., 1971; Spanne and Carlsson, 1971; section 8.5). For annealing times of the order of several hours, the dosimetry peaks in LiF are most stable at annealing temperatures of 400–500°C. The sensitivity is also dependent on the cooling rate from the anneal temperature.

Faster cooling rates increase the sensitivity but also accentuate the height of the lower temperature peaks relative to the main dosimetry peaks. All these effects are related to the concentration and state of aggregation of Mg in the crystal lattice, as discussed in section 4.4.5.

With suitable apparatus, the anneal time can be reduced to a few seconds; all that is required is to select a temperature such that there is a high probability of escape from the appropriate traps. Indeed, it has been shown (Carlsson et al., 1968; Carlsson, 1969) that changes in sensitivity from one readout cycle to the next can be reduced by minimising the annealing time and temperature. The anneal can in some circumstances, depending on the type of dosemeter and the application, be performed in the reader, in which case the dosemeter is held at or somewhat above the maximum readout temperature for a few seconds (Wallace, 1970; Marshall et al., 1971; Webb and Phykitt, 1971; Ehrlich, 1974). This is referred to as an internal anneal. Operational procedure is thereby simplified but at the expense of extending the overall readout time. The alternative is to anneal the dosemeter in a separate oven. This is referred to as an external anneal, and has the advantage that large numbers of dosemeters can be annealed simultaneously.

Overall, an internal anneal is generally preferred for the following reasons. Firstly, dosemeters can be cooled fast but reproducibly in the reader, and the sensitivity of the dosimetry peaks is thereby maintained at a level which is about a factor of about two higher than is achieved with an external anneal. Secondly, changes in sensitivity from one readout cycle to the next are minimised by the short annealing time. Thirdly, this short anneal is less likely to lead to random changes in surface condition due to accidental contamination with debris. A disadvantage of the fast cool is that the lower temperature peaks are accentuated, with an adverse effect on the stability of stored signal if the 80°C pre-irradiation anneal is not subsequently used. This is particularly noticeable with some solid forms of dosemeter, whose lower temperature peaks are also accentuated by
the method of manufacture (sections 8.5 and 9.5).

The efficiency of the internal anneal at removing residual signal depends on the type of dosemeter, and the temperature and duration of the anneal. Generally, 300°C for 16 seconds is sufficient to reduce the residual signal from most types of dosemeter to less than 0.1% of the previous dose. A higher anneal temperature can sometimes be used, but tends to cause larger changes in surface condition and transparency. In low dose measurements, a residual signal of less than 0.1% is generally acceptable. In high dose measurements it could still lead to significant error, and a residual signal of less than 0.01% would be preferable. The problem can sometimes be averted by allocating dosemeters to specific dose ranges. For example, if doses in the range 50 to 500 rad are to be measured, a dosemeter which has received 500 rad has this signal reduced to less than 0.5 rad by the internal anneal, and can subsequently be used for measuring a dose of as low as 50 rads with less than 1% additional error. However, a problem still remains if a dosemeter is used several times to measure a dose of 500 rad and then used to measure a dose of 50 rad.

An external anneal may thus be required (a) to increase throughput, or (b) to reduce residual signal to an acceptable level, or (c) to remove sensitization effects (see section 4.3.5). External annealing generally involves large numbers of dosemeters and therefore requires the use of a relatively high thermal capacity oven, which is slow to stabilize. Hence, although annealing times reported in the literature range from about 30 minutes to 20 hours, times of less than 30 minutes are rarely mentioned, probably due to uncertainty as to whether the sample has reached the desired temperature. A convenient annealing time that is generally recommended is 1 hour. The anneal temperature may be set to between 280 and 500°C, depending on the application. 1 hour at 400°C removes both the residual signal and the sensitivity enhancement in LiF.

The design of the oven should be such that temperature gradients in the region of the dosemeters are small. For this reason, forced circulation ovens with a fairly large internal volume are preferred. The dosemeters can conveniently be placed in a suitable jig (i.e. an annealing stand) in the middle of the oven, which is generally the region where thermal gradients are lowest. The oven lining should not generate fumes, which may cause spurious background signals if deposited on the surface of the dosemeter, and the oven should be specifically reserved for annealing to avoid contamination (see section 10.7). The method of cooling should be such that dosemeters cool uniformly and reproducibly. This criterion is most easily satisfied if a slow cool is used e.g. the oven door should not be
opened until the dosimeters have cooled to below about 100°C. If the 80°C anneal is also used, the oven door need not be opened until after its completion.

4.3.3. Low temperature pre-irradiation anneal

The low temperature pre-irradiation anneal may be used, after the high temperature anneal, to improve the stability of the stored signal. Cameron et al (1964) found that a pre-irradiation anneal of 80°C for about 16 hours practically eliminated the shallow traps responsible for glow peaks 2 and 3; this considerably reduced variations in the stored signal with time due to fading and migration and aggregation of traps. The low temperature traps are re-formed by the readout process, so that it is necessary to repeat the anneal before another re-use. Webb (1967c) showed that the glow curve structure was not significantly altered by varying the annealing time between 16 and 24 hours, which is operationally convenient. Glow curves obtained with and without the 80°C anneal are shown in figure 4.2. When the 80°C anneal is not used, the shape of the subsequent glow curve depends considerably on the cooling rate from the anneal temperature.

4.3.4. Post-irradiation annealing

An alternative method of reducing the effects of fading in LiF is to use a post-irradiation anneal. The phosphor is stored at such a temperature that the low temperature peaks fade rapidly, whilst the dosimetry peaks are not significantly affected; about 10 minutes at 100°C is sufficient to achieve this (Cameron, 1967). The post-irradiation anneal can conveniently be incorporated into the readout cycle as a 'preheat' stage (see section 9.5). A disadvantage of this latter technique is that wide variations in stored signal with time can still occur due to trap migration and aggregation, especially if the lower temperature peaks have been accentuated by fast cooling.

4.3.5. Sensitization

The sensitivity of LiF is enhanced by high doses. This phenomenon is known as 'sensitization' and is detectable above about 100 rads. It was originally thought that this was due to the formation of radiation-induced non-luminescent trapping centres, but recent research (Mayhugh, 1974; Mayhugh and Fullerton, 1974) supports Attix's (1974) track interaction model, in which sensitization is due to the formation of radiation-induced luminescent centres (see section 4.4.5).

The user has the options of either recalibrating the sensitivity or
returning the dosemeter to its original sensitivity by an appropriate annealing procedure. However, an operational problem which arises if the sensitization is not removed is that supralinearity is closely linked to sensitization, and the dose vs response curve may be significantly altered for subsequent doses. Wilson et al (1966) showed that the stability of the increased sensitivity followed first order kinetics and that the phenomenon could be treated as though it were due to a deep trap which on the Randall-Wilkins model has an activation energy of about 2.1 eV and a frequency factor of about $10^{12}$ s$^{-1}$. Annealing at 400°C for 1 hour removed the sensitization, whereas 280°C for 1 hour retained it.

Deliberate sensitization of LiF by a radiation dose of $10^4 - 10^5$ rads considerably improves the phosphor's characteristics for subsequent doses, providing the sensitization is retained by suitable thermal and optical treatments (Zimmerman and Cameron, 1964; Mayhugh and Fullerton, 1974). Sensitivity is increased by a factor of typically 5, the response is linear up to $10^4$ rads, no further sensitization occurs for subsequent doses of up to about $10^4$ rads, and the phosphor is more tissue equivalent. The improved tissue equivalence is due to the sensitizing dose preferentially enhancing the response to higher LET radiation. A disadvantage with the normal 280°C anneal for 1 hour, used to retain the sensitization, was that deep traps were not emptied and subsequently caused interference with low dose measurements. The background signal contained at least two components dependent on the sensitizing dose, (a) a signal due to thermal activation of deep traps, and (b) a signal due to photo-transference from deep traps to the dosimetry traps, caused by random exposure of the phosphor to natural lighting containing a uv component. There is also the possibility of transference from deep traps to the dosimetry traps by thermal activation during storage. Photo-transference could in some circumstances cause errors in measurements with sensitized phosphors even at radiotherapy levels. Linsley and Mason (1971b) have observed 1-2% regrowth of the dosimetry peaks when re-estimating dose by uv transference at room temperature. Even if a typical exposure to daylight during routine handling gives as little as 0.01% transference, this will lead to an apparent dose of 10 rads following a sensitizing dose of $10^5$ rads, and thus cause significant errors in subsequent measurements of up to $10^3$ rads.

However, Mayhugh (1974), and Mayhugh and Fullerton (1974) have shown that a 'uv anneal' removes the deep traps responsible for the high background signals but preserves the luminescent centres responsible for the sensitization. The uv-anneal consists of annealing the sensitized phosphor near 300°C for 30-60 minutes, whilst additionally exposing the phosphor to intense uv light. The technique is applicable to large batches of dosemeters.
Frank and Edelmann (1966) and Portal et al (1971) have also utilized sensitization to improve the performance of LiF of their own manufacture. Frank and Edelmann also noted interfering background signals but Portal et al did not, presumably because their phosphor has a different deep trap structure.

4.3.6. Dose re-estimation by photo-transferred thermoluminescence (PTTL)

PTTL in LiF is associated with deep traps, in particular with that responsible for peak 10, which occurs at about 395°C when a heating rate of 20°C per minute is used (Linsley and Mason, 1971b; Sunta et al, 1971; Sunta et al, 1974; Kathuria et al, 1974; Mayhugh, 1974). If dose re-estimation is required the maximum anneal temperature which can be used is 300°C. A uv-anneal should not be used, but the use of a uv-anneal as part of a sensitizing procedure does not preclude re-estimation of subsequent doses, i.e. the deep traps are still populated by subsequent doses. Linsley and Mason (1971b) obtained 1-2% regrowth of the dosimetry peaks at room temperature. By storing the phosphor at higher temperatures during the exposure to uv light the process may be made more efficient (Sunta and Watanabe, 1974), and up to 20% regrowth has been reported (Yorke, 1974; Mason, 1974).

4.4. Studies of the thermoluminescence of lithium fluoride doped with various activators

4.4.1. Introduction

At the time this particular research was started (1970) thermoluminescent grade LiF with repeatable characteristics was only available from one commercial supplier, the Harshaw Chemical Co. The disadvantage of a single source of supply are, of course, uncertainty in delivery and prices which have been arrived at in the absence of any competition. From the technical viewpoint, the LiF phosphors produced by Harshaw (TLD-100, TLD-600, and TLD-700) had two main disadvantages: their sensitivity was dependent on thermal and dose history and the complex glow curve structure often led to errors in measurement caused by fading and the migration and aggregation of trapping centres. LiF was therefore still open to improvement.

The Harshaw phosphors were prepared from single crystals grown by the Stockbarger technique, and were known to contain Mg, Al, and Ti among other impurities (British patent specification No.1059518, 1967). Rossiter et al (1970) had prepared similar materials by the addition of Mg and Ti to pure LiF, again by the Stockbarger method. Jones et al (1964 and 1965) investigated a large number of possible activators by adding impurities to pure LiF and simply melting the mixture in a graphite crucible. This method
is much simpler than controlled crystal growth and therefore would, if successful, result in a less costly product. It was decided to prepare samples of lithium fluoride, doped with various activators, by a similar technique since the equipment required was readily available.

The primary objective of this research was the preparation of a sensitive lithium fluoride with a simple glow curve structure. However, the possibility of finding out more about the basic thermoluminescent mechanism was another strong consideration. Although a considerable amount of research had been carried out into the thermoluminescent mechanism of LiF, most of this had utilised the Harshaw products, which had a well-defined activator type and concentration. It is clear that for a complete understanding the effects of varying activator type and concentration must be known.

4.4.2. Method of preparation

In all, about 60 samples were prepared. The following elements were investigated as possible activators: Mg, Ca, Ti, Mn, Cu, Zr, Ag, La, Dy, Ho, and Hf, listed in ascending atomic number. Selected compounds were added to pure LiF singly or as double or triple activators. Little is known of the effect on activation of the anion of an activator. Wherever possible the fluoride was used, but this was not always possible due either to non-availability or to the peculiar chemical nature of the compound.

The starting material was 'Optran' zone refined LiF, manufactured by BDH Chemicals Ltd. A typical mass spectrographic analysis of this material is given in Table 4.4. It can be seen that elements believed to contribute to thermoluminescence as a result of previous work, namely Mg and Ti, are present to the extent of 6 and 2.6 ppm (atomic) respectively, so that it could be expected that the starting material would show some thermoluminescence. The purity of the activators used was generally greater than 99%.

Preparation of samples was as follows. The 'Optran' LiF was ground to a fine powder (< 80 microns) by an agate mortar and pestle. Each sample weighed about 3.5g. Selected activators were added, some dry, others in solution. Generally 0.01% (100 ppm) by weight of activator was used, this being about the minimum weight that could reliably be measured on the balance. 'Wet' mixes were dried at 90°C for 2 hours. The mixture was placed in a lidded platinum crucible and placed in a muffle furnace, prestabilised at 900–950°C, for 2 hours, the surrounding gas being air. The furnace was then switched off and the crucible cooled at a rate of approximately 80°C per hour through the melting point (nominally 843°C for pure LiF).
Table 4.4. Typical mass spectrographic analysis (ppm atomic) 'Optran'
Lithium fluoride zone refined crystal pieces

<table>
<thead>
<tr>
<th>Element</th>
<th>ppm</th>
<th>Element</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium fluoride zone refined crystal pieces</td>
<td></td>
<td>Lithium fluoride zone refined crystal pieces</td>
<td></td>
</tr>
<tr>
<td>Uranium (U)</td>
<td>&lt; 0.02</td>
<td>Ruthenium (Ru)</td>
<td>&lt; 0.06</td>
</tr>
<tr>
<td>Thorium (Th)</td>
<td>&lt; 0.02</td>
<td>Molybdenum (Mo)</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Bismuth (Bi)</td>
<td>&lt; 0.02</td>
<td>Niobium (Nb)</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>&lt; 0.04</td>
<td>Zirconium (Zr)</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Thallium (Tl)</td>
<td>&lt; 0.03</td>
<td>Yttrium (Y)</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Mercury (Hg)*</td>
<td>20</td>
<td>Strontium (Sr)</td>
<td>&lt; 0.025</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>&lt; 0.02</td>
<td>Rubidium (Rb)</td>
<td>&lt; 0.07</td>
</tr>
<tr>
<td>Platinum (Pt)</td>
<td>&lt; 0.06</td>
<td>Bromine (Br)</td>
<td>&lt; 0.04</td>
</tr>
<tr>
<td>Iridium (Ir)</td>
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<td>Selenium (Se)</td>
<td>&lt; 0.06</td>
</tr>
<tr>
<td>Osmium (Os)</td>
<td>&lt; 0.05</td>
<td>Arsenic (As)</td>
<td>0.06</td>
</tr>
<tr>
<td>Rhenium (Re)</td>
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<td>Germanium (Ge)</td>
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<td>Tungsten (W)</td>
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<td>Gallium (Ga)</td>
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</tr>
<tr>
<td>Hafnium (Hf')</td>
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<td>Zinc (Zn)</td>
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<tr>
<td>Lutetium (Lu)</td>
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<td>Copper (Cu)</td>
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</tr>
<tr>
<td>Ytterbium (Yb)</td>
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<td>Nickel (Ni)</td>
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<tr>
<td>Trilium (Tm)</td>
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<td>Cobalt (Co)</td>
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</tr>
<tr>
<td>Erbium (Er)</td>
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<td>Iron (Fe)</td>
<td>0.02</td>
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<tr>
<td>Holmium (Ho)</td>
<td>&lt; 0.02</td>
<td>Manganese (Mn)</td>
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</tr>
<tr>
<td>Dysprosium (Dy)</td>
<td>&lt; 0.07</td>
<td>Chromium (Cr)</td>
<td>&lt; 0.07</td>
</tr>
<tr>
<td>Terbium (Tb)</td>
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<td>Vanadium (V)</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Gadollinium (Gd)</td>
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<td>Titanium (Ti)</td>
<td>2.6</td>
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<tr>
<td>Europium (Eu)</td>
<td>&lt; 0.04</td>
<td>Scandium (Sc)</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Samarium (Sm)</td>
<td>&lt; 0.07</td>
<td>Calcium (Ca)</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Neodymium (Nd)</td>
<td>&lt; 0.07</td>
<td>Potassium (K)</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Praseodymium (Pr)</td>
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<td>Chlorine (Cl)</td>
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<tr>
<td>Cerium (Ce)</td>
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<td>Sulphur (S)*</td>
<td>240</td>
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<tr>
<td>Lanthanum (La)</td>
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<td>Phosphorus (P)</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>&lt; 0.03</td>
<td>Silica (Si)</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>Caesium (Cs)</td>
<td>&lt; 0.02</td>
<td>Aluminium (Al)</td>
<td>0.02</td>
</tr>
<tr>
<td>Iodine (I)*</td>
<td>0.6</td>
<td>Magnesium (Mg)</td>
<td>6</td>
</tr>
<tr>
<td>Tellurium (Te)</td>
<td>&lt; 0.06</td>
<td>Sodium (Na)</td>
<td>0.2</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>&lt; 0.04</td>
<td>Fluorine (F)</td>
<td>Base</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>&lt; 0.06</td>
<td>Oxygen (O)</td>
<td>-</td>
</tr>
<tr>
<td>Indium (In)</td>
<td>&lt; 0.02</td>
<td>Nitrogen (N)</td>
<td>-</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>&lt; 0.07</td>
<td>Carbon (C)</td>
<td>-</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>&lt; 0.04</td>
<td>Boron (B)</td>
<td>0.8</td>
</tr>
<tr>
<td>Palladium (Pd)</td>
<td>&lt; 0.08</td>
<td>Beryllium (Be)</td>
<td>-</td>
</tr>
<tr>
<td>Rhodium (Rh)</td>
<td>&lt; 0.02</td>
<td>Lithium (Li)</td>
<td>Base</td>
</tr>
</tbody>
</table>

* Possible 'memory effect'
Approximately 2.5g of the sample formed into several large single crystals; the remaining fraction formed into large numbers of small crystals, generally where the sample contacted the crucible wall. The large crystal pieces were ground, again using an agate pestle and mortar; crystals between 80 and 200 microns were annealed at 400°C for 1 hour, rapidly cooled to room temperature, and subsequently used for the thermoluminescent experiments. The crucible was cleaned with hydrofluoric acid before the preparation of the next sample.

4.4.3. Results obtained on modified Con-Rad equipment

It was decided to investigate sensitivity and glow curve structure initially, with a more detailed study of any promising samples. The results reported earlier (Robertson and Gilboy, 1971) were obtained using a Con-Rad readout head which had been modified to hold a fixed sample tray, to which was attached a thermocouple to provide feedback for linear heating control. Samples were generally dosed to 30 rads in air with a Cobalt-60 source (dose-rate approximately 1.5 rads/hour) and read out 3 hours after completion of the irradiation. The glow curves between 25°C and 300°C were examined, using a linear heating rate of 5°C/sec. Table 4.5 shows peak temperature and relative peak heights per rad for a selected number of samples. Peak heights per rad are given relative to a value of 100 assigned to peak 5 of TLD-100. Peak temperatures quoted below are relative to a value of 210°C assigned to the peak temperature of peak 5 of TLD-100.

Figure 4.4 shows the glow curve structure of the starting material (1OptranLiF) in two ways. Curve 1 is the result of a dose of 500 rads at a dose-rate of 20 mrad/hr, i.e. over a period of several months. Low temperature peaks have decayed, and the higher temperature peaks are shown in greater detail. Three peaks are discernible, at 170, 210, and 280°C. Curve 2 was taken after irradiation to 40 rads at 1.5 rads/hr. The main peak is now at 140-150°C, with a smaller higher temperature peak. Curve 3 shows for comparison the glow curve of TLD-700. From Table 4.5 the 210°C peak in the Optran sample has less than 1% the sensitivity of the 210°C peak in TLD-700, but the lower temperature peaks are comparable. After a remelt, the sensitivity of the Optran sample low temperature peak dropped by a factor of 4.

Surprisingly, the addition of MgF₂ or MgCl₂ singly as activators produced little measurable thermoluminescence. However, the addition of Ti via various chemical compounds usually produced appreciable thermoluminescence in two well-defined peaks, a low temperature peak below 150°C and a high temperature peak above 170°C. Li₂TiF₆ (lithium hexafluorotitanate, manufactured by Alfa Inorganics Inc) was effective either when added alone
Table 4.5.

Performance of selected samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activators</th>
<th>Relative peak heights</th>
<th>Total light output</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$&lt;160^\circ C$</td>
<td>$&gt;160^\circ C$</td>
</tr>
<tr>
<td>1.</td>
<td>Optran</td>
<td>20</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2.</td>
<td>Optran: remelt</td>
<td>5</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>3.</td>
<td>TLD-700</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>4.</td>
<td>TLD-700: remelt</td>
<td>5</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>5.</td>
<td>MgF$_2$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>MgF$_2$ + ZrO$_2$</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>7.</td>
<td>MgF$_2$ + Li$_2$TiF$_6$</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>MnF$_2$</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>9.</td>
<td>MnF$_2$ + Li$_2$TiF$_6$</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>10.</td>
<td>CaF$_2$</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>11.</td>
<td>CaF$_2$ + CaCl$_2$ + Li$_2$TiF$_6$</td>
<td>95</td>
<td>28</td>
</tr>
<tr>
<td>12.</td>
<td>CaF$_2$ + CaCl$_2$ + TiSi$_2$</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Li$_2$TiF$_6$</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td>14.</td>
<td>TiF$_4$</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>15.</td>
<td>DyCl$_3$</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>16.</td>
<td>La$_2$O$_3$</td>
<td>4</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>17.</td>
<td>HoF$_3$</td>
<td>3</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>18.</td>
<td>SrTiO$_4$</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>19.</td>
<td>HfO$_2$</td>
<td>12</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
or with other compounds. The best results were obtained by the addition of calcium compounds and Li₂TiF₆ (sample 11) or titanium tetrafluoride (TiF₄; sample 14). Total light output from these samples was comparable to TLD-700. Strontium titanate (SrTiO₄) was the only other activator giving two well-defined peaks. With the other activators listed in Table 4.5, low sensitivity samples were produced. It is interesting (and significant, as is argued in section 4.4.6) that the thermoluminescent properties of TLD-700 were practically destroyed by a remelt and could not be restored by a 400°C anneal.

The shape of the glow curve and the overall sensitivity of both samples 11 and 14 did not change significantly when the samples were subjected to a pre-irradiation anneal of 80°C for 24 hours. This is in contrast to TLD-700, where the low temperature traps are largely removed by the same annealing cycle.

4.4.4. Some further results obtained on the Model 654 reader

Following the construction of the 'Toledo' Model 654 reader (described in Chapters 5 and 6), it was decided to repeat some earlier measurements under the more controlled conditions now available. In particular, the glow curve structure of samples 11 and 14 were compared with TLD-100 (see figure 4.5). Samples, consisting of about 28 mg of phosphor, were irradiated to a dose of 1.5 rads in air by a ⁹⁰Sr/⁹⁰Y beta source, at a dose-rate of about 150 mrad/sec, and read out within 5 minutes of irradiation. The heating cycle used was a linear ramp of 2°C/sec from ambient temperature to 400°C, and light was detected by a photomultiplier tube with a bialkali (K-Cs-Sb) photocathode, fitted with a Chance HA3 infra-red absorbing filter. Peak temperatures were calculated relative to a peak temperature of 210°C assigned to peak 5 of TLD-100. The expected peaks 1-5 were clearly present in the sample of TLD-100, peaks 2, 3 and 5 being at 123, 160, and 210°C respectively. In samples 11 and 14 there were only two peaks, occurring at 126 and 178°C in both samples. The total light outputs of samples 11 and 14 relative to TLD-100 were 1.51 and 1.15 respectively. The peak temperatures differ somewhat from those previously reported (Robertson and Gilboy, 1971) but this is no doubt due to the limitations of the earlier equipment.

The glow curve structure and sensitivity of samples 11 and 14 were not affected by a pre-irradiation anneal of 80°C for 24 hours, or by variations in the cooling rate from 400°C between 2°C/min (slow oven cool) and 20°C/sec (natural cool in readout instrument). The glow curve structure of the samples following exposure to uv light (365 nm) was also investigated, and is compared with TLD-100 in figure 4.6. Both samples 11 and 14 showed a
Figure 4.5.

Glow curve structure of samples 11 and 14, compared with TLD-100

(1) Sample 11
(2) Sample 14
(3) TLD-100
Figure 4.6.
Relative response of samples 11 and 14, and TLD-100, to uv light (365 nm)

Figure 4.7.
Normalised height of glow peak 5 in glow curves of sections from crystals with magnesium and titanium added. Dose 10 rads. (Rossiter et al, 1971)
large peak at about 290°C which was absent in TLD-100.

4.4.5. The thermoluminescent mechanism in LiF

The following summary of the generally accepted thermoluminescent mechanism in LiF is presented as background information preceding discussion of the above results. It includes some recent information that was not available at the time the research was originally carried out.

Mg$^{2+}$ centres are believed to occur in dipole formation with Li$^+$ vacancies, and in complexes of multiple dipoles, in proportions depending upon the degree of migration and aggregation resulting from various annealing procedures (Mayhugh et al, 1970, a and b; Jackson and Harris, 1970; Booth et al, 1972; Johnson, 1974). There is considerable evidence that dipoles consisting of the Mg$^{2+}$ ion and its associated Li$^+$ vacancy provide the trapping centres for peaks 2 and 3, and that aggregated complexes (or clusters) of dipoles constitute the traps for the dosimetry glow peaks (4 and 5). Dryden and Shuter (1973) suggest that trimers are primarily responsible for peaks 4 and 5. However, DeWerd et al (1974) believe that peak 5 is due to dimers. Crittenden et al (1974b) suggest that in all probability other forms of trap exist, such as Mg$^+$ or Mg in association with oxygen. Attix (1974) considers that all of these rather complex traps can probably serve either as electron or hole traps. It was thought earlier that the charge carriers released from traps during the heating process were holes (Klick et al, 1967; Claffy et al, 1968) but considerable evidence now exists that electrons are the charge carriers released (Mayhugh et al, 1970; Sunta et al, 1971; Christy and Mayhugh, 1972; Davies, 1974; Crittenden et al, 1974).

The sensitivity and glow curve structure of LiF are thus functions of the distribution of magnesium throughout the crystal lattice. After a quench from 400°C the distribution of Mg into dipoles or clusters will depend on the concentration of Mg. For low concentrations (<10 ppm by weight) almost all the Mg$^{2+}$ in the crystal will be paired with vacancies, and only a small fraction will be present in clusters or as free Mg$^{2+}$ ions (Dryden and Shuter, 1973). Peaks 2 and 3, which are probably associated with dipoles, will predominate in the glow curve structure, to the exclusion of peaks 4 and 5, which are associated with clusters. As the concentration of Mg is increased the probability of forming clusters increases, and the heights of peaks 4 and 5 correspondingly increase. Subsequent annealing procedures alter the glow curve structure by either causing clusters to separate into dipoles, or by causing dipoles and clusters to aggregate into higher complexes, depending upon the annealing temperature and the
rate of cooling from that temperature. In TLD-100, the loss of sensitivity as the cooling rate decreases is believed to be due to the aggregation of dipoles and trimers into higher complexes. For phosphor of grain size 75–200 \( \mu m \) the height of the dosimetry peaks (4 and 5) is optimised by magnesium concentrations of about 80 ppm by weight (Frank and Edelmann, 1966; British patent specification No.1059518, 1967; Rossiter et al, 1971).

Zimmerman and Jones (1967) and Rossiter et al (1971) have shown convincingly that Ti is involved with the photon emission process in LiF. Rossiter et al (1971) have further shown that very slight changes in Ti concentration can markedly affect the thermoluminescent properties of LiF, and that earlier discrepancies in experimental evidence can be explained by the Ti being associated with oxygen. The height of peaks 4 and 5 are optimised by a Ti concentration of about 8 ppm by weight. Davies (1974) investigated the EPR and ENDOR of titanium-doped LiF, and suggests that the active luminescent centre is associated with \( [Ti^{3+}F^-] \) or, more probably, \( [Ti^{3+}F^-_3O_2] \) complexes and that the luminescent centre is de-activated by \( Ti^{4+} \) converting to \( Ti^{4+} \).

Crittenden et al (1974b) believe that just one type of luminescent centre is responsible for peaks 2–5, since the corresponding emission spectra seem to be identical. Peaks 1 and 6 have different emission spectra, and it is proposed that these peaks arise from more intrinsic defects, possibly radiation damage. For peaks 2–5, their results are in general agreement with the model of Mayhugh et al (1970); trapped electrons are released from magnesium centres, interact with an intermediate defect such as a two hole trap (V3), and release the second hole to convert Ti3+ ions back to Ti4+ with the emission of blue light. However, Fairchild et al (1974) show that the principal emission centre for peaks 2 and 3 may be different from that for peaks 4 and 5. DeWerd et al (1974) have shown that hydroxide ion impurities play a major role in the thermoluminescent process. Their results suggest that either (i) the emission from glow peaks 2 and 3 is associated with a titanium-hydroxide complex, or (ii) the trapping centres for glow peaks 2 and 3 are affected in some manner by hydroxide ions.

Christy and Mayhugh (1972) suggest that luminescence centres may be formed by the combination of a radiation produced F-centre with a Ti centre (or complex).

A number of theories have been formulated to explain supralinearity, sensitisation, and LET effects (Cameron et al, 1968; Claffy et al, 1968; Attix, 1974). The track interaction model of Claffy et al (1968) accounts for current experimental evidence. Attix (1974) extended the track interaction model to cater for either holes or electrons. His summary of
the model is as follows:

(a) Electron-hole pairs are produced during ionizing irradiation, and these occur along the tracks of the secondary charged particles, such as Compton and photoelectrons in the case of incident \( \gamma \)-rays. Both the electrons and holes are trapped near the track.

(b) Some of the centres thus produced along these tracks are luminescence centres (Claffy et al. 1968 specified these as being F-centres, but that identification is not essential).

(c) When the phosphor is heated, one species of charge carrier (holes or electrons, it is not necessary to specify which) is released and migrates to the still-trapped oppositely charged carriers. They recombine, and in those cases where the centre happens to be a luminescent centre, thermoluminescence is emitted.

(d) For low doses the secondary electron tracks are widely separated so that released charge carriers only have access to luminescence centres in the same track. Thermoluminescent response vs dose is linear in this dose region.

(e) As the dose is increased, eventually the average separation of adjacent electron tracks is comparable to the average separation of luminescence centres along each track. More luminescence centres are then located within the migrating range of the released charge carriers; the TL efficiency thereby increases, and the TL output vs dose rises more rapidly than linearly.

(f) Most of the luminescence centres are not reached by a released charge-carrier during the heating cycle, and therefore most of these centres survive the TL readout process. A later radiation exposure and heating therefore exhibits enhanced TL efficiency, because of the added population of luminescence centres remaining from the previous exposure. This accounts qualitatively for the phenomenon of TL sensitisation.

The model is consistent with available data, and accounts for LET effects.

4.4.6. Discussion

The most surprising result with the 'home-made' phosphors was the failure of Mg to produce appreciable thermoluminescence. However, it became clear, when the thermoluminescence of TLD-100 was destroyed by a remelt, that the furnace cycle was such that most of the Mg was probably being precipitated out of the crystal lattice. The crucial factor is probably the cooling rate rather than the time spent by the sample above the melting point. Brunskill (1974) has since successfully produced LiF:Mg,Ti by a similar wet mix method, but using the following thermal cycle. The mixture is heated
in a graphite crucible in an argon atmosphere to a temperature of 950°C, at which it is held for 5 hours. The oven is switched off and the contents allowed to cool naturally. When the temperature reaches 680°C the temperature is held for 10 minutes after which the crucible is removed from the oven and cooled rapidly. The resulting phosphor has a sensitivity and properties very similar to TLD-100. Probably, the hold at 680°C ensures that the magnesium is evenly dispersed throughout the crystal lattice, and the rapid quench freezes it in the crystal. Correspondingly, in the author's experiments the slow cooling rate may have allowed the magnesium to precipitate out.

It is thus highly probable that the glow curve structure of samples 11 and 14 result in part from a low magnesium content (<10 ppm by weight). The term 'low' is used in comparison with TLD-100, which has a magnesium content of about 100 ppm by weight. Frank and Edelmann (1966) studied the effects of variations of Mg content on the glow curve structure and sensitivity of LiF. They found that the light sum due to peaks above 170°C (i.e. peaks 4 and 5) increased approximately linearly with Mg concentration for concentrations up to about 100 ppm by weight. For higher concentrations the light output from these peaks levelled out, and eventually fell. The light sum due to peaks below 170°C (i.e. peaks 1, 2, and 3) was greatest for low concentrations of Mg, decreased with increasing Mg concentration, reaching a minimum at about 100-200 ppm, and increased again for higher concentrations. At that time the effect of Ti was not known, but from their results it is probable that their starting material contained a few ppm of Ti. With Mg concentrations of 12 ppm or less they obtained a glow curve structure similar to samples 11 and 14, although they also noted small peaks at 210°C.

The 126°C peak in samples 11 and 14 is probably due to a mechanism similar to that causing peak 2 (123°C) in TLD-100. The slight difference in peak temperature can be explained by differences in trap concentration (Townsend and Kelly, 1973), and the increased sensitivity of 'peak 2' in samples 11 and 14 is in agreement with Dryden and Shuter (1973), who found that the height of peak 2 increases as the Mg content decreases (for a restricted range of Mg concentration). The identity of the 178°C peak in samples 11 and 14 is not easily established. Peaks 3 and 4 in TLD-100 occur at about 160 and 190°C respectively, relative to peak 5 at 210°C. It would seem that the 178°C peak corresponds more to the recently discovered peak 4b (Johnson, 1974) but, as mentioned above, peak temperature can be dependent on trap concentration. For example, Dryden and Shuter (1973) found that the temperature at which peak 5 occurred varied between about 190 and 210°C, increasing with magnesium concentration. There is
the additional possibility that the 178°C peak may be caused by some activator other than Mg.

The fact that the glow curve structure and sensitivity of samples 11 and 14 were not significantly affected by a pre-irradiation anneal of 80°C for 24 hours, or by large variations in the cooling rate from 400°C, provide further evidence of a low magnesium content. The independence of cooling rate indicates that the probability of dipoles meeting must be low, over the range of cooling rates studied. In contrast, in TLD-100 the reduction of the low temperature traps by dipoles aggregating into higher complexes with an 80°C anneal is a fairly rapid process. In TLD-100, with ~100 ppm Mg, the lower temperature peaks are reduced by about 90% by an anneal of 80°C for 16 hours, which illustrates the mobility of the Mg ions. If the concentration of Mg is <10 ppm, an equivalent reduction of the lower temperature peaks can be expected to take substantially longer, since the average separation between dipoles is much greater.

Both the peaks in samples 11 and 14 are asymmetric, the lower temperature edges being broader than the higher temperature edges. This is characteristic of a situation where the number of traps is less than the number of recombination centres (Townsend and Kelly, 1973) and in fact the absence of peaks at about 210°C could be correlated with a 'high' Ti content relative to TLD-100. Rossiter et al (1971) found that the optimum height of peak 5 was obtained with about 8 ppm by weight of Ti. His samples contained about 80 ppm by weight of Mg, i.e. very similar to TLD-100. Concentrations of Ti in excess of 8 ppm caused a concentration quenching effect (see figure 4.7), strongly decreasing the height of peak 5. Peak 4 was affected to a lesser extent, and peaks 2 and 3 were relatively unaffected. In samples 11 and 14, the added Ti activator was of the order of 50-100 ppm by weight, though probably this would not be evenly distributed, and it can thus be expected that severe concentration quenching of peaks 5 and 4 is taking place.

To summarise, the absence of peaks 4 and 5, and the magnitude of peak 2, are probably due to a combination of low magnesium and high titanium concentrations. The investigation was limited in that the light measurement system was optimised for the blue-green emission of TLD-100, and may not be so suited to some of these new materials. Additionally, the experiments were carried out over restricted doses and dose-rates.

From the subsequent work of Rossiter et al (1971), it is probable that the thermoluminescent characteristics of some of the samples were due in part to accidental cross-contamination with Ti in concentrations of ≤5ppm.
by weight, since its importance was not recognised at that time. However, the insensitivity to thermal history of some of the more promising samples is an interesting and potentially useful property and further work to establish the optimum concentrations of activators would seem worthwhile.

4.5. The future of TL materials research and development

4.5.1. The requirement for better analytical techniques

In retrospect, the discovery by Rossiter et al (1971) that concentrations of Ti of the order of 1 ppm by weight could significantly affect the thermoluminescent properties of LiF will probably be seen as a watershed in the history of TL materials research. Before then, research had centred on much higher impurity levels of the order of 100 ppm by weight. It is now clear that any detailed study of thermoluminescent materials must be backed up by excellent analytical services, the usual techniques being spark mass-spectrographic analysis or neutron activation analysis. It becomes apparent, when reviewing the literature on TLD research, that analytical discrepancies must have occurred even with impurity levels of the order of 100 ppm. Since the 'insignificant impurity' concentration must now be considered to be about 0.1 ppm or less, it would seem that TL materials research has reached a stage when it will have to wait for analytical and crystal preparation techniques to catch up before any further advances can be made. It is possible that in this respect some degree of 'bootstrapping' will be involved i.e. thermoluminescence may become an analytical aid.

Apart from doubts as to the validity or sensitivity of present analytical techniques, another factor deterring any programme of materials research is the high cost involved. A spark mass-spectrographic analysis of a single sample (by a commercial service) currently costs about £60. For this reason, none of the samples prepared in the investigation described earlier has been analysed, it being considered that the possible benefits do not warrant the cost. Due to the high costs involved, and the low chances of success, it is unlikely that any large programme of research will be undertaken by current commercial phosphor manufacturers, who will content themselves with producing established materials. Instead, further detailed work is more likely to be carried out by nationally supported pure research laboratories with good in-house analytical services.

In the context of phosphor purity, it is disturbing to note that in order to cut costs some of the current suppliers of LiF prepare their product simply by adding magnesium to rather impure starting material already containing the necessary titanium. This is not the way to establish a
material with repeatable characteristics; the effect of other impurities on the thermoluminescence of LiF is not yet known, and it is almost certain that the concentrations of these impurities will not be constant. The preferred way of producing a phosphor with repeatable characteristics is to start with the purest possible product and add known activators.

4.5.2. TL materials warranting further investigation

Assuming that analytical problems are resolved it is possible to assess the future prospects of various phosphors.

The three near tissue equivalent phosphors, LiF, Li$_2$B$_4$O$_7$, and BeO, are characterised by a low intrinsic efficiency of energy conversion. Although most TL materials research has been concentrated on LiF, it may be inferred from the low intrinsic efficiency that the thermoluminescent process in LiF is more complex than in most other phosphors, involving several steps with loss processes at each stage. The significant activators in LiF (TLD-100) are now believed known (Mg, Ti, O), but a large research programme might uncover a more efficient mechanism using other activators.

The most promising phosphor for future research is probably lithium borate, at present activated with manganese. Its intrinsic efficiency (0.073%) is higher than LiF but low dose measurements are complicated by the orange-red emission spectrum. It is not known whether the Mn acts as both trapping and luminescent centres or whether some other impurity, present in much lower concentrations, is also involved. Since its intrinsic efficiency is comparable with LiF, it is possible that the thermoluminescent mechanism is as complicated. Lambert (1971) has prepared lithium borate, activated with holmium, with a green emission spectrum but the intrinsic efficiency was an order of magnitude lower than lithium borate activated with manganese. However, taking into account the PM tube response, the effective efficiency was about the same. Moreno et al (1971) found that silver was also an efficient activator, but the main peak, at 140°C, was rather low.

It is probable that BeO could also be considerably improved, but the toxicity of this compound will deter many researchers. Sintered BeO discs are fairly safe to handle.

In contrast to the near tissue-equivalent phosphors many higher Z phosphors e.g. calcium sulphates, are characterised by an intrinsic efficiency of about 1%, which is approximately 25 times that of LiF. This is suggestive of a much simpler thermoluminescent mechanism than LiF, and it would be interesting to investigate the reasons for this; possibly the rare earth activators usually employed act both as trapping and luminescent centres. The addition of single rare earths to very pure LiF or Li$_2$B$_4$O$_7$, may therefore
be a fruitful line of investigation. In these phosphors an improvement in sensitivity by a factor of 10 and a simpler glow curve structure would be most welcome. It is clear that LiF:Mg must always have a complex glow curve structure with consequent dose measurement complications, due to the migration and aggregation of Mg complexes. The properties of available high-Z phosphors, such as CaSO₄:Dy or Tm, are already eminently suitable for the applications to which these phosphors are put, and little will be gained by further improvements.

4.5.3. Some commercial considerations

The materials research programme started by D. A. Pitman Ltd. in 1970 was justified, as explained above, by the existence at that time of only one source of LiF. Since then, LiF:Mg,Ti has become available from a variety of sources, with a consequent competitiveness in the pricing of LiF, and thus the only reason for producing it now would be if the profit on sales exceeded the capital and running costs of the requisite crystal growing equipment, amortised over a suitable period.

The production of established phosphors may not be economic, since difficulty is likely to be encountered in persuading potential customers that your product is just as reproducible as a competitive product which has established a reputation for repeatable characteristics over several years (e.g. Harshaw LiF). The competition can respond to any cut-price tactics, which also lower the profit margin. However, the production of a new phosphor with demonstrably superior characteristics may be economically justifiable, assuming one can achieve patent protection over a reasonable period.
5.1. Evolution of design philosophy

5.1.1. Early experience

The first type of reader manufactured by D. A. Pitman Ltd. was the Model 205A, based on a design by Walker and Webb (1968). This was a simple reader designed for short-term dose control in nuclear power stations, and capable of accepting only one type of dosemeter, a LiF/PTFE disc 12.7 mm diameter x 0.4 mm thick. The dose range with a disc containing 30% by weight of phosphor was 0.1 - 1000 rads. Reproducibility of readout was ± 20% over the higher dose ranges, but it was found that at the 100 mrad level it was at best ± 30%, even under ideal laboratory conditions. The main reason for this was that inert gas flow had not been provided for in the design with the result that any dirt or dust on the dosemeter could give rise to a high and variable background signal due to chemiluminescence.

The 205A reader was improved during the present studies by redesign of the dosemeter holder, introduction of inert gas flow, and the replacement of the original logarithmic DC amplifier and analogue meter by a linear DC amplifier and digital meter. The dose range was thereby extended downwards towards 10 mrads. Reproducibility of readout was then better than ± 10% over most of the dose range, falling to ± 50% at 10 mrads, as the effect of variations in background signal became significant. The improved reader was produced in two versions. The 205B (figure 5.1) was a specially ruggedized version which was manufactured to meet a Royal Navy specification, for use in nuclear submarines and naval dockyards. The 205C (figure 5.2) was produced to normal commercial standards, for personnel, extremity and criticality monitoring.

The 205C was a useful low cost instrument, but did not sell well, due to its rather limited capability and performance. Its deficiencies can be summarised as follows:

(a) Limited dosemeter configuration.
(b) Very tight machining tolerances on drawer required to avoid light leaks; normal wear and tear could lead to light leaks.
(c) Design of dosemeter holder and positioning of dosemeter both critical to ensure correct acceptance and heating of dosemeter.
(d) Limited heating profile.
(e) The efficiency of light collection is not accurately assessed by...
Figure 5.1. Model 205B TLD Reader

Figure 5.2. Model 205C TLD reader
the light source reading due mainly to the positioning of the infra-red absorption filter.

(f) Drift in light measurement system due to temperature coefficient of PM tube.

5.1.2. Market assessment

Following experience with the Model 205, the TLD market was reassessed. It was clear that a 'system' design approach had to be adopted. For example, a complete TLD system could comprise of (a) a basic readout instrument plus accessories such as data and glow curve recording equipment and dosemeter handling aids, and (b) various forms of dosemeter to suit different applications, plus dosemeter accessories such as badges and sachets, annealing ovens and stands, and a calibration facility. Potential customers do not usually have the time to 'shop around' for these separate items, and the convenience of being able to meet all their requirements with one order is often a deciding factor.

The market divides down into the following applications:

(a) Radiological protection: general personnel, extremity, and environmental monitoring; control and criticality dosimetry.
(b) Radiotherapy: the planning and checking of radiotherapy treatments.
(c) Research: investigations into materials, dosemeters, and basic dosimetry.

To cover all these fields a readout instrument needs to be versatile and very stable. The market also divides according to throughput. For high throughput requirements, such as large scale personal dosimetry, an automatic system is obviously desirable.

It was decided to produce initially a manual system for the lower throughput applications, with a view to embarking on an automatic system, incorporating the knowledge gained with the manual system, as the design was finalised. The reader itself is the central feature of any TLD system, and the design of the manual reader is discussed in this and the following chapter.

5.1.3. Manually operated readout instrument

The basic aim of the experimental programme was the production of a readout instrument which in itself contributed very little additional error to a dose measurement, but which simplified operational techniques as far as possible and was capable of accepting a wide variety of dosemeters, including phosphor/PTFE discs and microrods, loose powder, and hot-pressed, extruded and sintered types of dosemeter. Provision had to be made for extending the instrument capability to meet research applications, and for matching with a complete range of accessories. Reliability, and ease of
fault-finding and servicing, were of paramount importance.

This programme was carried through successfully and resulted in the advanced 'Toledo' Model 654 TLD reader (figure 5.3) which is now being marketed by D. A. Pitman Ltd. Several novel techniques were required to achieve these objectives, and their necessity and effectiveness are discussed in detail in the following sections.

5.2. Sources of error in TLD readers

The suitability of a reader design is best considered by examining the various sources of error and the methods used to reduce their effect. A TLD reader basically consists of means for heating a thermoluminescent dosemeter and means for measuring a constant fraction of the light emitted by the dosemeter as it is heated. The light output from the dosemeter is related to the radiation dose it has received, and unknown doses can be accurately measured by comparing the amount of light from dosemeters with unknown doses with the amount of light emitted by the same or similar dosemeters which have received a known radiation dose. Since any such calibration procedure is usually sequential the sensitivity of the reader should not vary significantly during the time interval between the readout of known and unknown doses. Sources of error within the reader can conveniently be classified into four groups:

1. Variations in the dosemeter heating cycle

The dosemeter must be passed through a closely controlled heating cycle, since in many cases the light output from the dosemeter is critically dependent on its thermal treatment. The method of heating invariably consists of placing the dosemeter in good thermal contact with a heating medium, thus there are two possible causes of variations in the dosemeter heating cycle:

i) Variations in the temperature cycle of the heating medium.

ii) Variations in the nett transfer of heat from the heating medium to the dosemeter.

2. Variations in the efficiency of light collection

A reader should be designed such that a constant and substantial fraction of the light emitted by a given type of dosemeter reaches the light detector. Possible sources of error are:

i) Variations in the positioning of the dosemeter with respect to the light detector and

ii) Variations in the optical properties of the dosemeter and its environment, and in the light path to the light detector.
Figure 5.3. 'ToLeDo' Model 654 reader

Figure 5.4. Section of Model 654 drawer assembly

- PM tube photocathode
- 'O' rings
- Path of inert gas flow
- Fixed polyimide plate
- Drawer
- Tray
- Heating element
- Thermocouple
- Heater electrode
- Flexible connector
- Electromechanical lift
- Infra-red absorbing filter
3. Variations in the sensitivity of the light measurement system

The low intensity light reaching the detector has to be transformed and amplified into a readable signal. The output signal per unit light input to the detector is generally termed the 'sensitivity'. Variations in the sensitivity of the light measurement system can be caused by drift in the gain of the light detector and the signal conditioning circuits. Additional errors can be incurred if the sensitivity is a function of the light input, i.e. if the output signal is not linearly proportional to the light input.

4. Variations in the background signal from the readout instrument

The background signal is defined as the reading obtained when an unirradiated dosemeter is read out in a given TLD reader. Although most of this reading is traceable to the dosemeter, there is also a contribution from the readout instrument itself arising from:

i) Noise in the light detector and the signal conditioning circuits.

ii) Infra-red radiation from heated areas.

iii) Chemiluminescence, i.e. light emitted during the oxidation of organic impurities such as oil and dust.

The description of the Model 654 has therefore been subdivided into four corresponding sections, the heating system, the efficiency of light collection, the light measurement system, and background signals. To clarify the interaction of the mechanical features, a cross-sectional view of the relevant section of the drawer assembly is shown in figure 5.4.

5.3 Determining the design of the heating system on the Model 654 TLD reader

5.3.1 Specification of the heating system

The first step in the design of the heating system was to specify its requirements. The heating system should accept most types of dosemeters in common use, thus it has to cope with dosemeters having a wide range of sizes, shapes, thermal capacities and conductivities. Dosemeter loading should be rapid and simple, and the design should be consistent with the necessity for maintaining constant the fraction of light collected from any given type of dosemeter. The dosemeters should be efficiently and reproducibly heated, and the temperature vs time heating profile should be versatile and easily adapted to suit different applications, e.g. routine or research use. The system should be reliable, and its performance easy to check and maintain.

5.3.2 Optimising the design of the heating system

The method adopted was to compare the various possible designs, and isolate
5.4. Methods of heating thermoluminescent dosemeters

5.4.1. A.C. resistive heating using low thermal capacity heaters

This is the form of heating most commonly used on commercially available readers; it has the advantage of being quick to respond to temperature changes and thus, by using temperature sensors and negative feedback, accurately programmable and versatile heating cycles can be generated to suit specific applications. Normally a metal heating element having a resistance of the order of 10 milliohms is connected across the secondary winding of a transformer. In many cases the heating element itself is the tray on which the dosemeter is placed, and may be shaped accordingly. The alternating voltage on the primary winding of the transformer is either varied or switched on and off at intervals to give the desired heating. The secondary winding and the connectors to the heating element should preferably have a resistance lower than the resistance of the heating element, otherwise a significant fraction of the power generated would be utilized in heating the transformer and the connectors. Hence the secondary winding is rated at a low voltage and a high current, and thick copper leads are used to connect it to the heating element.

This form of heating is discussed in greater detail following the description of other heating methods.

5.4.2. Resistive heating using high thermal capacity heaters

In some designs a resistive heater element is contained within a metal block of high thermal capacity, and the heated block is brought into contact with the dosemeter electromechanically. The Pitman Model 205 series and the reader described by Hartin (1966) use this method of heating. In the Model 205C the block is kept at a constant temperature by use of a Curie point thermostat, whilst Hartin's system employs a thermocouple embedded in the block.

The advantages of this form of heating are ease of manufacture and good mechanical reliability. During test trials on the Model 205, for example, the heated block system was tested over more than a hundred thousand operations. However, it has three major disadvantages. Firstly, the possibility of a versatile heating profile is lost. Secondly, much heat is dissipated and has to be removed to avoid overheating the apparatus, in particular the PM tube. Thirdly, it is not possible to quickly compensate for sudden changes in the surface temperature of the block caused by contact with dosemeters; e.g. on the Model 205C the heating efficiency is lower...
after reading out the first few dosemeters of a series, due to the lowering of the surface temperature of the block.

5.4.3. Hot gas heating

Readers employing hot nitrogen gas as the heating medium have been described by Petrock and Jones (1968), Botter-Jensen (1970), and Julius et al (1974). The advantages of nitrogen heating are (a) it gives highly reproducible heating as the dosemeter is completely surrounded by the heating medium; thus an excellent thermal contact is ensured and heat transfer problems are minimised, and (b) a very convenient dosemeter loading procedure can be employed, which lends itself to the development of automatic systems.

The disadvantages are (a) the method is only suitable for solid forms of dosemeter as it is difficult to feed in loose powder, and (b) the gas temperature cannot be changed quickly, thus it is not suitable for generating complex heating profiles.

5.4.4. Induction heating

A design using RF heating has been described by Brunskill (1968), and Brunskill and Langmead (1970). The dosemeter is placed in good thermal contact with a material such as aluminium or carbon, which is then inductively heated. The disadvantages of this method are, firstly, large amounts of RF power are consumed due to inefficient coupling between the induction coil and the heating tray and, secondly, it is difficult to accurately control the dosemeter heating cycle.

5.4.5. Other methods of heating

Cameron et al (1968b) have described a reader in which the dosemeter tray was heated by focusing onto it the light from a projector bulb. The system was limited by the necessity to exclude this light from the PM tube.

Kastner et al (1969) heated dosemeters ultrasonically, though this was not the effect they were investigating at the time. Heating systems employing microwaves and lasers have also been proposed, but these methods were not examined in detail since they all suffer in some degree from the various disadvantages cited above. D.C. resistive heating has also been contemplated, but its extra circuit complexity does not appear to offer any compensating advantages over A.C. heating.

5.4.6. Conclusion

The resistive heating of a low thermal capacity heating element is suitable for most forms of dosemeter, and is the method offering the most versatile and accurately controllable heating cycle. Therefore it was decided to investigate this method further with a view to using it in the Model 654 TLD reader.
5.5. Methods of controlling the dosemeter heating profile using an AC resistively heated low thermal capacity heater

5.5.1. Fixed power input

One of the first commercially available TLD readers, the Conrad 4100 and its successors, the 5100 and the 7100, simply timed the period over which a fixed current passed through the heating element, which held the dosemeter. The temperature vs time characteristic of the heating element is non-linear. Besides having the virtues of simplicity and low manufacturing cost the method lent itself to a system of interchangeable heating elements, each with the same external dimensions to clip into two heater jaws when the drawer was pushed home. Different configurations were provided in the central area of each type of element, to suit different types of dosemeter. The element suitable for loose phosphor and a number of high thermal conductivity solid forms of dosemeter has a circular central depression approximately 13mm in diameter. The element for heating phosphor/PTFE discs, which have a low thermal conductivity, has a mesh welded on to hold the disc in contact against the element. The element for heating phosphor/PTFE microrods has two metal rods welded to the tray such that the microrod can be clipped in between them. The removable nature of the elements allows them to be replaced as they tarnish, or if damaged.

This heating method is simple and works reasonably well, but has several disadvantages:

i) Only non-linear heating profiles can be generated, although the profile can be varied by adjusting the current through the tray and altering the timing period to suit. With the normal timing period the temperature of the heating element increases rapidly towards the end of the cycle, and this leads to large temperature gradients across the thickness of those dosemeters having poor thermal conductivity, such as phosphor/PTFE discs. It is thus difficult to set the heater current to ensure complete heating of these dosemeters without overheating them or generating too much infrared radiation. Webb (1966) evolved a method of taking the ratio of first and second readings to obtain the optimum signal/noise ratio. This is the most suitable method of setting the heating current; however, the optimum heating current is a function of the dosemeter, and the extra complexity involved in setting up the heating cycle led to a large number of user problems.

ii) The temperature of the heating element at the end of the cycle is dependent on its temperature at the start of the cycle. This necessitates waiting between readings for the element to cool to
near ambient temperature, or in using more than one element, so that one element is cooling whilst another is being used. Even so, variations in ambient temperature will cause variations in the temperature of the heating element at the end of the cycle.

**iii)** The heating cycle was not suitable for many routine and research applications. For example, a linear heating ramp is generally required in materials research; and in personnel monitoring, it is desirable to anneal dosemeters in the instrument, but to achieve that with this type of heating cycle would entail a signal/noise ratio much less than optimum. Additionally, it is not possible to accurately and reproducibly erase and gate out the light from the unwanted low temperature peaks in LiF and Li$_2$B$_4$O$_7$:Mn, since the temperature gradients across many types of dosemeter are too great to adequately resolve these peaks from the dosimetry peaks.

**iv)** The mechanical design is such that significant variations in geometrical efficiency of light collection can occur, due to positional variations of dosemeters with respect to the PM tube photocathode. With the microrod element the solid angle subtended by the microrod to the photocathode varies as the element flexes and the two guide rods move further apart or closer together. In addition, if the rods are too far apart, the microrod is not held firmly against the tray, and poor heating efficiency results. With the disc heating element, the efficiency of light collection will depend on the open area of the mesh. In practice it is very difficult to obtain meshes of the type used (electroformed) with exactly the same open area, thus each tray should be individually calibrated for use with a particular type of dosemeter.

**v)** Pushing home the drawer with a tray of loose powder requires care, since when the heater jaws are encountered the sudden extra mechanical resistance can cause powder to spill or become unevenly distributed. If an attempt is made to open the drawer whilst heating, a resistance weld of the tray to the heating jaws can result.

Despite the above listed drawbacks, many units were sold and with care functioned reasonably well, within their limitations.

**5.5.2. Negative feedback utilising thermocouple welded to heating element**

A common method of controlling the heating characteristic is to weld a thermocouple to the heating element in order to obtain a feedback signal for the heater control circuitry. Temperature vs time profiles can be obtained analogous to any voltage vs time profile that can be electronically generated.
This method can be extremely stable and accurate providing adequate compensation for the cold junction of the thermocouple is incorporated. A number of readers using this method of heating have been described, for example Rae (1968), Harris & Jackson (1968b).

The action of welding a thermocouple to the heating element immediately imposes certain constraints on the system. Heating elements become much less easily interchangeable; in fact the replacement of a heating element would, from the user's point of view, be a major operation not to be lightly undertaken. The heating element tends to tarnish with use and the decrease in reflectivity will alter the efficiency of light collection, which may require the heating element to be changed. A more far-reaching constraint is the limitation on the types of dosemeter that can be adequately heated e.g. in the majority of readers of this kind the fixed heating element has a circular depression in which the dosemeter is placed; it is not generally feasible to heat large phosphor/PTFE discs sufficiently by simply placing the disc on the circular depression, since the discs are often bowed and hence not in good thermal contact with the heating element.

5.5.3. Negative feedback utilising thermocouple not welded to heating element

To give a reasonable degree of control over the heating cycle without the constraints of the fixed heating element, some designs have resorted to using thermocouples which are simply mechanically pressed against the heating element. In general these arrangements are not reliable due to the varying nature of the contact with the tray. In the Teledyne Isotopes 7100 reader for example, a thermocouple is electromechanically lifted into contact with the tray when the drawer is closed. The thermocouple is not used to control the heating cycle directly, but only to provide an indication of tray temperature. The thermocouple wires are approximately 0.05mm thick, and are welded together to form a fine point; it is difficult to ensure that the fine point itself is always in contact with the tray, and thus reproducible readings are not easy to obtain. Additionally, the thermocouple has to be lifted vertically through different distances to suit the different heating elements, and the electro-mechanical arrangement is such that the pressure forcing the thermocouple against the tray is not constant.

In the Teledyne Isotopes 7300B, a different type of thermocouple probe (see figure 5.5) is used as a sensor for the control circuit. The flat design of this thermocouple joint gives more reproducible results than are obtained with other types of thermocouple, provided the pressure with which the thermocouple is applied to the tray remains constant; however, the same problem arises as on the 7100, namely the probe has to travel through
Figure 5.5. Thermocouple probe for the measurement of surface temperature (manufactured by Omega Engineering Inc.)

Figure 5.6. Heating trays for the Model 654 reader (loaded with various types of dosemeter)
different vertical distances to suit different trays. An additional problem is that the probe tip loses its springiness after some use, and this causes the pressure against the heating element and the area of contact to change.

5.5.4. Negative feedback utilising infra-red detector

The idea of using an infra-red detector as a sensor for a heater control circuit by measuring the infra-red radiation from the hot heating element appears at first sight to eliminate many of the problems associated with other devices. The author first heard of the idea from Wallace (1968).

An infra-red detector was incorporated into the Teledyne Isotopes Model 7300A. Another detector, shielded from the heating element emission, was used to provide ambient compensation. The system has one major disadvantage: the optical arrangement associated with the detector is situated directly beneath the heating element, and dust and other debris collect on it and reduce the infra-red signal reaching the detector. Consequently the feedback loop raises the temperature of the heating element to compensate, and thus careful and frequent cleaning of the optical arrangement is necessary to obtain a reproducible heating cycle. Two problems have been noted with the 7300A when this regular cleaning is not carried out. Firstly, with LiF and Li₂B₀.₂ Mn, the preheat temperature rises and erases a portion of the dosimetry peaks as well as the low temperature peaks. Secondly, with phosphor/PTFE dosemeters, the anneal temperature rises above 327°C, which is a transition temperature in PTFE, and changes the optical density and sensitivity of the dosemeters. Since the dosemeters are not generally overheated in a reproducible manner, the precision of sensitivity of a batch of dosemeters becomes much poorer.

5.5.5. Other methods of controlling the heating cycle

The 'fixed power input' method was described with respect to the Conrad series of instruments. Other readers have used this principle to programme heating cycles by varying the power input but unless a temperature sensor is used to provide a feedback signal the disadvantages listed in section 5.5.1 (i) and (ii) still apply.

A method of temperature control based upon measuring the resistance of the heating element has been proposed, but has not been applied to date.

5.5.6. Conclusion

Negative feedback is necessary for the accurate and reproducible control of a programmed heating cycle. The most suitable temperature sensor is a thermocouple welded to the heating element but this introduces constraints which need to be resolved by an appropriate mechanical arrangement. Before a
decision could be reached on whether this method could be used in the
Model 654 it was therefore necessary to investigate methods of achieving
efficient and reproducible heating of the range of dosimeters to be used,
together with reproducible efficiency of light collection.

5.6. Methods of achieving efficient heating of, and reproducible light
collection from different types of dosimeter

Dosimeters with high thermal conductivity, such as loose powder and many
compressed, sintered, or extruded forms, can conveniently be heated by
shaping the heating element to hold and centralise them. A simple
depression in the heating element is usually sufficient. Dosimeters having
a low thermal conductivity, such as phosphor/PTFE discs or microrods, are
more difficult to heat.

Considering first the phosphor/PTFE disc, it is not easy to heat these
efficiently since besides their low thermal conductivity they generally do
not lie flat on a heating element. Due to the manufacturing process discs
greater than 0.2 mm thick are slightly bowed and discs thinner than 0.2 mm
are crinkly. Very thin (e.g., 20 μm) discs tend to curl up when heated.
Generally the larger diameter discs are the most difficult to heat since when
simply laid on a heating element parts of them are not in direct contact with
the heating medium. In addition to heat transfer problems, the efficiency of
light collection is also affected. Previous attempts to heat the commonly
used 12.7 mm diameter phosphor/PTFE disc adequately have relied on trapping
the disc between two surfaces. The method used on Teledyne Isotopes
instruments is to slide the disc under a mesh or spring configuration
(Bjarngard and Jones, 1967). In the Pitman Model 205C the disc is held
between the heating block and a PTFE cruciform aperture. Jones (1968)
used a sprung ring of appropriate diameter to hold the disc firmly against the
heating element. Perry (1968) lifted the heater to press the disc against
a cruciform aperture. Knight (1967) used suction to hold the disc against
the heating element. With the phosphor/PTFE microrod, 1 mm diameter by
6 mm long, the problem of contact with the tray is not so great, but there is
a greater thickness of low thermal conductivity material through which heat
has to travel.

Only the Jones and Perry designs used thermocouples welded to the heating
element, but apart from this each of the above methods had disadvantages.
The Teledyne Isotopes system is very effective in holding the disc against
the heating element, but has the operational problem, more noticeable for
the thinner discs, of sliding the disc under the mesh or spring without
distortion. The Pitman Model 205C and the system due to Jones (1968) were
specifically designed for the 12.7 mm diameter disc and are not easily
adaptable to other dosimeters.
Perry's method had the advantage of simple dosemeter loading, and was the only system that had the welded thermocouple sensor essential for a reproducible and versatile heating cycle together with the potential to read out both the 12.7 mm diameter phosphor/PTFE disc and other forms of dosemeter. The system was investigated in more detail, and the following disadvantages were noticed. The Perry instrument was specifically designed for use with discs or loose powder, the latter being loaded into a metal tray and heated through the tray. The cruciform type of aperture severely restricted the other forms of dosemeter that could be used, due to the effect on the solid angle subtended by the dosemeter to the photocathode. Even in the case of powder the efficiency of light collection was affected by the distribution of the powder in the tray, and for small solid forms of dosemeter such as chips or microrods substantial variations in efficiency of light collection were possible. A circular heating element provided the surface immediately below the 12.7 mm diameter disc and was not easily accessible; inspection of its surface for changes in reflectivity therefore required a major stripdown. Its diameter was smaller than the diameter of the disc, thus the edges of discs were not heated, and this lead to problems when trying to reuse discs following only an internal anneal in the instrument, since due to positional variations discs were not necessarily heated over the same area each time, and remnants of previous doses could be recorded. The mechanical design also had limitations. The electromechanical lift was designed with the inclusion of a spring to ensure that a constant pressure was exerted on the dosemeter or tray, but due to incorrect positioning of the microswitch determining the 'heater up' position this spring was ineffectual. If the drawer was opened whilst the heater was up, the heating element could be damaged. Velvet cloth was used in conjunction with tight machining tolerances to prevent light leaks.

However, ways of overcoming these problems were worked out, and it was therefore decided to use a similar arrangement as the basis of the Model 654 heating system, which is now described.

5.7. The method of heating dosemeters on the Model 654

5.7.1. Heat transfer system

The efficiency with which a dosemeter can be read out in a given time depends on the temperature gradient across its thickness; the temperature gradient is a function of the dosemeter's conductivity and thermal capacity. It is easier to efficiently heat pure phosphor dosemeters such as loose powder and high sensitivity ribbons than the phosphor/PTFE range of dosemeters, which have a lower thermal conductivity, and this fact helped determine the design of the heat transfer system.
The method of heat transfer from the heating element to the dosemeter is illustrated in figure 5.7. It combines the concept of removable trays (for easier replacement or cleaning) with the accurate and repeatable temperature sensing (provided by the thermocouple welded to the heating element) necessary for the reproducible heating of dosemeters. In all cases the dosemeter is placed on a removable tray located in a depression in a sliding drawer unit, and when the drawer is pushed home an electromechanical lift, on which the heating element is mounted, moves vertically upwards and presses the tray against a fixed polyimide plate, thus ensuring good heat transfer from the heating element to the tray, which in turn heats the dosemeter. Different trays are provided to suit and centralise the various forms of dosemeter (figure 5.6) and their ease of replacement overcomes the problem of changes in reflectivity of the surface immediately in contact with the underside of the dosemeter since the state of this surface can easily be assessed, and trays replaced if required. The trays are constructed from 0.1mm thick stainless steel and the temperature gradient across their thickness was found to be less than 5°C at 250°C.

For solid forms of dosemeter, the use of vacuum tweezers results in an extremely rapid handling technique. Alternatively hand tweezers, or a combination of both hand and vacuum tweezers, may be preferred. Loose powder can be loaded with the tray either in the drawer or remote from the reader, and can be removed with vacuum tweezers (i.e. with an in-line powder trap) or by inverting the tray. A tray lifting device can be fitted to the front panel of the reader, below the drawer, to facilitate the positioning and removal of trays.

5.7.2. Design of heating element

Circular heating elements similar to Perry's design (figure 5.8) have several disadvantages: (a) They are difficult and costly to manufacture, having to be machined from a stainless steel bar, (b) to facilitate assembly, the heating element has to be soldered to two heater electrodes in such a way that the top surface remains parallel to the heater electrodes, (c) the top surface of the heating element should have low thermal gradients across it to ensure even heating of the dosemeter, but 'cold' spots are always formed at the sides nearest the heater electrodes, (d) to obtain an acceptably fast cooling rate the thermal capacity has to be quite small, and this can only be achieved at the expense of the robustness required for repeated use.

The system of removable trays meant that a circular design of heating element was no longer mandatory, and to overcome the above disadvantages the
Methods of heat transfer from heating element to dosemeter on the Model 654 reader

(a) Phosphor/PTFE discs, 0.13 - 0.4 mm thick by 11 - 12.7 mm diameter.

(b) Phosphor/PTFE discs, 0.02 mm thick

(c) Other dosemeters (Powder, chips, microrods, sintered discs)
Figure 5.8. Circular, heating element, similar to that used by Perry (1968).

Figure 5.9. Model 654 heating element.
form of heating element shown in figure 5.9 was designed. This is simple to manufacture and can be screwed to heater electrodes rather than soldered, so that the top surface can readily be made parallel to the heater electrodes. The heating element is constructed from 0.25mm thick stainless steel shim, and has a uniform temperature distribution over most of its 200mm² area. It cools reasonably fast, having a fairly low thermal capacity, and is bright nickel plated to eliminate oxidation problems up to a temperature of at least 400°C.

5.7.3. Thermocouple sensor

A thermocouple is welded to the underside of the heating element to provide the temperature sensing for the heating cycle control system. It is constructed, prior to attachment to the heating element, from 0.25mm diameter chromel and alumel (T1/T2) wires welded together by the tungsten inert gas (TIG) method. A small head is thereby formed at the tip, which is then conveniently welded to the centre underside of the heating element by a capacitive discharge method. A chromel/alumel thermocouple was chosen since it gave a fairly high voltage output which is reasonably linear with temperatures up to 400°C. Sufficient stocks of wire have been bought to ensure that all thermocouples are made from the same batch of wire. It is interesting to note that in principle the thermocouple wires could be attached separately to the heating element, but a much greater AC signal from the heating cycle is then developed across the resistance between the two wires, and has to be rejected by the thermocouple amplifier.

5.7.4. Methods of heating different types of dosemeter

The polyimide (Vespel, trademark of Du Pont de Nemours Ltd.) plate against which the trays are pressed by the heating element, is stable up to 400°C and has a low thermal conductivity, thus minimising heat losses from the trays and dosemeters. This plate has a 10mm diameter circular aperture through which light passes from the dosemeter to the light detector. Figure 5.7 (a) shows the method of heating large (11-13mm diameter) phosphor/PTFE discs of different thicknesses, which have a low thermal conductivity. The discs, which are slightly bowed, are placed convex side down in the appropriate tray (D or TD). The reason for the lip on the polyimide plate is that the depression in the trays was made reasonably deep to prevent the disc from sliding out of the tray if the drawer is closed sharply. Originally the design was such that the lip on the polyimide plate trapped the disc securely against the tray. However it was found that, due to the high coefficient of thermal expansion of PTFE, the disc tended to bend upwards away from the tray when heated. The problem was solved by the use of a slightly deeper tray which allows the disc to expand laterally when heated,
while remaining in close contact with the tray. For optimum results, each different thickness of disc should have an appropriate design of tray. Tray D is designed for discs $0.4 \pm 0.03\text{mm}$ thick. Tray TD is for discs $0.1 - 0.2\text{mm}$ thick. Since the heating element is larger than the disc all of the disc is heated and the problem of residual doses from previous readouts, due to non-reproducible positioning of the disc, is eliminated. The fixed aperture ensures a constant efficiency of light collection.

For most other dosemeters the method of heating shown in figure 5.7 (c), where the dosemeter simply rests on the tray, is sufficient. This is the usual method of heating loose powder, hot-pressed, and extruded dosemeters, all of which have fairly high thermal conductivities. Phosphor/PTFE microrods, which have a low thermal conductivity and are 1mm thick, are rather a special case. Attempts to hold microrods against the heating element can result in large variations in geometrical efficiency of light collection. The best solution appears to be to simply rest the microrod on the tray and to extend the read time to ensure efficient heating. Tray P has an 8mm diameter depression for loose powder or 8mm diameter phosphor/PTFE discs. Tray M has a 6mm diameter depression which is suitable for microrods, phosphor/PTFE discs less than 6mm in diameter, or extruded, hot-pressed, and sintered dosemeters. Trays with other diameter depressions could easily be manufactured to suit other forms of dosemeter.

Very thin phosphor/PTFE discs (e.g. $0.02\text{mm}$ thick 'ultrathin' discs) tend to curl when heated, and the heating method shown in figure 5.7 (b), using an overlying quartz disc, was devised for these. Holes are drilled through the quartz disc to allow nitrogen to reach the dosemeter. The method is not entirely satisfactory, as a signal is obtained from the quartz disc as well, and recent experiments indicate that better results may be obtained for example, (a) by simply placing the 'ultrathin' discs, which are 6mm in diameter, on Tray M, or (b) by using an electroformed mesh in place of the quartz disc. This can be positioned or removed by a magnetic handling device.

5.7.5. Flexibility of design

The mechanical arrangements for achieving heat transfer from the heating trays to the dosemeters are flexible, and other types of tray with meshes, and springs, or other means of retaining dosemeters can be used, if preferred. The methods described above were chosen because they simplified dosemeter loading. The design of the aperture in the polyimide fixed plate can similarly be varied, the present arrangement being a compromise dominated by the necessity of heating large phosphor/PTFE discs. To summarise the salient features of the overall method of heat transfer from the heating element to the dosemeter, this was chosen because it combined the concept of
various types of removable tray (easily replaced or cleaned) to suit different types of dosemeter with the repeatable and accurate temperature sensing (provided by the thermocouple welded to the heating element) necessary for the reproducible heating of dosemeters.

5.8. Model 654 heating cycle control system

5.8.1. General description

The heating cycle control system is described with reference to figure 5.10. It utilises negative feedback from a thermocouple transducer welded to the heating element to provide versatile, reproducible, and accurate control of the temperature of the heating element. The heating cycle generator simply provides a voltage vs time profile, $V(t)$, which is designed to simulate the required temperature vs time profile, $T(t)$, at the heating element. The thermocouple signal is amplified and a compensation voltage is added which allows for the cold junction being at a variable ambient temperature. The amplified signal (including compensation) is compared with the voltage output from the heating cycle generator, and the resultant error signal ($e$) varies the number of complete mains cycles per second switched into the primary of the heater transformer. Phase advance compensation is provided within the comparator, and is adjusted so that the response is critically damped. The heating cycle generator is self-contained on a removable module, and different modules can be provided to suit various applications.

The effects on the stability of the heating cycle of variations in ambient temperature and mains supply were found to be negligible under normal operational conditions. Variations in thermocouple amplifier linearity and in the accuracy of the cold junction compensation circuit were found to give rise to temperature uncertainties of about $0.25^\circ C$ over the working range.

A patent has been applied for (Robertson, Brabants, Davies, and Pettifer, 1974).

5.8.2. Theory of operation

A representation of the system from the point of view of control theory is also shown in figure 5.10. $G$ is a transfer function encompassing the mains-locked oscillator, optical coupler, zero-crossing switch, and transformer, and $H$ is the fraction of the output signal feedback.

From control theory:

$$T(t) = Ge$$

and $e = V(t) - HT(t)$

$$T(t) = G[V(t) - HT(t)]$$

$$\frac{T(t)}{V(t)} = \frac{G}{1 + GH}$$
Figure 5.10.

Heating cycle control system

Heating cycle Generator

Mains locked variable mark-space oscillator

Optical coupler

Zero crossing switch

Transformer

Heating element

Comparator with phase advance compensation

Mains

Amplifier

Thermocouple

Cold junction compensation

If GH ≫ 1 , T(t) = \( \frac{V(t)}{H} \)
If $G H \gg 1$, \\
\quad \frac{T(t)}{V(t)} = \frac{1}{H}$ \hfill (5.1)\\
i.e. $T(t) = \frac{V(t)}{H}$

Hence, if $G H \gg 1$, the temperature of the heating element is governed only by $V(t)$ (the output of the heating cycle generator) and $H$ (determined by the thermocouple, amplifier, and cold junction compensation). Therefore the complete system is largely independent of variations in the systems controlling the magnitude of $G$.

5.8.3. Heating cycles

The heating cycle generator is self-contained on a removable module, and different modules with varying capabilities can be provided to suit the application. Three types of heating cycle generator have been designed, and it is believed that these will satisfy most requirements. Their design was governed by the following considerations:

For many research applications, especially materials research, a linear heating rate is required so that the dosemeter temperature can be accurately matched to light output for glow curve analysis. Low heating rates, of the order of $0.3 - 2^\circ C/sec$, are generally used to reduce the difference between the indicated temperature and the actual average dosemeter temperature by minimising temperature gradients throughout the dosemeter, and thus improving the resolution of the different glow peaks. Readout times are therefore in the range of 5-15 minutes, which is tolerable in research applications, but unacceptably long for routine measurements. However, if the linear heating rate is increased to reduce the readout time, this leads to higher temperature gradients across the dosemeter, with the following disadvantages:

(a) Resolution of the glow curve structure is degraded. This is of concern when attempting to discriminate the dosimetry peaks from other (usually lower temperature) peaks.

(b) A higher end-of-cycle temperature is required to achieve adequate heating efficiency with the result that the signal/noise ratio is degraded, since the background signal contains several components whose magnitude and variability increase rapidly with temperature.

These effects are accentuated with dosemeters having a low thermal conductivity such as LiF/PTFE discs. For example, with a linear ramp of $30^\circ C/sec$, the temperature gradient across a 30% loaded, 0.4 mm thick disc is 72°C when the heated face is at 280°C (Perry and Preston, 1970). Perry and Preston (loc.cit) reduced the temperature gradient across LiF/PTFE discs with a reasonably fast heating rate by incorporating a top heater, in the form of a mesh, in a similar position to that occupied by the polyimide plate on the
Model 654. The mesh was connected to the secondary winding of the heating transformer, and by suitable choice of step down ratio a low temperature gradient was achieved. This method has the disadvantage, when applied to a reader which has to measure all shapes of dosemeters, that the geometrical efficiency of light collection will vary for small dosemeters such as chips and microrods, depending on which part of the mesh pattern the dosemeter is pressed against. Additionally, there is the more general problem of manufacturing the top heater, and selecting the secondary tapping so that its temperature is the same as the lower heater, over the temperature range. It was therefore decided not to use a top heater on the Model 654, but to reduce the temperature gradient across phosphor/PTFE dosemeters by using a different type of heating profile.

For routine measurements a linear heating ramp is not generally necessary and the alternative 'plateau' type of heating offers several advantages. This consists of an initial fast ramp to a given temperature, and a hold at that temperature until the dosemeter is sufficiently heated. Although the temperature gradient across the dosemeter is high during the fast ramp, it is considerably reduced during the hold period and for routine applications this results in several advantages compared with a linear ramp over the same time. With a linear heating ramp, lower and upper temperature discriminators are used to define a read zone which separates the dosimetry peaks from lower temperature peaks and background signals respectively. In contrast, a complete plateau heating cycle can consist of three plateaux, the preheat, read, and anneal zones (McCall et al, 1970; Johns et al, 1970; Webb and Phykit, 1971), and again only the light emitted during the read zone is used for dose measurement. In each zone the lower average temperature gradient across the dosemeter is advantageous, compared with the linear ramp. The preheat zone can be employed to give better separation of the dosimetry peaks from lower temperature peaks. In the read zone, variations in background signal are reduced since a lower average temperature is required to obtain an adequate heating efficiency. The anneal zone is used to further reduce any residual signal remaining after the read zone; with phosphor/PTFE discs, the residual signal can be reduced to an extent impracticable with a fast linear heating ramp due to the crystalline transition point in PTFE at about 327°C. The cooling zone must be considered as an integral part of the dosemeter heating cycle, since the sensitivity of some phosphors, such as LiF:Ti,Mg, is dependent on the cooling rate from the read or anneal temperature, and the cooling rate must therefore be reproducible from one readout cycle to the next. Figure 5.11 shows a typical 'multi-plateau' heating cycle and its corresponding glow curve from a routine measurement on a 7LiF/PTFE disc, (12.7mm diameter by 0.4mm thick) with 30% phosphor loading. The preheat,
Figure 5.11. Typical 'multi-plateau' heating cycle and corresponding glow curve from $^{7}$LiF/PTFE disc, 12.7mm diameter by 0.4mm thick, with 30% phosphor loading (no 80°C anneal).

Figure 5.12. Standard Module : Heating cycle
read, and anneal zones are each of 16 seconds duration.

The various factors determining the optimum heating profiles for LiF/PTFE discs are considered in chapter 9. A potential source of error that has to be considered with a plateau heating profile is non-linear response of the light measurement system due to the increased rate of light output during the fast ramp.

The various heating cycles designed for the Model 654 reader are described in the following sections (5.8.4 - 5.8.6). The specification of the heating cycle modules, and data on the reproducibility of their parameters, are summarised in Tables 5.1 and 5.2 respectively. The temperatures, times, and related settings on the standard module were determined by experiments described in chapters 9 and 10. Parameters such as the variable temperature ranges on the research modules can be chosen to suit special requirements.

5.8.4. Standard Heating Cycle Module

The sensitivity assigned to a particular dosemeter is critically dependent on its heating cycle and, in some cases, its thermal history. In order to precalibrate dosemeters a standard heating cycle has therefore to be specified, and this is provided in the Model 654 by the Standard Heating Cycle Module, which has been designed primarily for routine measurements. The standard heating cycle is believed to be optimum for many types of dosemeter, and is preset in the Pitman laboratories with fixed preheat, read, anneal, and cool zones (see figure 5.12).

The preheat and anneal zones can be independently switched in or out so that the user can select between internal or external annealing. The anneal zone temperature can also be switched to either 300°C or 400°C to suit either phosphor/PTFE or other dosemeters respectively. A choice of two read zone temperatures and times allows the optimum read zone to be selected for the most commonly used types of dosemeter.

5.8.5. Research Heating Cycle Module A

This module has eight variables and, as its name suggests, is primarily intended for research applications. The heating cycle is shown in figure 5.13. Preheat and anneal zones can be switched in or out as before. Purely linear heating rates can be set by switching out the preheat and anneal zones and varying the read time to suit the linear heating rate chosen.

5.8.6. Research Heating Cycle Module B

A disadvantage of Research Module A is that it is not possible to discriminate against low temperature peaks or infra-red radiation on the linear heating ramp. This is sometimes desirable, especially in materials research, and the heating cycle shown in figure 5.14 was accordingly designed to meet this
Research Module A: Heating cycle

- Variable Anneal Temp.
- Variable Read Temp.
- Variable Preheat Temp.

Start of cycle

Variable preheat time -> Variable read time -> Variable anneal time

End of cycle

Controlled cool variable from natural cooling rate down to 1°C/sec slowest cooling rate.

Research Module B: Heating cycle

- Variable Hold Temp.
- Variable upper limit of integration
- Variable lower limit of integration

Start of cycle

Variable Time

End of cycle

Controlled cool variable from natural cooling rate down to 1°C/sec slowest cooling rate.
requirement. Lower and upper discriminators can be varied over appropriate
temperature ranges, and the heating time can be varied to suit the linear
heating rate or to provide a hold period.

5.8.7. Thermocouple amplifier and cold junction compensation

The thermocouple amplifier has to be extremely stable, due to its position
in the feedback loop of the heater control system (figure 5.10), and also
linear to facilitate the interpretation of the temperature of the heating
element. It is assumed that the thermocouple characteristic is stable with
temperature cycling up to 400°C. The EMF developed by the thermocouple is
a function of the difference in temperature between its hot junction (at
the heating element) and its cold junction, which is the terminal block to
which the two thermocouple wires are led. Both wires are secured at the
terminal block by identical metal connectors, this being an essential
condition for obtaining the stated response from the thermocouple. The
terminal block is at near ambient temperature and can thus vary over a wide
range, normally about 15°C in many climates. Additionally, it is in the
same sealed box as the heating system, and will warm up above ambient as
dosemeters are read out and heat is dissipated. A cold junction circuit is
provided to obtain temperatures with respect to the Celsius temperature
scale (to which thermocouple tables are referenced). This circuit
effectively generates a voltage which is dependent on the temperature of the
terminal block and is added to the EMF developed by the thermocouple such
that the sum is equivalent to the EMF from a thermocouple with its hot
junction at the temperature of the heating element and its cold junction at 0°C.
The thermocouple amplifier itself is of standard design, apart from a unique
and highly accurate cold junction compensation circuit. For the chromel-
alumel thermocouple used, the function of EMF (V volts) versus temperature
(T°C) is accurately described by an equation of the form

\[ V(T) = k \left[ \exp(BT) - 1 \right], \]  \hspace{1cm} (5.2)

where k and B are constants, over the range 0 - 50°C, i.e. the region of
interest for cold junction compensation. The function of resistance \( R_1 \)
versus temperature (T) of a silicon resistor is accurately described by an
equation of the form

\[ R_1(T) = R_0 \exp\left(\alpha(T-T_0)\right), \]  \hspace{1cm} (5.3)

where \( R_0 \) is the resistance at a temperature \( T_0 \) and \( \alpha \) is a constant. By
incorporating a fixed resistance \( R_F \) of suitable value in parallel with \( R_1 \)
it is possible to match the two functions exactly at 25°C, and accurately
over the range 0 - 50°C. \( R_F \) is determined by the equation
A circuit description and the derivation of equation 5.4 is given in full in Appendix 1, since this research into the problem of cold junction compensation is potentially useful in other applications. Experimental results on the thermocouple amplifier and cold junction compensation circuit are given in Table 5.3.

5.8.8. Safety Features

The temperature of the heating element is given by

\[ T(t) = \frac{V(t)}{H} \quad \text{(5.1)} \]

If the thermocouple breaks or becomes detached from the heating element the feedback signal \( H \) will tend to zero and \( T(t) \) will quickly increase and within a few seconds cause permanent damage to the heating element. An auxiliary protection circuit (which senses resistance) therefore switches off the power to the heater in the event of this occurring, and a 'thermocouple fault' indicator illuminates on the front panel. Additionally, the front panel temperature meter indicates past full scale. A fault in the thermocouple amplifier could also cause a similar problem, but could be detected by an unexpected reading on the front panel temperature meter. A circuit breaker limits the current that can be applied to the primary of the heating transformer and this not only limits the temperature the heating element can reach but also safeguards against any fault in the heater control system that could place a large DC voltage component on the primary.

5.9. Other comments on the Model 654 heating system

5.9.1. Temperature gradients

The temperature indicated by the thermocouple (welded to the heating element) is not necessarily the same as the dosemeter temperature, due to thermal gradients in the heat transfer system. Thermal gradients were measured by two methods: a surface temperature probe (STP) utilising a laminated thermocouple (figure 5.5) and temperature indicating devices (TID's) based on colour changes. These latter are specified to be accurate within \( \pm 1\% \). The temperatures indicated by the TID's at 240° were between 1 and 5°C higher than those indicated by the STP. It is thought that this may have been due to the STP creating more of a 'cold spot', because of its higher thermal capacity.

The average temperature of the heating element is higher than the temperature of the thermocouple since the thermocouple produces a cold spot where it is welded to the heating element, and the heater control circuit increases the temperature of the heating element to compensate. For example, with the
thermocouple indicating 240°C, the temperature of the top surface of the heating element varies from about 250°C to 235°C over a central circular area of 13mm diameter, only falling below 240°C at the two edges nearest the heater electrodes. In practice, the thermal capacity of the heating tray helps to smooth out these cross-gradients. The temperature gradient across the thickness of the heating trays is a function of temperature but is about 4°C at 240°C. There is also a gradient across the diameter of the heating trays; the edge of the depressions in Type P and M trays are about 5°C cooler than the centre, and in Type D about 10°C cooler. These gradients bring the average tray surface temperature down to near the thermocouple temperature, counteracting the cold spot effect. By careful choice of the diameter of the thermocouple wires, the average temperature of the central region (≈8mm diameter) of the top surfaces of the heating trays, i.e. the lower surfaces of the dosemeters, was brought to within 2°C of the temperature indicated by the thermocouple. The optimum diameter of thermocouple wire to achieve this was found to be 0.25mm.

The temperature gradients across dosemeters are dependent on their size, shape, and thermal conductivity, and on the rate of nitrogen flow. For 30% loaded LiF/PTFE discs, 0.4mm thick, the gradient across the dosemeter is about 15°C at a constant tray temperature of 240°C. For pure PTFE discs of the same thickness the corresponding gradient is about 25°C, thus illustrating the marked influence of the thermal conductivity of the LiF in the previous example. Pure phosphor forms of dosemeter such as hot pressed chips or sintered dosemeters have corresponding gradients of less than 10°C. Nitrogen flow further cools the top surfaces of dosemeters, though any such cooling detected by the thermocouple is compensated for by the heater control circuit. A nitrogen flow rate of 400 ml/min has a cooling effect of less than 5°C.

In practice, optimum dosemeter heating cycles are found by experiment and related to the temperature of the thermocouple welded to the heating element. However, a knowledge of the temperature gradients is essential when checking the efficiency and reproducibility of heat transfer from the heating element to the dosemeter, and for these purposes the information contained in figure 5.15 would be useful. In this figure the true temperatures are estimated from both STP and TID measurements.

5.9.2. Phase advance compensation

The phase advance compensation circuit provides anticipatory (derivative) control to critically damp the response of the heating cycle control system. The most suitable component values were determined by the use of the surface temperature probe, since it was found that the thermocouple welded to the
Figure 5.15.

Temperature gradients in Model 654 heating system

- Temp. of centre of heating element
- Temp. of centre of heating tray
- Temp. gradient across tray
- Temp. of top surface of 30% loaded LiF/PTFE disc 12.7mm dia x 0.4mm thick
- Temp. of top surface of pure PTFE disc 12.7mm dia x 0.4mm thick

True surface temperature (°C)

Thermocouple temperature (°C)
heating element did not adequately respond to fast transient temperatures, owing to its relatively high thermal capacity. The overshoot in plateau temperatures was investigated for the standard heating cycle. As expected, overshoot decreases with increase in thermal capacity. The circuit parameters were adjusted so that the maximum overshoot on the surface of a heating tray following a fast ramp from ambient to any plateau temperature below 300°C was less than 5°C. In practice overshoot is generally only 1 or 2°C, since the preheat, read, and anneal zones split up the temperatures between which a fast ramp is occurring. Additionally, the thermal capacity of the dosemeter smooths out the response. Overshoot is negligible for ramp rates of less than 10°C/sec.

5.9.3. Power dissipated in drawer assembly

It is desirable to minimise the power dissipated during the heating cycle to avoid an excessive temperature rise in the drawer assembly, which could affect the stability of the internal light source and also cause an increase in the PM tube dark current (see chapter 6). The efficiency of the transformer, which has a 100A, 0.6V, secondary winding, is 80-90%. The resistance of the flexible connectors from the transformer secondary to the heating element and its electrodes is about 1 milliohm, compared with a value of 7 milliohm for the heating element itself at room temperature. The resistance of the transformer secondary winding and the heater electrodes are not significant. Large area contacts reduce contact resistance to a minimum and all copper components are tinned to prevent corrosion, which could lead to high resistance joints. Thus about 70% of the power into the primary of the transformer is actually utilised in heating the heating element, and this percentage increases as the heating element warms up and its resistance increases. About 15W is supplied to the primary to maintain the heating element at 400°C. The average power used in heating a LiF/PTFE dosemeter, from the beginning of one standard heating cycle to the next, is about 5W and continuous readout of dosemeters over a 10 hour day produces a temperature rise in the drawer assembly of less than 10°C relative to ambient, the nitrogen flow helping to dissipate the heat from the drawer assembly.

This completes the description of the Model 654 heating system. The light collection and measurement systems are described in the following chapter.
Table 5.1. Specification of Model 654 heating cycle modules

(a) **STANDARD MODULE** Zone temperatures can be varied by the operator if required.

<table>
<thead>
<tr>
<th>Preheat zone</th>
<th>Switchable in or out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed ramp (30°C/sec)</td>
</tr>
<tr>
<td>Read zone</td>
<td>Fixed profile, 135°C for 16 secs.</td>
</tr>
<tr>
<td></td>
<td>Fixed ramp rate (approx. 30°C/sec)</td>
</tr>
<tr>
<td></td>
<td>Choice of two temps. (240°C or 270°C)</td>
</tr>
<tr>
<td></td>
<td>Choice of two times (16 or 32 secs)</td>
</tr>
<tr>
<td>Anneal zone</td>
<td>Switchable in or out</td>
</tr>
<tr>
<td></td>
<td>Fixed ramp (approx. 30°C/sec)</td>
</tr>
<tr>
<td></td>
<td>Choice of two fixed profiles</td>
</tr>
<tr>
<td></td>
<td>300°C for 16 secs or 400°C for 16 secs.</td>
</tr>
<tr>
<td>Cooling zone</td>
<td>Natural cooling rate only</td>
</tr>
</tbody>
</table>

(b) **RESEARCH MODULE A**

<table>
<thead>
<tr>
<th>Preheat zone</th>
<th>Switchable in or out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed ramp (approx. 30°C/sec)</td>
</tr>
<tr>
<td></td>
<td>Variable hold temp. (ambient to 185°C)</td>
</tr>
<tr>
<td></td>
<td>Variable time (0-99 secs)</td>
</tr>
<tr>
<td>Read zone</td>
<td>Variable linear ramp rate (0-40°C/sec)</td>
</tr>
<tr>
<td></td>
<td>Variable hold temp. (185-375°C)</td>
</tr>
<tr>
<td></td>
<td>Variable time (0-999 secs)</td>
</tr>
<tr>
<td>Anneal zone</td>
<td>Switchable in or out</td>
</tr>
<tr>
<td></td>
<td>Fixed ramp (approx. 30°C/sec)</td>
</tr>
<tr>
<td></td>
<td>Variable time (0-999 secs)</td>
</tr>
<tr>
<td></td>
<td>Choice of two variable temperature regions</td>
</tr>
<tr>
<td></td>
<td>(275 to 320 or 370 to 410°C)</td>
</tr>
<tr>
<td>Cooling zone</td>
<td>Cooling rate variable from approx. 1°C/sec to natural cooling rate</td>
</tr>
</tbody>
</table>

(c) **RESEARCH MODULE B**

<table>
<thead>
<tr>
<th>Preheat zone</th>
<th>Depends on read zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Read zone</td>
<td>Variable linear ramp rate (0-40°C/sec)</td>
</tr>
<tr>
<td></td>
<td>Variable lower limit of integration (ambient-200°C)</td>
</tr>
<tr>
<td></td>
<td>Variable upper limit of integration (200°C-400°C)</td>
</tr>
<tr>
<td></td>
<td>Variable hold temp. (200°C-400°C)</td>
</tr>
<tr>
<td></td>
<td>Variable time (0-999 secs)</td>
</tr>
<tr>
<td>Anneal zone</td>
<td>Depends on read zone and hold time</td>
</tr>
<tr>
<td>Cooling zone</td>
<td>Cooling rate variable from approx. 1°C/sec to natural cooling rate</td>
</tr>
</tbody>
</table>
Table 5.2. Experimental results on Model 654 heating cycle generators (applicable to all modules)

1. Effect on plateau temperatures of variations in mains supply: -
   < 0.01°C per V, in range 200-260 volts AC
2. Effect on plateau temperatures of temperature coefficient of heating cycle generator: -
   < 0.04°C per °C, from 0°C to 50°C
3. Temperature coefficient of timing intervals: -
   < 50ppm per °C, from 0°C to 50°C
4. Effect on timing intervals of variations in mains supply: -
   < 2ppm per V, in range 200-260 volts AC
5. Effect on linear heating ramp of temperature coefficient of heating cycle generator: -
   < 0.1% per °C, from 5 to 50°C
6. Effect on cooling rates of temperature coefficient of heating cycle generator: -
   Varies from zero at natural cooling rate to about 0.5%/°C at slowest cooling rate (1°C/sec), from 5-50°C.

Table 5.3. Experimental results on thermocouple amplifier and cold junction compensation circuit

1. Resistance vs temperature characteristic of Texas Instruments Ltd. TM1 10KΩ silicon resistor: -
   \[ R(T) = R_0 \exp\left(\alpha(T - T_0)\right) \]
   where \( \alpha = 0.0078 ± 0.0002 \)
2. Accuracy of cold junction compensation circuit: -
   ± 0.1°C at 25°C, ± 0.6°C at 0°C and 50°C
3. Effect on plateau temperature of the temperature coefficient of the thermocouple amplifier: -
   < 0.02°C per °C, from 0°C to 50°C
4. Thermocouple amplifier linearity: -
   ± 0.25°C, from 0°C to 470°C
CHAPTER 6. INSTRUMENTATION II: THE LIGHT MEASUREMENT SYSTEM

The Model 654 light collection and measurement systems, and components for the minimisation of background signals are described in this chapter.

6.1. Efficiency of light collection on the Model 654

6.1.1. Geometrical efficiency of light collection

The dosemeter reading and the signal/noise ratio of the light detector (usually a photomultiplier tube) are directly proportional to the efficiency of light collection which should therefore be constant, to ensure good precision, and high, to minimise the effect of noise in the light detector. In practice, the positioning of the photomultiplier tube photocathode relative to the dosemeter is limited by mechanical and thermal considerations, so that the maximum solid angle that can be subtended by the photocathode is about $\pi$ steradians.

The method of light collection on the Model 654 is illustrated in figure 5.4. The axial distance from the photocathode to the (lifted) tray is 15mm, and the effective diameter of the photocathode is 44mm. An uninterrupted view of the photocathode is presented to the depressions in the Type P and M trays. The 10mm diameter aperture in the polyimide plate is determined by the heating method for large LiF/PTFE discs (section 5.7.4.) and necessarily limits the collection efficiency from the Type D tray. However, this is advantageous in that small variations in the positioning of these discs are not a source of error since they are masked by the aperture.

The effect of small variations in the positioning of the dosemeter relative to the photocathode have been discussed by Karzmark et al. (1965). They found that the axial distance between the dosemeter and the photocathode critically affects the geometrical efficiency of light collection. Increasing this distance reduces the effect, but then dark current in the photomultiplier tube and noise in the signal conditioning circuits become more significant. On the Model 654 a variation of 0.25mm in the axial distance of 15mm changes the geometrical efficiency by about 1%. The distance between the top surface of the dosemeter tray and the photocathode is determined by (i) the depth of the tray and (ii) the fixed distance from the lower surface of the polyimide plate to the photocathode (figure 5.4). Thus only variations in tray depth influence this distance, and these are held to tight tolerances to minimise variations from tray to tray.

The effects of transverse displacements of the dosemeter are not nearly so critical; typically a transverse displacement of 0.25mm will change the geometrical efficiency by about 0.1%. In the Model 654, transverse displacements are limited by the use of trays with different diameter depressions to suit and centralise the various dosemeters. A constant
efficiency of light collection is most difficult to achieve with loose powder, due to the difficulties of placing the powder in the tray in a reproducible manner. Solid forms of dosemeter do not present so much of a problem.

The above discussion has been confined to dosemeters, but similar considerations apply to the efficiency of light collection from any reference light source used in the light measurement system. The aperture, in particular, influences the design of the light sources.

Changes in the light path between the top surface of the dosemeter and the PM tube photocathode (e.g. as could be caused by dust on the infra-red filter) are compensated for by the light sensitivity control system (section 6.5).

6.1.2. Tray reflectivity

The reflectivity of the heating tray can have a marked influence in the light output from some dosemeters (section 9.1.3). For example, with loose powder differences of up to 20% have been reported between trays of high and low reflectivity. Variations in tray reflectivity are not so critical for some solid forms of dosemeter, notably the translucent 0.4mm thick phosphor/PTFE discs. For example, a change in the coefficient of reflectivity from about 0.9 to about 0.1 alters the response from 0.4mm thick LiF/PTFE discs, with 30% phosphor loading, by only 3%. However, variations in reflectivity are significant when using thinner phosphor/PTFE discs, microrods, and chips, which are all more transparent.

The original trays, which are manufactured from 0.1mm thick stainless steel shim, were plated first with bright nickel, to prevent oxidation and give a high reflectivity, and then finished with a semi-transparent layer of rhodium to give a hard-wearing surface. The rationale was that (a) a higher reflectivity would give a higher signal from the dosemeter, (b) a low emissivity in the infra-red region would reduce thermal radiation (Cameron et al, 1968), and (c) without the plating, the tray surface would oxidise, causing the reflectivity to vary. However, on considering the problem more deeply, it was realised that a high reflectivity was not really essential. Although the signal could be increased, little or no improvement in the signal/noise ratio from the dosemeter itself would result, since the noise from the dosemeter would similarly increase. The only advantage would be a decrease in the effect of noise in the light measurement system, but this was generally not significant compared with noise from the dosemeter.

The effect on the thermal radiation from the tray of variations in tray reflectivity were assessed (figure 6.1) by comparing the thermal signal from
Figure 6.1.

Comparison of thermal radiation from trays of varying reflectivity

(1) Tray plated with bright nickel and rhodium

(2) Tray coated with colloidal graphite

Thermal radiation (arbitrary units)

Maximum tray temperature, °C
an empty tray plated with bright nickel and rhodium with the signal from a tray coated with colloidal graphite (T115, Acheson Colloids Ltd.). The heating cycle used was a fast ramp (30°C/sec) to the indicated maximum temperature, plus a hold at that temperature for a time such that the overall cycle time was 32 seconds. No significant difference in thermal radiation was observed for temperatures up to 280°C, and it was concluded that for most dosimetry applications the effect of tray reflectivity on its effective thermal radiation was not important, but it should be noted that this conclusion only holds for the particular combination of infra-red absorbing filter and PM tube photocathode used (see section 6.5.6).

The oxidation of unplated trays was not found to be a problem for temperatures of up to 400°C. The only noticeable effect was a discolouring if heated for long periods at 400°C without inert gas flow. In practice, i.e. with inert gas flow, the rate of discolouration was not significant in comparison with other effects, such as burnt-in dust. The fairly rapid deterioration in tray reflectivity due to burnt-in dust is unavoidable, and although it can be minimised by frequent tray cleaning, this is not operationally desirable.

It was concluded that to minimise changes in tray reflectivity with time, low reflectivity trays should be used from the start (cf. Karzmark et al, 1965); this does not lead to any significant increase in thermal radiation in the Model 654. Unplated stainless steel trays are now supplied with this instrument. When new, their reflectivity is quite high, but is rapidly reduced with use by burnt-in dust and other debris. If it is desired to lower the tray reflectivity from the start, this can be achieved by heating the trays in air at 400°C for 1 hour. An annealing oven can conveniently be used for this purpose.

In some reader designs the variation in reflectivity of other surfaces between the dosimeter and the photocathode may also need to be taken into account.

6.2. TLD light measurement systems

The peak light intensities corresponding to doses of from $10^{-4}$ to $10^{-6}$ rads are typically $10^{-14}$ to $10^{-4}$ lumens, i.e. approximately $10^2$ to $10^{12}$ photons sec$^{-1}$ steradian$^{-1}$, for photons of wavelength 450 nm. This range may be marginally altered by different dosimeter formats and sensitivities, but there is often a compensating effect in that, for example, high sensitivity dosimeters are generally most suitable for the measurement of low doses, and vice-versa. Considering possible light detectors, only a photomultiplier tube (PM tube) is capable of covering this entire range of intensities, although photodiodes can be used for the higher intensities. Schematics of practical light measurement systems utilising PM tubes are shown in figure 6.2.
Figure 6.2. TLD light measurement systems

(a) Digital counting

(b) Analogue measurement

(c) Photon counting
A signal is generated at the PM tube anode proportional to the light input at the photocathode. A high tension D.C. supply (generally referred to as the EHT (extra-high tension) generator) is required to drive the tube. The PM tube sensitivity is usually expressed in amperes output current per lumen input, and can be varied by adjusting the EHT supply to the dynode chain. The PM tube is usually run in the current measurement mode, in which case a current is obtained at the anode proportional to the light input. In most instruments this current is measured as follows:

Either 
(a) Referring to figure 6.2.(a), the current is converted to a pulse rate proportional to the current by a charge-to-pulse convertor (CTPC). The CTPC is sometimes referred to as a current-to-frequency convertor (CTFC). The light signal can be integrated over a desired time interval by feeding the pulses from the CTPC to a scaler. A glow curve can be obtained by converting the CTPC pulse train to an analogue signal via a ratemeter, the output of which can be connected directly to a chart recorder. Glow curves can also be obtained in a form suitable for computer analysis by feeding the CTPC output to a multi-channel analyser (MCA) in the multiscaling mode (Harris & Jackson, 1968b). The digital output from the MCA is often in the form of punched paper tape, which can be used to transfer the data to a computer, if required.

Or 
(b) Referring to figure 6.2.(b), the current is amplified by an electrometer (i.e. a low current DC amplifier). The integrated light reading can be obtained by integrating the output current with a capacitor to give a voltage which can be displayed on a meter, and the glow curve can be simply obtained by connecting the output of the electrometer to a chart recorder.

The first method, being digital, is generally preferred since a 6-decade dynamic range can be achieved without the necessity for range-changing, as is required with the DC method, and it is simpler (electronically) to achieve simultaneous measurement of both integrated readings and glow curves.

The major disadvantage of using the anode current of the PM tube as a measure of the light input is that the current output is directly proportional to the overall sensitivity of the PM tube, which is dependent on a number of variables (section 6.3). The alternative method, (Aitken, 1968; Schlesinger, 1971) is photon counting, i.e. to count individual pulses arriving at the PM tube anode. Each pulse corresponds to a single photon striking the photocathode and variations in PM tube gain only affect the height of the pulse, therefore photon counting variations can be minimised by choosing a suitable discriminator setting. The reason why this method is not incorporated into commercial systems is that the dynamic range is limited by pulse pile-up
Effects to 3 or 4 decades, thus it can only be used in applications where
the equivalent dose is expected to fall within this range, i.e.
archaeological dating. The discriminator setting in single photon counting
can also be used to partially reject PM tube dark current or thermal
radiation, which may have a lower average pulse height than the light
being measured. Spanne 1974 has shown that dark current can be reduced
only by a factor of about 1.4, which is not usually significant. For
most dosimetry applications, thermal radiation is not a problem when the
heating cycle is selected to optimise the signal/noise ratio from the
dosemeter e.g. by use of a 'plateau' heating cycle, and the discriminator
setting is then only effective at reducing dark current. However, it is
probable that photon counting is more effective in reducing thermal
radiation in some archaeological dating applications, where the phosphors
used have higher glow peak temperatures than the phosphors used in
dosimetry.

6.3. Photomultiplier tubes

The light detector in a TLD system has to have a large area photocathode
(to ensure a good light collection solid angle at typical phosphor to
photocathode separations) and a high sensitivity-to-noise ratio, and in
practice only a PM tube is suitable. A general introduction to the PM
tube can be found in the handbook issued by EMI Ltd. (1973). The important
characteristics relevant to TLD are summarised below.

6.3.1. Spectral response

The majority of PM tubes are ideal for measuring the light output from
LiF, since the peak quantum efficiency is generally at a wavelength close
to the peak emission (400 nm) of this phosphor. The quantum efficiency is
also a good match for CaF$_2$ and CaSO$_4$:Dy phosphors. However, the quantum
efficiency falls sharply as the wavelength moves towards the peak emission
of Li$_2$B$_4$O$_7$:Mn. The problem is not resolved for this latter phosphor simply
by choosing the tube with the highest quantum efficiency in the orange-red
region, since the infra-red signal from the hot dosemeter and tray may also
thereby be increased. The signal/noise ratio will thus also depend on how
far the 'tail' of the quantum efficiency vs wavelength curve extends into
the infra-red region. Typical curves for several types of photocathode are
shown in figure 6.3. Even the relative response of tubes of the same type may
vary considerably since the quantum efficiency is critically dependent on
the production process, which involves many possible variables.

The spectral response of a PM tube is slightly temperature dependent (EMI
Ltd, 1974), but the effect is too slight to be of concern in TLD.
Figure 6.3.
Typical spectral response curves for photocathodes (EMI Ltd., 1973)

Figure 6.4.
Transmission vs wavelength characteristic of the infra-red filter used in the Model 654 reader. (Chance HA3, 4mm thick)
6.3.2. Optical filters

Filters may be used to discriminate against thermal radiation and thereby increase the signal/noise ratio. The choice of filter will depend on the phosphors that are to be used with the instrument. To cover all phosphors in current use it is necessary to fit a filter design to cut out all radiation of wavelength longer than about 700 nm. If the readout of Li$_2$B$_4$O$_7$:Mn is not required, the cut-off wavelength can be shortened to about 600 nm to further reduce the thermal radiation contribution to background signal.

6.3.3. Overall sensitivity

The overall sensitivity of a PM tube is a function of (a) the quantum efficiency, $Q(\lambda)$, of the photocathode and (b) the gain, $M$, of the dynode structure (see section 3.1.2), and is dependent on a number of variables:

(i) A 0.1% change in EHT will produce a change in sensitivity of about 1%; thus the EHT should be very stable and have minimum ripple.

(ii) The sensitivity is dependent upon the temperature of the PM tube; the measured temperature coefficient varies from tube to tube, but for a bialkali tube is typically from $-0.5\%$ to $-1\%$ per °C from 0°0 to 40°0.

(iii) When exposed continuously to 'strong' light sources, i.e. recording a current of $10^{-6}$ amps or more, tubes suffer from fatigue effects. The sensitivity falls gradually, but after a period of hours the rate of change of sensitivity decreases. The effect of PM tube fatigue as applied to TLD has been studied by Karzmark (1965).

(iv) Tubes are affected by magnetic and electrostatic fields. A mu-metal screen (at cathode potential in the current measuring mode) can reduce both these effects. Karzmark et al (1965) calculated on the basis of available data that DC currents through the dosemeter heating element could produce a magnetic field which would have a significant effect on sensitivity, but stated that AC currents should produce no significant effect. However, both Saunders (1971), and Forslo et al (1974) have reported significant changes in PM tube sensitivity due to AC heater currents altering the magnetic field in the environment and structure of the PM tube. Changes of the order of 10% were observed with a heating element to photocathode distance of 15mm, but became insignificant when this distance was increased to 90mm. These effects have not been observed with the Model 654 (see Table 6.2.(a)).
6.3.4. **Dynode chain**

When the tube is used in the current measuring mode the cathode is placed at high negative potential and the anode near ground potential. The current through the dynode chain must be very much greater than the maximum signal current drawn from the tube if the latter is to be linearly proportional to the light input, but cannot be too high, otherwise the dynode chain resistors would be overheated. In practice, a compromise is reached between the current through the dynode chain and the power handling capability, and therefore the physical size, of the dynode chain resistors.

6.3.5. **Dark current**

The dark current is the signal detected in the absence of any excitation by light, and should be as low as possible to minimise any variations in dosemeter background readings. Although variations in dark current at any one temperature are small, dark current is strongly temperature dependent, approximately doubling with a 8°C rise in temperature. The parameter given by dark current divided by sensitivity is virtually constant over a wide range of sensitivity, thus little improvement in signal/noise ratio can be obtained by running the tube at one particular EHT.

The major portion of the dark current signal is due to thermionic emission and can be appreciably reduced by cooling the PM tube. Bialkali tubes (K-Cs-Sb photocathode) have the lowest dark current at room temperature. The dark current at a specified sensitivity can vary considerably between tubes of the same type; it is thus advisable to specify a maximum dark current at a certain sensitivity (generally 200 amps/lumen) when ordering a PM tube. This involves a surcharge, but is considerably less expensive than a cooling system. One other cause of apparently high dark current is leakage from the high voltages on the other dynodes or cathode to the anode. This can take place across the base of the glass envelope of the PM tube, or across the socket, or through or across the insulation of the connection to the anode, if it happens to touch a high voltage point. A reduction in dark current can thus sometimes be achieved by ensuring that the relevant areas are clean and free of moisture (i.e. by increasing the resistance between the anode and high voltage points). On some EMI and Centronic tubes, the two pins on the glass base on either side of the anode pin are not internally connected, and it is possible to paint a circular colloidal graphite or silver guard ring through these pins, earthing it through the socket. However the insulation resistance of the glass envelope is such that if the surface is clean the leakage from the high voltage pins across
the glass envelope should be an order of magnitude less than the thermionic dark current. Leakage through a clean PTFE socket should also be minimal. The connection between the anode point on the socket and the signal connector on the PM tube housing should be sleeved with a high resistance insulator, e.g. PTFE sleeving. Dirt and moisture can effectively be removed by cleaning with pure ethyl alcohol, which should be allowed to evaporate thoroughly before the tube is returned to the housing.

6.4. Setting the sensitivity of the light measurement system to a desired level, and stabilisation at that level

6.4.1. Use of light sources

The relation between the EHT on the PM tube, and the sensitivity (i.e. output signal/light input) of the light measurement system is a rather complex function, and different for each PM tube. It is therefore usual to set the sensitivity of the light measurement system to a certain level, and check its stability, by means of a low intensity solid state light source, since the light source reading is linearly proportional to sensitivity. The light source can either be external to the instrument, in which case it is placed in the drawer for the check, in the same position that the dosemeter would normally occupy, or internal, in which case it is often permanently positioned in the drawer so that it is presented to the PM tube photocathode when the drawer is fully extended. For the check, the light output is integrated over a reproducible time period to give a reading on the instrument display.

It should be noted that the light source reading only checks out the sensitivity of the light collection and measurement system, and does not provide any indication that other parts of the overall system, e.g. dosemeter heating and background reduction, are functioning correctly. To check out overall instrument performance the use of sensitivity and background calibration dosemeters is advised. Assuming, however, that the instrument is functioning correctly, the light source reading can be a useful guide in the setting of the sensitivity of the light measurement system to a value suitable for a particular type of dosemeter operating over a given dose range.

6.4.2. Suitable light sources

Light sources suitable for TLD have been described by Facey (1966), Blase and Rutland (1966) and Karzmark, Fowler and White (1965). Nearly all the sources consist of a radioactive source either mixed with or in intimate contact with a plastic scintillator or a thermoluminescent material.
The light source surfaces should obviously be protected from dust and mechanical wear and tear. In addition the surfaces surrounding the light source, e.g. the light source holder and the immediate environs, should have a constant reflectivity. If the light source is exposed to ambient lighting, it should either be insensitive to ambient light or the sensitivity should decay within an acceptable period once the source has been removed from ambient light.

The light source emission spectra should match that of the dosemeter as closely as possible, as the spectral response of the PM tube may vary with time. This condition is especially critical if it is intended to use the light source reading to provide some form of precalibration for particular types of dosemeter, which may be read out in a large number of instruments, each of which may have a PM tube with a different spectral response. These problems are accentuated for phosphors with emission spectra far removed from the phosphor with which the light source is matched. The solution is either to match the light source to the most popular phosphor, or to provide a different light source for each phosphor.

6.4.3. Problems in stabilising the sensitivity of the light measurement system at the desired level, and previous attempts to overcome these problems

The sensitivity will soon deviate from the desired setting due to a number of causes and will need frequent correction. Factors influencing this are described below.

(i) Drift in the sensitivity of the PM tube

The temperature coefficient of the tube's sensitivity is the main cause of short term drift, being typically - 0.5% to - 1% per °C. There are three distinct effects. Firstly, ambient temperature changes will take full effect after a delay of 1 or 2 hours, due to the intrinsic structure of the PM tube. The second effect is even more short-term. If the tube is positioned vertically above the dosemeter, heat will rise from the hot dosemeter and alter the temperature of the photocathode. If a heat filter is interspersed between the photocathode and the dosemeter, the heating of the photocathode, and the time interval over which such heating takes effect, will depend largely on the thickness of the heat filter and the degree of contact between the heat filter and the photocathode, and also on the duty cycle of the instrument. The third effect is due to dissipation of heat from the instrument itself. The Pitman Model 205C, for example, has a heater which is permanently on at a constant temperature, and this leads to the PM tube housing warming up by about 6°C during the first two hours after switch on, with a corresponding drop in gain. Following this, changes in gain reflect ambient temperature changes.
Various methods have been used to overcome the above problems. Karzmark, et al (1965) placed a methyl methacrylate light pipe between the dosemeter and the photocathode to remove the latter from the immediate vicinity of the dosemeter whilst still maintaining adequate light collection efficiency. This method is also used by Brunskill (1968), Hartin (1966), and others. Richey and Carlsson (1968) position the PM tube horizontally, with a lens and mirror system to collect the light. Whilst these innovations remove the short-term dosemeter heating effect, they do not compensate for ambient temperature changes. The light collection efficiency is also decreased significantly, and the EHT has to be increased to compensate; this increases the dark current, and the signal-to-noise ratio of the light measurement system thereby decreases. In all the instruments described in the above references the PM tube housing is cooled to around 10°C to reduce dark current and to maintain the tube at a constant temperature. Thermo-electric cooling is generally used on commercial instruments. However it should be noted that even this does not overcome other PM tube problems, such as fatigue and ageing, and susceptibility to magnetic fields.

On the Pitman Model 205C a temperature sensitive resistor in the EHT generator is used to partially compensate for the PM tube gain drift due to temperature changes, but it is not very successful, for two reasons. Firstly, the temperature of the resistor is not usually the same as the temperature of the PM tube. Secondly, temperature coefficients of PM tubes vary from tube to tube, and individual calibration is not feasible.

(ii) Changes in EHT

As discussed in an earlier section, the EHT on the PM tube should be highly stabilised, with low ripple. Even expensive units may have appreciable temperature coefficients, and a given percentage change in EHT causes about 10 times that change in sensitivity.

(iii) Changes in the signal conditioning circuits

The signal conditioning circuit may be either (a) a CTPC or (b) a DC amplifier plus integrator. Temperature coefficients should be small, and long-term stability good, in both cases.

(iv) Reduction in sensitivity due to changes in the light path

Dust can build up on a heat filter, photocathode, or light-pipe. To maintain sensitivity the EHT has to be increased to compensate for the light attenuation. In time, the dust build-up will be quite severe, and yearly cleaning of optical surfaces is recommended. Generally a build-up of dust in the light path between dosemeter and photocathode will affect a light source reading to the same extent as the light output from the dosemeter. The Model 205C, however, has a major disadvantage in that the mechanical
design is such that dust build-up on the heat filter attenuates the light output from the dosemeter, but does not affect the light output from the light source. This places a limitation on the accuracy with which the dosemeter sensitivity can be related to the light source reading.

(v) Light leaks

Any extraneous light can add to either the dosemeter or light source reading thus giving an erroneous result. It is extremely unlikely that a light leak would give a constant error, being a function of ambient lighting. Additionally, the most likely path for a light leak into the reader is through the drawer entrance, and is liable to vary as the drawer wears through continued use.

(vi) Apparent variations due to the light source

If the stability of the light measurement system is assessed on the basis of light source readings, it should be noted that those readings may vary due to effects associated with the light source, such as (a) statistical fluctuations due to the random nature of radioactive decay, (b) changes in light output with temperature, (c) radiation damage, (d) changes in reflectivity and transmission at the surfaces of the light source (e) variations in the solid angle subtended by the light source to the PM tube photocathode, and (f) variations in the timing period over which the light source is counted.

6.5. The light measurement system on the Model 654

6.5.1. Introduction

The light detector is a PM tube run in the current measurement mode, and generates a current proportional to the light input. The current is converted to a pulse train by a charge-to-pulse convertor, and the pulses are fed to a scaler and its associated 6-digit display. Thus, at any sensitivity setting, the light output from the dosemeter can be measured over 6 decades. An 'Overrange' lamp illuminates if the scaler store is exceeded.

The light measurement system on the Model 654 is novel in that it utilises variable negative feedback both to set the sensitivity to a desired level and to automatically maintain that level, thus greatly simplifying operational procedures. The sensitivity can be adjusted linearly over 3 decades, thereby simplifying calibration techniques, since adjustments to compensate for differences in dosemeter sensitivities can readily be made. Once the desired sensitivity has been set the system automatically compensates for drift in photomultiplier tube sensitivity, the temperature coefficient of the signal conditioning circuits, and changes in the light path between
the dosemeter and the photocathode. This automatic correction is based on a highly stable light source to which reference is made whenever the drawer is fully opened in order to change the dosemeter.

The major problems associated with earlier designs of light measurement system have thus been eliminated or reduced. System sensitivity is governed by a five digit thumbwheel switch, which provides a variable signal to which the output from the PM tube due to an internal light source automatically adjusts. This enables the operator to reproducibly set the instrument to suit any dosemeter range and sensitivity in a matter of seconds, and is a great improvement on the old 'hit and miss' system employed on other instruments, whereby the high voltage on the PM tube is repeatedly adjusted until the internal light source reaches the desired setting. Patents have been applied for in the U.K. (Robertson, Davis, Brabants, and Marshall, 1973) and in the U.S.A. (Robertson, Davis, Brabants, Marshall and Pettifer, 1973).

6.5.2. System operation

The operation of the system is best described with reference to figure 6.5. Whenever the drawer is fully opened an internal light source (ILS) of strength $U$ is brought into position under the PM tube photocathode, and a microswitch closes the feedback loop, i.e. puts the system into the 'sample' mode. The resultant current output from the PM tube due to the ILS is proportional to both the PM tube sensitivity and the light output of the ILS, and is converted into a pulse rate ($f_0$) by the charge to pulse convertor (CTPC). The signal can then be counted over a set time period by a scaler. The pulses from the CTPC are fed into a ratemeter, the gain of which is controlled by the sensitivity and calibration controls such that its output voltage is a linear function ($H$) of the input frequency. This voltage is compared with a reference voltage ($f_1$). The resultant error signal ($e$) alters the output voltage of the integrator, which in turn controls the voltage on the PM tube, hence the PM tube gain. Thus, if the sensitivity of the overall system alters from the desired sensitivity an error signal is generated which adjusts the PM tube gain to compensate.

Whenever the drawer is not fully extended the feedback loop is opened i.e. the system is in the 'hold' mode, and the high voltage on the PM tube is held at its value when the drawer started to close. Uncorrected drift can occur during the 'hold' period and in order to maintain the system sensitivity the drawer must be fully opened at intervals; this is normally carried out as a matter of course when changing dosemeters. The underlying assumption in the system design is that sensitivity drift will be
Figure 6.5.

Light sensitivity control system

Reference voltage → a) Sample or b) Hold → Integrator → EHT Generator → PM tube → CTPC → Scaler

a) Internal light source or b) Dosemeter

Fault indication

Ratemeter

To (optional) glow curve ratemeter and chart recorder

Sensitivity control

Calibration

\[ f_o = \frac{f_i}{H} \]

If \( GH \gg 1 \),

For monochromatic light, sensitivity = \[ f_o = \frac{f_i}{U} \]
negligible during the readout of a dosemeter, and this has been verified experimentally.

6.5.3. Theory of operation

A representation of the system from the point of view of control theory is also shown in figure 6.5. G is a transfer function encompassing the integrator, EHT convertor, PM tube, and CTPC. From control theory:

\[ f_0 = G e \]
\[ e = f_i - H f_0 \]
\[ f_0 = G(f_i - H f_0) \]
\[ f_0 = \frac{G}{1 + GH} f_i \]

If \( GH \gg 1 \),
\[ f_0 = \frac{f_i}{H} \] \hspace{1cm} (6.1)

Thus the relation between \( f_i \) and \( f_0 \) is dependent only on the ratemeter, provided that \( GH \) is very much greater than unity. The sensitivity \( S \), defined as the output frequency of the CTPC per unit light input into the PM tube photocathode, is established in the sample mode.

Thus,
\[ S = \frac{f_0}{U} \] \hspace{1cm} (6.2)

Substituting for \( f_0 \),
\[ S = \frac{f_i}{HU} \] \hspace{1cm} (6.3)

The sensitivity is thus dependent only on \( f_i \), \( H \), and \( U \) (providing \( GH \gg 1 \)), and these can readily be made very stable.

The sensitivity control, which is a five digit thumbwheel switch on the front panel, varies \( H \) linearly to give the 3 decade linear adjustment in sensitivity (see section 6.5.8). The 'calibration' control is an internal fine adjustment to enable all readers to have the same sensitivity when switched to the same sensitivity setting, thus enabling some degree of precalibration. Equation 6.3 is only strictly true for monochromatic light, or if the response of the photocathode (no optical filters) is independent of \( \lambda \), which is not generally the case. In practice the sensitivity is also a function of the dosemeter emission spectrum, the light source emission spectrum, the spectral response of the photocathode, and the effect of any optical filters. With the notation of section 3.1, the sensitivity is given by

\[ S = \frac{f_i}{H \int_U U(\lambda) F(\lambda) Q(\lambda) d\lambda} \]
and on this sensitivity setting the reading $R'$ from a dosemeter will be

$$R' = \frac{\int L(\lambda)F(\lambda)Q(\lambda) d\lambda}{\int U(\lambda)F(\lambda)Q(\lambda) d\lambda}$$

(cf. eqn.3.3)

6.5.4. The internal light source (ILS)

The stability of the light source is critical to the correct operation of the light measurement system. The type of light source used is similar to that described by Facey (1965) and consists of 5 μCi of $^{14}C$ (benzoic acid (carboxyl), Radiochemical Centre, Amersham) uniformly dispersed in a plastic scintillator (NE 120, Nuclear Enterprises Ltd.) The light source is 12.5 mm in diameter by 3 mm thick, and has a mean temperature coefficient (below 40°C) of about $-400 \text{ ppm } ^\circ\text{C}^{-1}$. Facey (loc.cit) has calculated that internal radiation damage should have a negligible effect on light output over at least ten years. A problem was experienced in ensuring a constant reflectivity at the surfaces of the light source in contact with its holder, the light source being relatively transparent, but it was solved by vacuum depositing a coating of aluminium on these surfaces. The emission spectrum peaks at around 425–450 nm, and thus is well matched to LiF and to most photocathodes.

The temperature coefficient of the light source is the major limitation on the reproducibility of the sensitivity of the light measurement system. From eqn.6.3, if the light output decreases the sensitivity increases, as the EHT rises to maintain the GTPC output constant. The ILS will actually move through a greater temperature range than the ambient temperature swing, as it is necessarily positioned in the drawer assembly, near the heating element, and the temperature of the drawer assembly will rise as the frequency of dosemeter readings increases. An efficient nitrogen flow through the assembly helps to limit this temperature rise.

The ILS reading is given by

$$f_0 t = \int_0^1 f_1 t$$

where $t$ is the timing interval. This is independent of $U$, the intensity of the light source, hence variations in $U$ are not observable from the ILS reading, and one of the reasons why an external light source is also supplied is to check for variations in the ILS, e.g. due to any dust or debris collecting on its surface.

Several precautions have been taken to keep the top surface of the ILS absolutely clean, and have been proved successful over two years operational experience. A dust filter is inserted in the input side of the nitrogen line, and the design is such that nitrogen blows over the surface of the ILS while a reading is taken. In experiments with layers of debris placed on a light source it was found that all the debris could be removed.
by opening the flowmeter valve fully, with the nitrogen line at normal operational pressure (0.35 - 0.7kg m\(^{-2}\)).

A slight sensitivity to light has been noticed with this type of light source. When exposed to daylight an almost immediate decrease in intensity of about 2% occurs. When the light source is removed from ambient lighting it gradually recovers to its original intensity over a period of about five days. Since the ILS is not normally exposed to light, the stability of the light measurement system is unaffected.

6.5.5. The external light source (ELS)

The ELS is supplied (a) to check for any leakage in 'hold' mode (see section 6.5.12), and (b) to check for any variations in the ILS. It is placed in the drawer for the check, in the same position that the dosemeter would normally occupy. The ELS reading is only an approximate check for any variations in the ILS, and in practice apparent variations of less than 2% are not considered significant, since the ELS reading may vary due to (a) positional tolerances, (b) temperature variations, and (c) the effect of exposure to light. However, a gradually increasing ELS reading may be indicative of a build-up of dust on the ILS.

6.5.6. The photomultiplier tube

The photomultiplier tube is an 11-stage venetian blind tube with a bialkali (K\(_2\)CsSb) photocathode, and is available from EMI Ltd. (9757B) or 20th Century Ltd. (Centronic P4232B). The specification on the dark current is that it should be less than 10\(^{-10}\) amps at 200 amps/lumen sensitivity. The quantum efficiency of the photocathode is shown in figure 6.3. The tube is fitted with a mu-metal magnetic screen maintained at cathode potential. Also incorporated into the PM tube housing (see figure 5.4) is a Chance HA3 heat-absorbing filter, 4mm thick, which is positioned directly above the aperture in the fixed polyamide plate. The transmission characteristic of this filter is shown in figure 6.4. The PM tube photocathode is thermally isolated from the optical filter by an O-ring.

The current output due to the ILS varies between about 10\(^{-9}\) to 10\(^{-6}\) amps, depending on the system sensitivity. The dark current is a factor of about 10\(^4\) less than the ILS signal, and has negligible effect on the feedback system. The dynode chain is shown in figure 6.6. The negative high voltage on the cathode is typically varied from 500 to 1100 volts (with respect to earth) to alter the PM tube sensitivity from 0.25 amps/lumen to 250 amps/lumen, i.e. the range over which this tube is normally used. Due to individual variations between PM tubes an EHT generator designed for this purpose should be able to vary from about 400 to 1500
Figure 6.6. Dynode chain used on Model 654 reader

E.H.T.
(from EHT generator)
volts. The total resistance of the dynode chain is 1.4 megohms, thus the current through the chain can vary from approximately $3 \times 10^{-4}$ to $10^{-3}$ amps. To preserve linearity within 1% the signal current should be less than 1% of the current through the dynode chain i.e. at minimum EHT the signal current should be less than $3 \times 10^{-6}$ amps, and at maximum EHT less than $10^{-5}$ amps. The cathode-D1 voltage should be approximately 150V for the best signal/noise ratio and immunity to magnetic fields. The PM tube manufacturers thus recommend a 150V zener diode in this position. Alternatively a 200kΩ resistor may be preferred as in figure 6.6 on component reliability grounds. The voltage across this resistor is approximately 150V with an EHT of 1000V (which is about the usual working voltage) and varies from 80 volts to 220 volts according to the EHT. The 80 volts is sufficient to ensure efficient electron collection, and 220 volts is well below the maximum safe voltage. A 200kΩ resistor is also placed between D9 and D10, as this improves linearity at high signal currents, by reducing the possibility of space charge limiting.

6.5.7. The charge-to-pulse convertor (CTPC)

This is a modification of earlier designs by Perry (1968) and Botter-Jensen (1970). A MOSFET input ensures that leakage currents are much lower than the PM tube dark current, and the frequency of the output is linearly proportional to input current up to 2.5 MHz. The conversion factor is 1 pulse per $10^{-10}$ coulomb. The unit is contained in a sealed and desiccated box which provides electrostatic and electromagnetic screening, and ensures that the leakage current remains low even in conditions of high humidity.

The temperature coefficient of the unit is such that significant drift does not occur during the 'hold' mode (e.g. during a heating cycle), following an initial 10 minute warm-up period.

6.5.8. The ratemeter

This unit has to be extremely stable, as it governs the feedback ratio and thus, along with the reference voltage, sets the closed loop gain. On the prototype unit, the average temperature coefficient from 0 to 50°C was found to be less than 20ppm °C⁻¹, i.e. very much less than the temperature coefficient of the ILS, which is thus the limiting factor on stability. The ratemeter is a switched constant current type, and the feedback ratio can be varied by 1000:1 by means of the 5 digit 'Sensitivity' thumbwheel switch to give the same degree of variation in sensitivity (see eqn.6.3*). The 'Sensitivity' switch is the only sensitivity control routinely available to the operator. The first digit is a decade multiplier, and can be set to positions 0, 1, or 2, which respectively multiply the relative sensitivity
by $x\ 1$, $x\ 10$, and $x\ 100$. This is achieved digitally by a dual decade counter. Digits $2 - 5$ can be switched nominally between 0000 and 9999, but the logic on the second digit has been rewired so that position 0 is the same as position 1, and thus these digits are effectively adjustable between 1000 and 9999, correspondingly altering the relative sensitivity from '1.000' to '9.999'. The switch setting is thus related to the relative sensitivity of the light measurement system as shown in Table 6.1.

Table 6.1.

<table>
<thead>
<tr>
<th>Sensitivity control</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Five digit thumbwheel switch)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Digits used on switch</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 = $x\ 1$</td>
<td>1.000 - 9.999</td>
</tr>
<tr>
<td>1 = $x\ 10$</td>
<td>x</td>
</tr>
<tr>
<td>2 = $x\ 100$</td>
<td></td>
</tr>
</tbody>
</table>

Examples

<table>
<thead>
<tr>
<th>Switch setting</th>
<th>Relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>01000</td>
<td>1.000</td>
</tr>
<tr>
<td>09999</td>
<td>9.999</td>
</tr>
<tr>
<td>11000</td>
<td>10.00</td>
</tr>
<tr>
<td>13756</td>
<td>37.56</td>
</tr>
<tr>
<td>19999</td>
<td>99.99</td>
</tr>
<tr>
<td>21000</td>
<td>100.0</td>
</tr>
<tr>
<td>29999</td>
<td>999.9</td>
</tr>
</tbody>
</table>

It was decided to use this wide range thumbwheel switch as the sensitivity control since (a) one is not limited to a small number of precalibrated settings, and (b) the variation in sensitivity with digits $2 - 5$ is achieved by close tolerance high stability resistors. The resolution of sensitivity varies with switch setting. For example, with the last four digits on 9999 the resolution is 0.01% (1 part in 9999), but on 1000 the resolution is 0.1%.

The 'calibrate' control (a high stability potentiometer) can also adjust the feedback ratio by about $\pm\ 20\%$, and is used in conjunction with a Master External Reference Light Source (MERLS) to set the sensitivity of each instrument to the same value for the same sensitivity setting. For this adjustment the timing period over which the light source is integrated.
has to be the same on each unit. On the Model 654 this timing period is 16 secs ± 0.03%.

6.5.9.  The reference voltage
This also has to be extremely stable as, from eqn.6.3, the sensitivity is directly proportional to it. On the prototype unit, the temperature coefficient was less than 10ppm per °C. It is derived from a zener diode.

6.5.10. The Comparator
The output of the comparator is held at a negative potential (the reference voltage) in the absence of an output from the CTPG. At initial start up this ensures that the integrator output voltage is positive and EHT is generated. When the light source is presented to the PM tube the resultant pulse input to the ratemeter generates a voltage counteracting the negative potential, thus reducing the error voltage on the output of the comparator as the desired EHT is reached. Equilibrium is attained when the output of the comparator averages zero volts. If the system sensitivity alters from that set by the 'Sensitivity' switch, an error signal is generated which adjusts the EHT until the output of the comparator again averages zero volts. If the 'Sensitivity' switch setting is altered, the EHT adjusts to maintain zero comparator output, thus resetting the sensitivity.

6.5.11. Sample or hold
This is achieved by means of a reed relay operated by a microswitch in the drawer assembly. The relay is opened in 'hold' mode and effectively becomes a high resistance (> $10^{14}$ ohms).

6.5.12. Integrator
The integrator is a low input current MOSFET operational amplifier with capacitive feedback. The output voltage reaches a steady value when the input current averages at zero. When in the 'hold' position, the output will be held at a constant voltage, the constancy being conditional on negligible leakage through the operational amplifier, capacitor, sample-and-hold relay, and protection diode. Any such leakage would cause the EHT voltage to gradually deviate from the correct voltage, and the unit is housed in a sealed and desiccated box to minimise the effect, which is in fact negligible over the maximum period of ten minutes during which the circuit can be in the 'hold' position without resampling.

The reference voltage $f_1$ is in fact modified by the input offset voltage of the integrator, and the temperature coefficient of this offset voltage is responsible for an initial upwards drift in ILS readings of typically 0.2 - 0.3% during the first few hours after switch-on.
6.5.13. **EHT generator**

The EHT generator is a D.C. to D.C. convertor giving a rectified and smoothed high voltage supply of up to -1500 volts. The EHT output voltage is linearly proportional to the output voltage of the integrator. The stability has to be such that significant drift does not occur during the 'hold' mode.

6.5.14. **Stepped drawer system** (Robertson, 1974)

For correct operation of the light measurement system, it is essential that extraneous light does not add to the internal light source when the system is sampling, with the drawer fully out. In addition, stray light should not add to the dosemeter reading when the drawer is fully closed. The most probable path for stray light to enter the head unit is through the drawer entrance, and special attention was paid to the drawer design to achieve negligible light leakage over the working life of the instrument.

One common feature of many other TLD readers is the rather stiff drawer action, due to the close machining tolerances which are required to exclude light leaks. In such designs, the drawer eventually works loose, due to wear and tear; it is then prone to light leaks, especially with the drawer fully open. Another practical problem, which occurs when closing a stiff drawer containing powder, is that sudden movements due to uneven motion of the drawer can cause the powder to spill or be rearranged incorrectly in the tray.

On the Model 654 light leaks with the drawer fully open must be less than 0.1% of the strength of the internal light source for the feedback system to function accurately. Consequently, a 'stepped' drawer has been designed (see figure 6.7) which completely eliminates light leaks of this nature but enables some mechanical tolerances to be relaxed to provide a smooth drawer action and increased mechanical reliability. Referring to figure 6.7, when the drawer is fully open, a step along the bottom and sides of the drawer interrupts the path of light entering through the front of the drawer. It is not possible to extend this step around the top of the drawer since this would necessitate a gap, between the top of the drawer and the fixed polyimide plate, which is undesirable as the vertical travel of the dosemeter and the chances of its lateral displacement are thereby increased. Therefore, to complete the light seal, an opaque roller drops under the action of gravity into a groove across the top of the drawer. When the drawer is fully closed, it is possible to have a full step around the drawer opening, and this provides an effective light seal.

Note that the smooth drawer action also facilitates the design of any automatic sample changer which may be incorporated into the system.
Figure 6.7.

Stepped drawer system

a) Side view (drawer open)

Drawer

Tray position

Opaque roller

PM tube housing

Front panel

b) Top view (drawer open)

Internal light source
The response times of three distinct operations have to be taken into account.

(a) Time taken to stabilize at any given sensitivity from initial switch on:
A plot of sensitivity vs time is shown in figure 6.8(a). The sensitivity stabilizes to within 0.1% of the final value after about 120 seconds. The initial period during which the sensitivity remains at zero is because the output of the integrator has to build up to a critical value before the EHT generator starts to operate.

(b) Time taken to stabilize after the drawer is fully opened following a dosemeter reading:
As the drawer is closed, the EHT is held, but the output of the comparator rises to the reference voltage level. When the drawer is fully opened, e.g. following a dosemeter reading, there is a delay of 2 seconds before the system switches from 'hold' to 'sample' to allow the output of the comparator to fall to near zero, and thus avoiding a momentary increase in the EHT. Following this, the system compensates for any sensitivity change which might have occurred during the 'hold' period with an effective time constant of about 7 seconds. Thus a change in sensitivity of 1% would be reduced to less than 0.3% after 7 seconds, and less than 0.1% after about 14 seconds. It is assumed that the drift in sensitivity during one dosemeter readout, which normally takes a maximum of 1 minute, would be less than 1%, and auxiliary control circuitry inhibits the automatic start of another read cycle until the drawer has been fully opened for at least ten seconds, which is felt to be a reasonable mandatory delay from the operational point of view. In practice, the process of changing dosemeters and noting the previous reading takes about ten seconds to accomplish. A plot of sensitivity vs time is shown in figure 6.8(b).

(c) Time taken to stabilize after the sensitivity is changed:
Sensitivity vs time is illustrated in figure 6.8(c) which shows the response following the maximum possible change in sensitivity of 3 decades. The sensitivity stabilizes to within 0.1% of the new level within 60 seconds. The drawer must of course be fully opened during this period. A convenient method of timing the period is incorporated in the operation of the reader.

6.5.16. Reproducibility of sensitivity setting

When the circuit is changed to the hold mode by the action of starting to close the drawer, the sensitivity is not held at exactly the same value each time due to statistical fluctuations in the light output from the internal light source. The coefficient of variation (one standard deviation expressed as a percentage of the average reading) in the sensitivity setting is determined by two factors, the strength of the light source and the effective time constant of the feedback loop. A coefficient of variation in the sensitivity
Figure 6.8. Light measurement system: response times

a) Switch on

```
<table>
<thead>
<tr>
<th>Sensitivity</th>
<th>Final level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time since switch on</td>
<td>120 secs</td>
</tr>
</tbody>
</table>
```

b) Drawer opened

```
<table>
<thead>
<tr>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Hold mode'</td>
</tr>
<tr>
<td>'Sample mode'</td>
</tr>
<tr>
<td>Corrected sensitivity</td>
</tr>
<tr>
<td>Initial sensitivity</td>
</tr>
<tr>
<td>2 secs</td>
</tr>
<tr>
<td>10 secs</td>
</tr>
</tbody>
</table>

Drawer fully opened

```
<table>
<thead>
<tr>
<th>Time</th>
</tr>
</thead>
</table>
```

c) Sensitivity changed

```
<table>
<thead>
<tr>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original sensitivity</td>
</tr>
<tr>
<td>New sensitivity (lower level)</td>
</tr>
<tr>
<td>60 secs</td>
</tr>
</tbody>
</table>

```

<table>
<thead>
<tr>
<th>Time</th>
</tr>
</thead>
</table>
setting of about 0.1% has been achieved with a light source consisting of 5 uCi of $^{14}C$ in a plastic scintillator and a time constant of about 7 seconds. Decreasing the time constant leads to faster response times but greater fluctuations in sensitivity, and vice-versa. It was decided not to increase the strength of the light source to avoid the possibility of internal radiation damage reducing the light output.

One other factor which could contribute to the deviations in sensitivity, but which has not been detected experimentally, is the speed at which the drawer is closed. The changeover from 'sample' to 'hold' takes about 10 ms, due to anti-bounce circuitry associated with the 'drawer out' microswitch. At a drawer speed of say 2.5 cm per second, the drawer, and therefore the internal light source, would move a distance of 0.25mm before the EHT was held. As the drawer speed varies, the position of the ILS relative to the photocathode at the instant of changing from 'sample' to 'hold' will vary, thus the geometrical efficiency will change slightly. Two factors will minimise this effect; first, the time constant of the feedback circuit is very much greater than 10 ms; secondly, the light source is 12.5mm in diameter compared with the aperture in the polyimide plate which is only 10mm in diameter and this reduces considerably the change in geometrical efficiency for small displacements.

6.5.17. Experimental determination of the standard deviation in sensitivity

The 'Sensitivity' switch was set to a certain value and the drawer was fully opened to position the ILS under the PM tube. Special test equipment was used to allow switching from sample to hold mode and vice-versa, independent of the position of the drawer. Once the sensitivity had stabilized in sample mode, the system was switched to hold mode and an ILS reading taken. The system was then switched back to sample mode for a few seconds to reset the sensitivity, and then once again switched to hold mode to obtain another ILS reading. This procedure was repeated to give a total of 20 readings for a reasonable statistical interpretation. The coefficient of variation of these readings was found to be 0.14%, but a contribution to this figure is due to counting statistics, and was determined to be about 0.06% by obtaining a series of 20 ILS readings at one particular 'hold' setting. The coefficient of variation in the sensitivity is thus

$$\left( (0.14)^2 - (0.06)^2 \right)^{1/2} = 0.12\%$$

This figure does not vary significantly over the range of 'Sensitivity' settings (excluding inaccuracies due to insufficient resolution on the display).

6.5.18. Theoretical calculation of ILS counting statistics

The strength of the light source is 5 uCi( ± 20%)
No. of disintegrations/sec. = 5 x 3.7 x 10^4

The effect of the polyimide aperture is such that light from approximately 60% of disintegrations is detected.

No. of disintegrations/sec. detected = 5 x .6 x 3.7 x 10^4
= 11.1 x 10^4

The coefficient of variation of counts from a radioactive source is given by
\[ \left( \frac{N}{T} \right)^\frac{1}{2} \]

where \( N = \) No. of disints/sec detected, and \( T = \) counting time.

\[ \text{Coefficient of variation} = \frac{100}{\left(11.1 \times 10^4 \times 16\right)^\frac{1}{2}} = 0.075\% \]

This is in good agreement with the experimentally determined value of 0.06%, considering the uncertainty in the strength of the light source and the approximations made.

6.5.19. Auxiliary protection circuits

(a) Time limit to 'hold' mode

Uncorrected drift can occur during this period due to changes in the PM tube, EHT, integrator, or CTPC. In normal operation the sensitivity is reset after every dosemeter reading, and the assumption is made that the mandatory ten second period with the drawer fully open is sufficient for correction to take place. However, if the drawer is left in for longer than usual, a greater drift in sensitivity could take place than can be corrected for in the ten seconds. Therefore, if the drawer is not set to the fully out position during a period of more than ten minutes, a warning 'RESET' lamp flashes, and the drawer must then be fully opened for a minimum period of 60 seconds before automatic operation can recommence. This 60 second period is sufficient to fully compensate for even very large changes in sensitivity.

(b) Feedback loop break indication

A major failure in the light measurement system will in many circumstances result in the absence of a feedback signal; a large error signal will then be present continuously, and will soon cause the EHT generator to reach a maximum level at which point a 'MAX EHT' lamp will illuminate, indicating a fault in the light measurement system. The maximum EHT is preset for each tube at a voltage which is below the safety limit.

6.5.20. Experiments on light measurement system

A series of experiments were carried out to test the sensitivity of various components in the light measurement system to various factors, and the results are summarised in Table 6.2. The rationale of each experiment is self-evident. Many of the effects are clearly negligible, and in practice there are generally
only two factors which limit the overall performance, (a) the temperature coefficient of the internal light source, and (b) the temperature coefficient of the input offset voltage of the integrator.

6.6. Limitations to the accuracy of dosemeter precalibration

The 'calibration' control in the light measurement system is an internal fine adjustment to enable all readers to be normalised to the same sensitivity when switched to the same sensitivity setting. In principle this facilitates some degree of dosemeter precalibration, since all types of dosemeter manufactured by D. A. Pitman Ltd. can be calibrated on the "master" Model 654 reader in the Pitman Laboratories, and the calibration figures can be related to a 'Sensitivity' setting which will be valid for all other Model 654 readers, assuming the same heating cycle is used. In practice, the following factors limit the accuracy of dosemeter precalibration in this way to about 5–10%:

(a) Any such calibration figure can only meaningfully be given for the average sensitivity of a batch of dosemeters. A statistically significant proportion of the batch would be calibrated using an irradiation facility which has been related to an absolute standard. The uncertainty in the calibration of the mean batch sensitivity should be less than about 2% at the 99% confidence level, but for individual dosemeters there is the additional error of variations in sensitivity relative to the mean batch sensitivity. This error is generally 2–5%, depending on the type of dosemeter.

(b) Reproducibility of the heating cycle:— For each form of dosemeter a definite proportionality is assumed between dose and light output; this is critically dependent on the dosemeter heating cycle, and may vary slightly from one reader to the next.

(c) Uncertainty in the calibration of the light measurement system:— With care, statistical and resolution errors can be made very small (~0.1%), but the accuracy of calibration is limited by variations in (i) the temperatures of the light sources involved (ii) the timing period (iii) the solid angle subtended by the 'master' external reference light source (MERLS) used in the calibration, and (iv) the stability of MERLS. Of these, the last contributes most to the uncertainty. To reduce random errors, the relative responses to a set of 5 MERLS are compared at intervals, but as yet a method of checking for systematic drift is not operational. Eventually it is hoped to check a MERLS at intervals against a photometric standard at the National Physical Laboratory, but from a preliminary investigation it would seem that the uncertainty involved in this comparison would be of the order of 3–5%, due to the relatively low intensity.
(d) Reproducibility of the sensitivity of the light measurement system

The short-term reproducibility is of the order of $0.1\% \pm 0.05\%$ per $^\circ$C, but in the longer term will be dependent on the stability of the ILS.

(e) Differences in spectral response between PM tubes

These differences will not lead to appreciable calibration errors for LiF dosemeters (as the emission spectrum of LiF matches that of the light sources fairly well), provided that the spectral response of a PM tube is stable with time. However, the precalibration for dosemeters emitting in substantially different spectral regions, e.g. Li$_2$B$_4$O$_7$Mn, will be dependent on variations in PM spectral response from tube to tube relative to the response to the light source emission spectrum.

The calibration will only be valid for dosemeters with a stable sensitivity. In practice the sensitivity of a dosemeter may be dependent on pre-dose and post-dose storage conditions, radiation and thermal history, surface condition and other factors. The dosemeter background signal will be an additional complication at low doses.

6.7. Background signals

6.7.1. PM tube dark current

The photomultiplier tube used in the Model 654 is specially selected for low dark current (section 6.5.6). When reading out LiF/PTFE discs, 12.7mm diameter by 0.4mm thick, with 30% phosphor loading, the dark current at 20°C is equivalent to less than 1 mrad. Variations in dark current at a constant temperature are of the order of 0.1 mrad for this type of dosemeter. However, the dark current is dependent on temperature, and when reading out large numbers of dosemeters it is advisable to check the dark current at intervals to determine whether it has changed significantly. Dark current variations are easily assessed and are not a limiting factor in low dose measurements.

6.7.2. Noise in the signal conditioning circuits

Noise in the signal conditioning circuits is negligible, due to the low leakage MOSFET 'front end' of the CTPC (section 6.5.7).

6.7.3. Thermal radiation

Most of the thermal radiation signal during readout originates from the hot dosemeter, and thus varies with the type of dosemeter, but is minimised by the use of an efficient infra-red absorbing filter (Chance HA3) and by the selection of heating cycles with the highest signal/noise ratio. The transmission vs wavelength characteristic of the infra-red filter is shown in figure 6.4. Thermal radiation from the heating tray itself is a negligible factor even in low dose measurements.
6.7.4. **Chemiluminescence and inert gas flow**

The chemiluminescence signal from a dosemeter is considerably reduced by an efficient inert gas purge, which removes any oxygen from the readout area. Nitrogen or argon can be used, but nitrogen is preferred on cost grounds. The chemiluminescence signal from the empty sample tray is negligible when nitrogen flow is used. The main function of the inert gas flow is to suppress chemiluminescence signals (see chapter 10) but it also performs the following functions:

1. **It minimises the temperature rise in the drawer assembly, and thus reduces variations in the ILS due to temperature.**
2. **It prevents the heating trays and heater assembly from oxidising.**
3. **It can be used to blow dust from the top surface of the ILS and reduce the necessity for periodic dismantling and cleaning.**
4. **It flows across the face of the infra-red filter, thus cooling the filter, which is positioned above the heated dosemeter, and improving the thermal isolation of the PM tube photocathode, which is itself separated from the infra-red filter by an 'O' ring. This thermal isolation is required to minimise short-term drift in PM tube gain during the 'hold' mode.**

For optimum results, the nitrogen should be dry, dust-free, and have an oxygen content of less than 100 ppm. It was found experimentally that a nitrogen flow rate of greater than 1 litre/min caused appreciable interference with the readout of some forms of dosemeter. For example, phosphor/PTFE microrods show a loss in sensitivity and precision due to a cooling effect, and loose powder samples were displaced from the centre of the tray to the edges. Although efficient suppression of chemiluminescence signals was noted for flow rates as low as 100 ml/min, an operational flow rate of 400 ml/min was chosen to aid in the performance of the other functions. The inert gas flow is controlled by the flowmeter in conjunction with an electrically activated valve. To conserve gas supplies the valve is only open during read cycles, and in typical applications a standard nitrogen cylinder containing 6.2 m³ is sufficient for about 10⁴ readings.

6.7.5. **Background subtract facility**

A two digit thumbwheel switch gives provision for fast, reproducible and accurate insertion of predetermined dosemeter backgrounds, which are then automatically subtracted from the display reading.

6.8. **Concluding remarks**

This concludes the design philosophy and description of the Model 654 reader. A more detailed description of the electronic circuitry and mechanical features can be found in the instruction and service manuals,
available from D. A. Pitman Ltd. A full range of accessories, such as
glow curve and data recording equipment, and dosemeter handling aids,
have also been developed. The smooth drawer action lends itself to
automation, and a prototype automatic sample changer capable of handling
up to 30 dosemeters of any type normally accepted is currently undergoing
trials (J. C. Stewart, private communication). The necessary control
signals from the reader were anticipated and are already provided for in
the design. To date (Sept. 1974) 27 readers are in operation (6 overseas)
and another 60 are under construction. Users' comments have been
favourable and no serious design faults have been found.

In the next chapter different forms of dosemeter and criteria for
comparing them are discussed.
Table 6.2. Experiments on Light Measurement System

(a) Experiments not utilising internal EHT generator

1. Measurement of short-term drift in CTPC:—
   Approx. 2% during first 20 minutes after switch on.
   Thereafter, < 0.1% in any 10 minute period.

2. Detection of light leaks:—
   Drawer out: No measurable difference in ILS reading (< 0.1%)
   Drawer in: No measurable difference in dark current.

   < 0.1% in any 10 minute period with or without dosemeter read cycles.

4. Effect of internally generated magnetic fields on sensitivity:—
   No measurable effect (< 0.1%)
   See also section 6.3.3. (iv). These effects have not been observed
   with the Model 654 even though the heating element to photocathode
   distance is only 15mm. This is believed to be due to the nature of
   the heating cycle control circuit (section 5.8), which employs
   complete cycle firing and a zero-crossing switch.

5. Temperature coefficient of light source:—
   < 400 ppm°C⁻¹, 20°C - 50°C.

(b) Experiments on stability of sensitivity in 'sample' mode

1. Variations in sensitivity with mains voltage:—
   < 2 ppm V⁻¹, from 200 - 260 VAC

2. Variations in sensitivity with temperature of reference voltage and
   ratemeter:—
   < 40 ppm°C⁻¹, from 0 - 50°C

3. Temperature coefficient of 1pps timer:—
   < 50 ppm°C⁻¹, from 0 - 50°C.

4. Drift in ILS readings:—
   < 0.3% during first 5 hours after switch-on (see section 6.5.12).
   Thereafter, < 0.1% ± 0.05% per °C.

5. Time taken to stabilise at a certain sensitivity from switch on:—
   Within 0.1% after 120 secs.

6. Time taken to stabilise after the sensitivity setting is changed:—
   Within 0.1% after 60 secs, following maximum possible change of
   3 decades.

7. Time taken to correct for any sensitivity drift after the drawer is
   fully opened following a dosemeter reading:—
Corrects with an effective time constant of about 7 seconds.

8. Ability of the system to cope with large changes in $G$ (see section 6.5.3):
   (a) Variation in ILS reading with temperature of the PM tube:
       $< 3 \text{ppm} \, \text{°C}^{-1}$, from 10 - 44°C.
   (b) Variation in ILS reading with temperature of EHT convertor, CTPC and integrator:
       $< 10 \text{ppm} \, \text{°C}^{-1}$, from 0 - 50°C.
   (c) Variation in ILS reading with strength of ILS:
       No measurable change ($< 0.1\%$) with 100% increase in ILS strength.

9. Ratio of ILS signal to dark current (depends on temperature):
   (a) Typically 10,000 : 1
   (b) Minimum 2,000 : 1

10. Variation in sensitivity with 'Sensitivity' switch setting:
    Linear, within 0.15%.

    Experiments in 'hold' mode

1. Drift in sensitivity during the maximum (10 minutes) 'hold' time:
   $< 0.1\%$.

2. Reproducibility of sensitivity at each sensitivity setting
   (corrected for any drift in ILS reading):
   Coefficient of variation $< 0.1\% \pm 0.05\%$ per °C.

3. Linearity of response, at each sensitivity setting:
   Depends on the ratio of the peak signal current to the current through the dynode chain. The peak signal current is a function of the type of dosemeter, dose, and the heating profile. The current through the dynode chain is a function of the sensitivity setting. Taking all these factors into account, for readings of up to $10^5$ digits the response should be linear within 1%, and considerably better than this in most cases. For readings of $10^6$ digits the response will typically be 2% low, but could conceivably be up to 10% low in extreme situations.

4. Drift due to PM tube fatigue effects, following exposure to maximum measurable light intensity for 10 minutes:
   $< 0.1\%$ during the maximum 10 minutes 'hold' time.

(d) Miscellaneous

1. Non-linearity due to changes in the spectral response of the PM tube with EHT:
Not measurable (<0.5%) from about 400nm (LiF) to 600nm (Li$_2$B$_4$O$_7$:Mn).

2. Effect of small variations (within microswitch limits) in position of opened drawer on sensitivity: $< 0.1\%$.

3. Effect of mains spikes:
Not noticeable (<0.1%) since incorporation of mains filter. However, extra filtration may be required on very noisy lines.

4. Temperature rise in drawer assembly: $<10^\circ C$ relative to ambient, for constant use (with nitrogen flow) over 10 hours.

5. Sensitivity of ELS to ambient light:
Variations of up to 2% observed, depending on intensity of ambient light.
CHAPTER 7. THERMOLUMINESCENT DOSEMETERS

In this chapter different types of thermoluminescent dosemeter and criteria for comparing them are discussed.

7.1. Criteria for comparing different types of thermoluminescent dosemeter

7.1.1. General physical characteristics

For solid dosemeters made from pure phosphor, the resistance to environmental or chemical attack is generally similar to that of powdered phosphor. However, if the dosemeter consists of a phosphor intimately mixed with, or in contact with, other materials, these properties of the dosemeter may differ from that of the pure phosphor. For example, Li$_2$B$_4$O$_7$Mn is hygroscopic, but its resistance to humidity can be greatly improved by incorporating it within a PTFE matrix. Sometimes, however, the thermal and mechanical stability of a dosemeter may be limited by the matrix material. Phosphor/matrix dosemeters are usually not so mechanically rigid as pure phosphor dosemeters, which may endow both advantages and disadvantages. Light transmission through solid dosemeters will be a function of the crystalline state and also the light transmission characteristics and refractive indices of the phosphor and any matrix material.

7.1.2. Available phosphors and configurations

There are generally constraints on the shapes and forms in which a particular type of dosemeter can be produced, and sometimes also on the phosphors which can be used. For phosphor/matrix dosemeters, there is an upper limit in the percentage loading of phosphor of about 30%, above which the mechanical stability is impaired. Discs or chips are good shapes for general purpose applications. Small rods are useful for in vivo applications. Skin and beta-particle dosimetry requires the use of dosemeters which are either very thin, or have a small 'effective thickness'. In the design of automatic systems, the ease with which a multi-element coded dosemeter can be constructed from suitable single element dosemeters is obviously a basic consideration. Some multi-element dosemeters contain several different types of dosemeter for mixed field measurements and photon energy spectrometry.

7.1.3. Dose range

The dose range of a dosemeter is determined by its sensitivity, response vs dose, and variations in the various sources of background signals.

The sensitivity and glow curve structure of a phosphor may be altered by the incorporation of the phosphor into a solid form. For example, sensitivity
will be dependent on the transparency of the dosemeter to its internally generated thermoluminescence. The glow curve structure of LiF:Mg,Ti dosemeters is also dependent on the detailed dosemeter form. It is shown in this thesis (section 8.5) that this is a function of the grain size of the powder from which the dosemeter is constructed, and may be related to the concentration and distribution of Mg.

The minimum detectable dose is determined by variations in background signals due to chemiluminescence, triboluminescence, thermal radiation, sensitivity to light, electrostatic discharges, or residual dose. Triboluminescence signals are greatly reduced in most solid forms of dosemeter, compared with loose powder. Any matrix material will contribute to background variations, and may even be slightly thermoluminescent. The maximum dose is effectively limited by the onset of saturation.

7.1.4. Precision

The precision required is determined by the application. The precision of measurement of a given dose can refer to either (a) the spread in readings obtained with a batch of dosemeters all of the same nominal sensitivity, or (b) the spread in readings obtained by repeated measurements with a single dosemeter. A discussion on precision is necessarily linked to the range of dose measurement. For doses such that the thermoluminescence signal is very much greater than variations in the background signal, the precision is determined by variables associated with (a) the method of manufacture and (b) the dosemeters' case-history since manufacture. For lower doses, where the background signal constitutes a significant portion of the total signal, the precision is limited by the above variables and variations in background signal.

Mathematically: If $\sigma_D$ is the standard deviation in dose $D$ of a series of measurements, $\sigma_B$ is the standard deviation in background signal, and $\sigma_S$ is the coefficient of variation in sensitivity, then

$$\sigma_D^2 = \sigma_B^2 + \left( \frac{\sigma_S}{100} \right)^2$$

At high doses, $\sigma_S$ dominates. At low doses, $\sigma_B$ dominates.

The precision, relative to the mean dosemeter sensitivity, with which a batch of dosemeters can be manufactured, is to some extent related to ease of production and cost. If the form of dosemeter and the production process are such that uniform dosemeters can easily be manufactured, then there would be no problem, but this is not usually the case. Generally very good precision can be achieved only by maintaining stringent manufacturing tolerances and quality control, and possibly some form of preselection. This results in a higher unit cost, and may still not lead to adequate
precision for some applications. A compromise is to adopt a production procedure that results in a reasonably priced dosemeter, and to recommend individual dosemeter calibration in those applications for which the batch precision is unacceptably low. Individual dosemeter calibration is essential for high precision applications since, even if the precision of a batch of dosemeters is initially acceptable, the sensitivity of individual dosemeters may change with re-use, being a function of thermal and dose history, and surface condition.

The preferred characteristics of a dosemeter to ensure reproducible heating and efficiency of light collection are a stable shape and a high thermal conductivity.

7.1.5. Cost

The cost of the phosphor is often the major factor in determining the total dosemeter cost. Pure phosphor solid dosemeters generally contain more than 30mg of phosphor, this being a constraint of the manufacturing techniques used in producing large batches of uniformly shaped dosemeters. Similarly, a loose powder measurement is sometimes obtained with as little as 15mg, but more often with 20-30mg since more precise measurements can usually be obtained thereby. However, dosemeters in which the phosphor is distributed in an inert matrix can often be considerably cheaper than pure phosphor dosemeters, since the proportion of phosphor can be related to the application and the sensitivity required. For example, phosphor/PTFE dosemeters can be manufactured which contain only small amounts of phosphor (~2mg) but with sufficient sensitivity for radiotherapy or other high dose applications. The cost of a dosemeter will also be related to the amount of extra effort required to obtain uniformity of response, as discussed in 7.1.4.

To minimise the cost per read-out it is obviously desirable to be able to re-use the dosemeters as often as possible. Most forms of dosemeter can be re-used at least 30 times without serious degradation of desirable characteristics, provided reasonable care is taken to preserve the surface condition. Any deleterious effects of thermal and dose history can be counteracted by appropriate operational techniques.

7.1.6. Response to different radiations

The relative response of the phosphor to different photon energies will be modified by the presence of any matrix or support material. Considering a phosphor uniformly distributed within a matrix, if the phosphor grain size is sub-micron the response is essentially that of the matrix, but if the grain size is greater than about 70μm, then the response is similar to the phosphor (Bassi et al, 1971; Charles and MacFarlane, 1974). This dependence
on grain size is related to the ranges of the secondary electrons. The response to neutrons will be influenced by the neutron interaction cross-sections of the phosphor elements and of the matrix material. The response of the dosemeter to non-penetrating radiations is determined by its transparency and thickness, as discussed in section 3.3.4 and chapter 11. With solid forms of dosemeter the thickness of any support material is often a critical factor.

7.1.7. Convenience of handling

Solid forms of dosemeter can conveniently be handled with hand or vacuum tweezers. Loose powder samples are either weighed individually or dispensed volumetrically. With most types of dosemeter, it is not possible to identify individual dosemeters directly and identification jigs are required to keep track of them. An advantage of phosphor/PTFE discs is that they can conveniently be identified by writing on one surface. To minimise variations in light output, this surface is placed away from the light detector during read out.

7.2. Measurements with loose powder

Loose powder, i.e. small grains of phosphor, encapsulated in plastic containers suitable for the application, was the first form of thermoluminescent dosemeter, and is still widely used. It has the advantage of flexibility, since a variety of shapes and sizes can be contrived by altering the container. Furthermore, sensitivity variations within a large batch can be averaged out by thorough mixing. The disadvantages of TLD powders are (a) the general inconvenience of handling powdered materials, and (b) a sensitivity variation with particle size due to light scattering and other effects (e.g. for LiF, Spiers and Zanelli, 1966; Zanelli, 1968; King, 1974; and the present work). For low dose measurements it is essential to use inert gas flow to suppress large non-radiation induced signals (triboluminescence and chemiluminescence).

The grain sizes generally used for routine measurements are in the range 75-200 μm, since they are free running and convenient to handle. Smaller grains tend to stick to each other and to their container due to electrostatic charges, while larger grains result in too few particles per sample for adequate averaging out in sensitivity, and they also exhibit complex light scattering effects. The particle size distribution changes with re-use, as smaller grains are produced by handling.

Generally about 30mg of powder is used per read-out, though the optimum weight may vary from about 10-40mg, depending on the design of the heating tray. After correcting individual readings for weight, coefficients of
variation of as low as 0.5% can be obtained. The limiting factor on precision is then the reproducibility with which the powder can be distributed in the heating tray. Although most accurate results are obtained by individually weighing each sample, vibrating volume powder dispensers can be used to dispense weights with a coefficient of variation of less than 1%.

In particular applications, the powder container may be designed to hold sufficient powder for several read-outs, to allow averaging and checking of results. This is the method often used in radiotherapy. For less stringent applications, such as extremity monitoring, the powder sachet is usually designed to hold exactly the right amount of powder for one read-out. However, the effective precision in weight may be reduced if some loss of powder occurs during the transfer from the sachet to the reader.

7.3. **Solid and encapsulated forms of dosemeter**

Solid and encapsulated forms of dosemeter are desirable since they have the advantage over loose powder of handling convenience. However, loose powder is still generally a first choice when accuracy is of paramount importance, despite intense development by dosemeter manufacturers. The various forms of dosemeter that have been developed are described below, and the properties of commercially available dosemeters are compared in Table 7.1.

7.3.1. **Encapsulation in glass matrix (enamel)**

The encapsulation of CaF$_2$:Mn in a glass matrix (Schulman et al, 1960a) was one of the first attempts to manufacture a pre-packaged or solid form of dosemeter. The dosemeter had the limitations of a large photon energy dependence, a high non-radiation induced light signal, and poor beta response. A similar form of dosemeter has been developed by Mihailovic (1966).

7.3.2. **Miniature valves**

Schulman et al (1960b), continuing their work on pre-packaged CaF$_2$:Mn, produced the first practical pre-packaged dosemeter, which consisted of CaF$_2$:Mn phosphor coated on a heater filament inside an evacuated glass bulb. The vacuum reduced background signals and prolonged heater life. A perforated tin filter was used to make the photon energy response approximately tissue-equivalent. Schayes et al (1965) developed a similar system, coating CaF$_2$: natural onto a cylindrical nickel tube, around which was spiralled a tungsten heating filament. The beta response is low due to the thickness of the glass envelope.
Table 7.1. Comparison of some commercially available forms of thermoluminescent dosemeter

<table>
<thead>
<tr>
<th>Quality</th>
<th>Loose powder</th>
<th>Phosphor/PTFE</th>
<th>Sintered</th>
<th>Hot pressed</th>
<th>Single crystals</th>
<th>Glass capillaries</th>
<th>Miniature valves</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Suitable phosphors</td>
<td>Wide</td>
<td>Wide</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Wide</td>
<td>Limited</td>
</tr>
<tr>
<td>2. Geometrical configurations available</td>
<td>Wide</td>
<td>Wide</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
<td>Limited</td>
</tr>
<tr>
<td>3. Uniformity of large batch</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Generally poor</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>4. Approximate tissue equivalence possible (LiF) without energy shield</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>5. Direct identification of individual dosemeters</td>
<td>Possible</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Possible</td>
</tr>
<tr>
<td>6. Currently widely used in personnel monitoring (photons and charged particles)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>7. Minimum detectable dose with LiF</td>
<td>&lt;10 mrad</td>
<td></td>
<td>Not known</td>
<td>Not known</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Suitable for measurement of non-penetrating radiations</td>
<td>Yes</td>
<td>Yes</td>
<td>Possibly</td>
<td>Yes</td>
<td>Possibly</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>9. Suitable for extremity monitoring</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>10. Currently widely used in radiotherapy</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>11. Suitable for in vivo measurements</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>12. Currently used in automatic systems</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>13. Relative cost per dosemeter</td>
<td>Low to moderate</td>
<td>Low to moderate</td>
<td>Moderate to high</td>
<td>Moderate to high</td>
<td>Moderate to high</td>
<td>Moderate to high</td>
<td>High</td>
</tr>
<tr>
<td>14. Relative size</td>
<td>Depends on container</td>
<td>Small</td>
<td>Small</td>
<td>Small</td>
<td>Small</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>15. Usual maximum operating temperature</td>
<td>400°C</td>
<td>300°C</td>
<td>400°C</td>
<td>400°C</td>
<td>400°C</td>
<td>400°C</td>
<td>Not known</td>
</tr>
<tr>
<td>16. Ruggedness</td>
<td>Depends on container</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
<td>Fair</td>
</tr>
</tbody>
</table>

Note: "Not known" indicates data not available or not applicable.
7.3.3. Glass capillaries

Further miniaturization was achieved by the development of small glass capillary needles (~1mm in diameter by 12mm in length) filled with either CaF$_2$:Mn or LiF in an argon atmosphere (e.g. Booth et al, 1971). The glass surround modifies the photon energy response of the phosphor, and the beta response is very low due to the wall thickness.

7.3.4. Single crystals

The use of cleaved LiF single crystals has been investigated by Suntharalingam et al (1965), and Suntharalingam and Cameron (1966). Individual calibration of crystals is required to correct for sensitivity variations. A recent development in the manufacture of single crystals is the continuous growth method (LeBelle and Mlavski, 1971; LeBelle, 1971), which allows the dimensions of the crystal to be controlled independently of the growth rate. Jarrett et al (1971) have investigated the thermoluminescence from LiF single crystals grown in this way; under some conditions impurities can be controlled, so that it is conceivable that LiF:Mg,Ti could be manufactured in the form of single crystals having fixed dimensions and reproducible sensitivity. Al$_2$O$_3$ could similarly be produced.

7.3.5. Phosphor/PTFE dosemeters

Phosphor/PTFE dosemeters (Bjarnard et al, 1965; Bjarnard and Jones, 1966; 1967) consist of fine grains of phosphor uniformly dispersed within a PTFE matrix. A wide variety of shapes and forms, with different phosphors and various percentage phosphor loadings, can be manufactured to cover most dosimetry applications. Discs have been manufactured, varying in diameter from 2-13mm, and in thickness from 0.02 to 0.5mm. Rods 1mm diameter by varying lengths have been produced, primarily for in vivo applications. Tape can be produced in various configurations, and can be used as a multi-element dosemeter in an automatic TLD system (Dauch, 1974). The maximum operational temperature for phosphor/PTFE dosemeters is generally about 300°C, due to a crystalline transition in PTFE at 327°C.

The average grain size of phosphor in phosphor/PTFE dosemeters is about 10 μm, and the photon energy response of the phosphor is thus affected by the PTFE. The effective atomic number of PTFE is 8.4, i.e. close to LiF, and the photon energy response of LiF/PTFE dosemeters is thus very similar to pure LiF. The energy response of LiF/PTFE dosemeters has been studied by Endres et al (1970) and Casbolt et al (1973). The energy response of CaSO$_4$:Dy/PTFE dosemeters will be very dependent on phosphor grain size, due to the high effective atomic number (15.3) of CaSO$_4$:Dy. At 30 keV, the pure phosphor will over-respond by a factor of 11.3 compared with $^{60}$Co. However,
the corresponding factor for a typical batch of CaSO$_4$::Dy/PTFE dosemeters is 7.0 (Teledyne Isotopes Product Bulletin). It has been calculated (M. W. Charles, private communication) that if the average grain size of CaSO$_4$::Dy was less than 1 $\mu$m, the over-response of CaSO$_4$::Dy/PTFE dosemeters at 30 keV would be about 2.0.

D. A. Pitman Ltd. have a particular commercial interest in this type of dosemeter, and the design, manufacture and performance of phosphor/PTFE dosemeters is described in detail in chapters 8-11.

7.3.6. Phosphor/silicone dosemeters

Cameron et al (1968) report that a dosemeter consisting of about 30% by weight of LiF powder embedded in a silicone rubber product was produced by Madison Research Inc. The silicone rubber was slightly thermoluminescent and sensitive to room light, which limited low-dose measurement. Bassi et al (1971) have shown that, if the grain size of LiF is larger than 70-80 $\mu$m, a LiF/silicone dosemeter has a response as a function of photon energy similar to that of LiF. Webb and Bodin (1971) have described the manufacture of extremely thin, but uniform, phosphor/silicone dosemeters. The silicone they used was not noticeably thermoluminescent or sensitive to room light. Nakajima (1968), and Brunskill and Langmead (1970) have also described the manufacture of dosemeters utilising silicone. Since silicone rubber is unstable above about 280°C, a characteristic of all phosphor/silicone dosemeters is that the hottest read out profile which can be used is about 280°C for a few seconds.

7.3.7. Sintered dosemeters

Solid dosemeters can be formed from pure phosphor by compressing powder to the desired shape in a press, followed by a sintering at a high temperature (of the order of 650°C). The sintering process is necessary to achieve mechanical strength. Christensen (1968 and 1970) has prepared sintered Li$_2$B$_4$O$_7$:Mn discs. Portal et al (1970) and (1971) and Niewiadomski et al (1971) have produced sintered LiF discs and rods. Discs up to 13mm in diameter have been produced, but a preferred diameter seems to be about 5mm. Dosemeters thinner than about 0.5mm are difficult to produce, and are very fragile. However, dosemeters with a very low effective thickness can be produced using colourants (Koczynski et al, 1974).

BeO (Scarpa et al, 1971) and Al$_2$O$_3$ (McDougall and Rudin, 1970) can also be obtained in a sintered ceramic form.

7.3.8. Hot pressed and extruded dosemeters

Solid dosemeters can also be formed from pure phosphor by hot pressing or
extrusion techniques, in which the dosemeter is formed in a high pressure and high temperature environment. Dosemeters produced in this way can have a high transparency, with a consequent improvement in light output. Blair (U.S. Patent 3,567,922) developed the hot press method for manufacturing CaF$_2$:Mn dosemeters. Cox (1968) describes the characteristics of LiF dosemeters produced by extrusion and hot pressed methods. CaSO$_4$ and Li$_2$B$_4$O$_7$:Mn dosemeters can also be produced (Cox, 1970), but for the latter it is necessary to use a binding material.

A variety of geometries can be manufactured, but there are practical and economic constraints on size. The largest dosemeter so far produced is about 6.4mm square; the thinnest dosemeter is 0.25mm thick, but this requires careful handling, since it is rather fragile. The most popular formats are 'chips' (3.2 x 3.2 x 0.9mm) and square cross-section microrods (1 x 1 x 6mm). Hot pressed dosemeters are more sensitive and uniform than extruded dosemeters.

7.3.9. Layer of phosphor attached to a backing material

Hartin (1967) has described a dosemeter fabricated by bonding LiF powder to a high melting point plastic with a transparent high temperature binder. In the present work (see chapter 12) a dosemeter is described consisting of a layer of Li$_2$B$_4$O$_7$:Mn phosphor sandwiched between two layers of FEP (fluoroethylene polymer) - coated polymide tape, which are bonded together under controlled temperature and pressure conditions. LiF dosemeters can be similarly fabricated.

7.3.10. Multi-element, coded dosemeters

Multi-element, coded dosemeters, for use in large scale automatic systems, can be constructed from the various types of single element dosemeters described above. The dosemeter has to be provided with identification numbers which can be read both by machines and humans.

The NRPB dosemeter (Dennis et al, 1974) consists of two phosphor/PTFE discs in an aluminium plaque coded with a series of holes. The Teledyne Isotopes 'Radiguard' multi-area dosemeter (e.g. Dauch, 1974) consists of a piece of phosphor/PTFE tape, having the same shape as a radiation monitoring film. This is coded by a number (readable by machine or human) printed directly on its surface. The Harshaw Chemical Co. dosemeter consists of two or three hot pressed chips, mounted individually between FEP foil in a coded plaque (Harshaw Chemical Co., 1974). Jones (1968; 1971) has also described a multi-element dosemeter using hot pressed chips, while Botter-Jensen and Christensen (1971), Widell (1974), and Portal et al (1974) have utilised sintered dosemeters.
7.4. Advantages and disadvantages of phosphor/PTFE dosemeters

In considering the virtues of phosphor/PTFE dosemeters in comparison with other types of dosemeter, their chief advantage obviously lies in the wide variety of available formats. This results in the ability to cover most general and specialised dosimetry applications, often at a significant cost advantage over alternative types of dosemeter. An additional characteristic which is extremely useful when individually calibrating dosemeters for high precision applications is that discs can be directly identified by a marking agent. Disadvantages are all associated with the precision of dose measurement. Their low thermal conductivity and flexible shape makes them more difficult to heat reproducibly, and can also lead to changes in the efficiency of light collection. Various background signals associated with the PTFE can cause difficulty when making low dose measurements. For this reason the parameters which limit the precision of measurements made with phosphor/PTFE dosemeters have been closely investigated, and are described in detail in the following chapters (8, 9, and 10). The work is basically concerned with LiF/PTFE discs, but from it conclusions can be drawn which apply to other types of phosphor/PTFE dosemeter. It is shown that with appropriate instrumentation (e.g. the Model 654 reader) and operational techniques the precision obtainable with phosphor/PTFE dosemeters is more than adequate for applications such as radiotherapy and radiological protection.

Precision at high dose levels is limited by the intrinsic and extrinsic variables described in chapters 8 and 9 respectively. Low dose measurements are described in chapter 10.
CHAPTER 8. SOURCES OF SENSITIVITY VARIATIONS WITH
LiF/PTFE DISCS I- INTRINSIC VARIABLES

This is the first of two chapters describing sources of sensitivity variations in LiF/PTFE discs. Intrinsic variables are defined as those which lead to differences in sensitivity among dosemeters of the same batch as a result of the manufacturing process. Although this chapter deals only with LiF, the results are generally applicable to other phosphors. Extrinsic variables, i.e. those associated with the treatment of the dosemeter following manufacture, are described in the next chapter.

8.1. The production of phosphor/PTFE dosemeters

The production of phosphor/PTFE dosemeters was first described by Bjarnegard et al (1965). The commercial rights are protected by patents (e.g. British Patent Specification 1,140,028), and D. A. Pitman Ltd. manufacture phosphor/PTFE dosemeters under license from the patent holders, Teledyne Isotopes Inc.

The process is based on a thorough mixing of phosphor powder of grain size less than about 80 μm with a fine PTFE powder. The average phosphor grain size is about 10 μm for LiF. Both components should be dried to remove water vapour, which would otherwise cause clogging. The optimum mixing time should be determined experimentally for each design of mixer and amount of mix; too short a time will result in an uneven phosphor distribution, whereas if the phosphor and powder are mixed for too long a time the phosphor grains, coated with fine PTFE powder, tend to separate out. Electrostatic charges probably play a part in this phenomenon.

The mixture can be moulded into bars of typically 5 to 15 mm diameter, or extruded, typically as 1 mm diameter rod. For moulding, the highest content of phosphor is about 30% by weight, since at higher concentrations the mechanical properties of the dosemeter deteriorate. For extrusions, the maximum loading is about 10%. To produce moulded bars, the mixture is compressed in a mould, and then sintered at 365°C for about 1 hour. The cooling rate from the sintering temperature has to be very slow to achieve a uniform optical density throughout the bar. Discs are produced from bars by parting off on a lathe or, for very thin discs, on a microtome. Most thermoluminescent phosphors can be incorporated into PTFE in this way. In general their thermoluminescent properties are not changed by their incorporation into PTFE, which is very chemically inert. The emission spectra are unchanged, since PTFE does not have any absorption bands in the region of visible light. When overheated (i.e. above about 400°C) PTFE may give off poisonous gases, and due precautions should be taken to avoid thermal runaway.
Figure 8.1.

Weight distribution of a batch of 365 LiF/PTFE discs, 30% phosphor loading, 12.7 x 0.4mm

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Figure 8.2.

Practical method of measuring the optical transmission of LiF/PTFE discs in the Model 654 reader

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either during the readout cycle or in the annealing or sintering ovens.

8.2. Size, shape and optical transmission

8.2.1. Dosemeter size and shape

The phosphor/PTFE bars are made slightly oversize (a) to allow for shrinkage during sintering and (b) to enable the sintered bar to be turned down to an accurately known diameter, removing surface debris and discolouration in the process. The diameter of a bar can be quite easily machined to within about \( \pm 10 \mu m \) of the desired diameter, so that variations in the diameter of a disc are negligible. It is more difficult to part off discs of a reproducible thickness, and the problem becomes particularly acute with thinner discs. Discs of thickness greater than about 0.1mm are generally parted off on an automatic lathe, and their reproducibility of thickness therefore depends on the accuracy with which the lead screw has been cut. However, greater uniformity is obtained by this procedure than by the alternative method of extruding sheet and stamping out discs from it.

The parting-off tool is ground to a fine edge to avoid wastage, and discs are produced somewhat bowed as a result. The curvature is initially uniform but does change with usage (see section 9.1). A general purpose dosemeter in widespread use is a disc 12.7mm in diameter by about 0.4mm thick, loaded 30% by weight with \(^7\)LiF. These are manufactured from 150mm long bars; about 350 discs can be obtained from each bar. The discs from a complete bar were inspected and weighed in the order in which they were cut, to obtain information on their weight distribution and the influence of variations in the lead screw on the lathe. Figure 8.1 shows the weight distribution of the 365 discs cut from the bar. The mean weight was 109.9 mg, with a coefficient of variation of 2.1%, excluding the one disc well outside the normal variation. Assuming a constant disc diameter and density, the weight of a disc will be proportional to its average thickness. Thus the standard deviation in average thickness is 2.1% of 0.4mm, i.e. 8.4 \( \mu m \), which is remarkably good, considering the flexibility of PTFE. If this standard deviation was solely characteristic of the lead screw, it would be independent of the thickness of disc; however, it is probably partially due to other factors e.g. the vibration pattern of the parting-off tool, which may be different for other thicknesses of disc.

There is a correlation between the coefficient of variation in weight, and any foreign inclusions such as dust and other debris, which were either present in the original phosphor or PTFE powder, or entered during the mixing or moulding processes. In all, 44 of the 365 discs had visible inclusions, which generally occurred in groups along the bar. In Table 8.1 the weights of two groups of 20 discs are listed in the order in which they
Table 8.1. Effect of inclusions on the coefficient of variation in weight of LiF/PTFE discs, 12.7mm diameter x 0.4mm thick, containing 30% by weight of phosphor

<table>
<thead>
<tr>
<th>Disc No.</th>
<th>Group A</th>
<th>Group B</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (mg)</td>
<td>Weight (mg)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>111.4</td>
<td>110.6</td>
<td>slight inclusion</td>
</tr>
<tr>
<td>2</td>
<td>112.1</td>
<td>107.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>111.8</td>
<td>113.0</td>
<td>slight inclusion</td>
</tr>
<tr>
<td>4</td>
<td>110.9</td>
<td>104.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>109.7</td>
<td>113.0</td>
<td>slight inclusion</td>
</tr>
<tr>
<td>6</td>
<td>106.5</td>
<td>107.4</td>
<td>slight inclusion</td>
</tr>
<tr>
<td>7</td>
<td>110.7</td>
<td>113.6</td>
<td>slight inclusion</td>
</tr>
<tr>
<td>8</td>
<td>109.5</td>
<td>107.8</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>110.3</td>
<td>114.5</td>
<td>inclusion</td>
</tr>
<tr>
<td>10</td>
<td>110.1</td>
<td>109.3</td>
<td>inclusion</td>
</tr>
<tr>
<td>11</td>
<td>108.0</td>
<td>106.1</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>109.0</td>
<td>110.4</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>108.1</td>
<td>106.0</td>
<td>inclusion</td>
</tr>
<tr>
<td>14</td>
<td>112.4</td>
<td>109.9</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>109.5</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>110.5</td>
<td>110.5</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>109.4</td>
<td>109.6</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>108.5</td>
<td>107.9</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>111.4</td>
<td>112.8</td>
<td>inclusion</td>
</tr>
<tr>
<td>20</td>
<td>109.3</td>
<td>109.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mean weight</th>
<th>Coefficient of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group A</td>
<td>110.0</td>
<td>1.4%</td>
</tr>
<tr>
<td>Group B</td>
<td>109.8</td>
<td>2.6%</td>
</tr>
</tbody>
</table>
were cut off the bar. Group A were cut from a section of the bar with no
inclusions. The coefficient of variation of the weights is 1.4\%. Group B
were cut from a section of the bar with some inclusions; these inclusions
were first noted on examination of the cut discs, and are indicated in Table
8.1. The coefficient of variation of the weights of Group B discs was 2.6\%,
thus inclusions cause a degradation in precision as well as in appearance.
Note that in the section of the bar with inclusions, an unusually high
weight is often followed (or preceded) by an unusually low weight. This
phenomenon was usually seen wherever inclusions occurred along the length
of the bar. It would seem that the position of the cutting tool is slightly
disturbed by the change in resistance felt as it encounters an inclusion.

8.2.2. Optical transmission

The light output from dosemeters of the same size is dependent on the
transmission through the dosemeter of its internally generated light (see
sections 3.1 – 3.3). The optical transmission through PTFE is dependent on
the rate of cooling, from the sintering temperature of 365\(^\circ\)C, through a
crystalline transition point at 327\(^\circ\)C. During the manufacture of phosphor/
PTFE discs it is necessary to cool the bar slowly (at a rate of about
0.6\(^\circ\)C/min through the transition temperature and down to at least 250\(^\circ\)C) to
stress-relieve the PTFE. This slow cooling rate also results in uniform
light transmission throughout the bar. The results of this chapter (and
chapters 9 and 10) were obtained with discs which had not been heated above
300\(^\circ\)C since their manufacture, and some of the conclusions may not be
applicable to discs which have been heated above the transition temperature,
due to changes in their shape and surface texture (see sections 9.4.1 and
12.4.2).

The transmission characteristics of LiF/PTFE discs were initially studied
with a spectrophotometer. Monochromatic light of wavelength 400nm was used,
to simulate the emission spectrum of LiF. However, light scattering at the
incident surface of the disc resulted in an abnormally low value for the
transmission. The observed transmission was dependent on the distance between
the disc and the monochromator; the greater the distance, the lower the
transmission. Additionally, the discs are somewhat bowed due to the
manufacturing process and the curvature is not constant from disc to disc,
being a function of handling and usage (after discs have been readout a few
times, they become flatter), and it was found that variations in the angle
between the incident light and the normal to the surface of the disc at the
point of incidence caused appreciable differences in light scattering, and
thus in apparent transmission. A typical average transmission of a batch
of 20 LiF/PTFE discs, 0.4mm thick, loaded 30% with phosphor, was 0.07.
The discs are actually far more transparent to internally generated light than this, their opaque appearance being due to scattering of ambient light. To obtain a more accurate measurement, the effective transmission of various batches of discs was measured by a development of the method described in section 3.2.6. Another advantage of this method is that the effective transmission is averaged over the whole disc. The light source used was a thin (0.4mm thick) source of the type used in the Model 654 TLD reader with an emission spectrum very similar to that of LiF. All readings were obtained on the Model 654 by integrating the light over a period of 16 secs. Several problems were encountered and solved. It is almost impossible to remove the optical coupling compound (Dow Corning 20-057), which was employed to reduce light scattering between the disc and the light source, from the surface of the disc. Therefore, the disc cannot subsequently be heated, e.g. for correlation of transmission with sensitivity, since the surface of the disc discolours during readout, as the compound oxidises. A second problem is that, due to the curvature of the discs, the effective transmission depends on whether the convex or the concave side of the disc is uppermost (i.e. nearest the light detector). The transmission is higher for concave side upwards (by 3 - 4%); it is evident that this should indeed be so from a consideration of the efficiency of light collection from concave and convex surfaces.

To overcome these problems, the method shown in figure 8.2 was adopted. A washer is placed on top of the light source, and the disc can be positioned on the washer, reproducibly with respect to the light source, and either convex or concave side up. Optical coupling compound is not used, and consequently there is some light scattering. Correction factors (of the order of 20%) were experimentally determined to relate the transmission as measured by this method to the effective transmission as measured with optical coupling compound, using representative sets of discs which were not required to be subsequently heated. The correction factors were calculated for flat discs, the assumption being made that the average reading of a disc read both convex and concave side up was equivalent to that from a flat disc.

The above solution is a compromise, and there is undoubtedly some error due to variations in light scattering between discs. The coefficient of variation in transmission of a single disc read repeatedly was 0.4%, the disc being removed and replaced before each reading. Another source of error is prompt phosphorescence from the PTFE, following exposure to daylight. However, this decays to an insignificant level about 10 seconds after removal from daylight, and an appropriate delay was allowed before commencing a measurement.
The effective transmissions of sets of LiF/PTFE discs, 0.4mm thick by 12.7mm diameter, and with different phosphor loadings, are given in Table 8.2. The discs were cooled through the transition temperature at a rate of about 0.6°C/min.

Table 8.2. Effective transmission of LiF/PTFE discs, 0.4mm thick

<table>
<thead>
<tr>
<th>Phosphor loading (% by weight)</th>
<th>Effective transmission, ( t ) (average of 20 discs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.76</td>
</tr>
<tr>
<td>15</td>
<td>0.55</td>
</tr>
<tr>
<td>20</td>
<td>0.52</td>
</tr>
<tr>
<td>25</td>
<td>0.48</td>
</tr>
<tr>
<td>30</td>
<td>0.43</td>
</tr>
</tbody>
</table>

It is apparent from this table that variations in transmission could also be due to slight departures from the nominal phosphor loading. For example, the transmission through a nominally 30% loaded disc is altered by about 0.7% by a 1% change in phosphor loading.

8.2.3 Variations in sensitivity with thickness of disc

With the notation of the theory of thermoluminescent dose measurement developed in chapter 3, the light output (L) from a uniformly irradiated disc of thickness T is obtained by eliminating \( k_1 \) from equations 3.7 and 3.1.

Thus,

\[
L = \frac{P(\lambda)k_2D_0G}{bT} \left(1 - \exp\{-bT\}\right) \left(1 + r \exp\{-bT\}\right)
\]

where \( b \) is related to the coefficient of attenuation by the dosimeter of its internally generated light.

\( P(\lambda) \), the light generated per unit absorbed dose, is linearly proportional to T, therefore

\[
P(\lambda) = TP'(\lambda),
\]

where \( P'(\lambda) \) is the light generated per unit absorbed dose and per unit thickness, and is independent of T. Hence

\[
L = \frac{P'(\lambda)k_2D_0G}{b} \left(1 - \exp\{-bT\}\right) \left(1 + r \exp\{-bT\}\right) \quad \text{............}(8.1)
\]

If variations in \( P(\lambda), k_2, D_0, G, \) and \( b \) are insignificant for a batch of nominally uniform discs of slightly varying thickness, irradiated and readout under identical conditions, then

\[
L(b = \text{constant}) \propto \left(1 - \exp\{-bT\}\right) \left(1 + r \exp\{-bT\}\right)
\]
If the diameter and density are constant for a batch of dosemeters, then

\[ T \propto W, \text{ where } W = \text{disc weight} \]

i.e. \[ T = kW, \text{ where } k = \text{a constant} \] ... (8.2)

\[ L(b = \text{constant}) \propto (1- \exp(-bkW)).(1+r \exp(-bkW)) \] ... (8.3)

As an example of sensitivity variations with thickness, consider LiF/PTFE discs, 12.7mm diameter \( \times \) 0.4mm thickness, and loaded 30% with phosphor. The average weight of such a disc is 0.110g. The average effective transmission, \( t_m = 0.43 \) (from Table 8.2).

Now, \( t_m = \exp(-bT) \)

... (see section 3.2.6)

\[ b = -\frac{\ln t_m}{T/kW} \]

Thus, \( bk = 7.67 \).

\[ T = 90 \text{ mg cm}^{-2}, \text{ therefore } b = 9.38. \]

Substituting this value for \( bk \) in equation 8.3,

\[ L(b = \text{constant}) \propto (1- \exp(-7.67W)).(1+r \exp(-7.67W)). \] ... (8.4)

Equation 8.4 is plotted in figure 8.3, for \( r = 0 \) and \( r = 1 \). Both curves are normalised to a light output of 1 for a disc weight of 0.100g, although at this weight the actual ratio of light outputs is given by:

\[ \frac{L(r = 1)}{L(r = 0)} = 1.47 \text{ (W = 0.100g)} \]

From figure 8.3, it can be calculated that for a disc of nominal weight 0.110g (i.e. 0.4mm thick), a 1% increase in weight will lead to a corresponding increase in light output of 0.7%, if \( r = 0 \), or 0.4%, if \( r = 1 \).

Also shown in figure 8.3 are some experimentally obtained points for discs irradiated to the same dose and having weights varying between 0.03 and 0.17g. It can be seen that they are closest to the curve for \( r = 0 \), which suggests that the readout conditions approximated to this, even though a high reflectivity tray was used. Presumably the effective reflectivity is greatly reduced by the air gap between the tray and the disc (see also section 9.1.3).

### 8.2.4 Variations in sensitivity with optical transmission

\[ L = \frac{P'(\lambda)k_2D_0G(1-\exp(-bT))}{b}(1+r \exp(-bT)) \] ... (8.1)

If variations in \( P'(\lambda), k_2, D_0, \) and \( G \) are insignificant, then

\[ L \propto \frac{(1-\exp(-bT))}{b}(1+r \exp(-bT)) \]

Substituting for \( b \) and \( bT \) (\( t_m = \exp(-bT) \)),

...
Figure 8.3.

Variation in light output with weight of LiF/PTFE discs, 30% phosphor loading, 12.7 x 0.4mm

\[ \text{Relative light output (L), normalised to 1.0 for a weight of 0.1g} \]

\[ \text{bk = 7.67 (b = 9.38)} \]
This equation is plotted in figure 8.4, for constant \( W \) (i.e. constant \( T \)) and \( r = 0 \) and 1. For LiF/PTFE discs, 0.4mm thick, and containing 30% phosphor, \( t_m = 0.43 \). From figure 8.4, a 1% increase in transmission will lead to a corresponding increase in light output of 0.4%, if \( r = 0 \), or 0.7%, if \( r = 1 \).

8.2.5. Correlation of sensitivity variations in LiF/PTFE discs, containing 30% phosphor by weight, with weight and optical transmission

The coefficient of variation in sensitivity of LiF/PTFE discs is improved by correcting for weight and transmission, as is illustrated in Table 8.3 for two batches of uniformly irradiated discs, both containing 30% by weight of LiF. Corrections for weight were made on the basis of equation 8.4. The corrected reading for each disc, \( L' \), is given by

\[
L' = \frac{L}{(1- \exp[-7.67W]).(1+r \exp[-7.67W])}
\]

where \( L \) is the observed light sum from the disc and \( W \) is its weight.

Corrections for weight and transmission were made on the basis of equation 8.5. The corrected reading for each disc, \( L'' \), is given by

\[
L'' = \frac{-L \ln t_m}{W(1-t_m).(1+rt_m)}
\]

where \( L \) and \( W \) are as above, and \( t_m \) is the disc's optical transmission.

Note that equations (8.4) and (8.5) both assume a constant percentage phosphor loading, since variations in \( P'(\lambda) \) were assumed to be insignificant.

Table 8.3.
Correlation of sensitivity variations with weight and transmission.

<table>
<thead>
<tr>
<th>Coefficient of variation (%)</th>
<th>Batch A (20 discs)</th>
<th>Batch B (25 discs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>4.4</td>
<td>31.9</td>
</tr>
<tr>
<td>Weight</td>
<td>1.4</td>
<td>31.4</td>
</tr>
<tr>
<td>Sensitivity, corrected for weight ( (r = 0) )</td>
<td>4.2</td>
<td>8.7</td>
</tr>
<tr>
<td>Sensitivity, corrected for weight ( (r = 1) )</td>
<td>4.2</td>
<td>13.9</td>
</tr>
<tr>
<td>Transmission (not corrected for weight)</td>
<td>2.3</td>
<td>12.8</td>
</tr>
<tr>
<td>Sensitivity, corrected for weight and transmission ( (r = 0) )</td>
<td>3.7</td>
<td>7.1</td>
</tr>
<tr>
<td>Sensitivity, corrected for weight and transmission ( (r = 1) )</td>
<td>3.5</td>
<td>11.3</td>
</tr>
</tbody>
</table>
Figure 8.4.
Calculated dependence of light output on transmission (for constant disc thickness)

Figure 8.5.
Dependence of light output on % phosphor loading for LiF/PTFE discs, 0.4mm thick

- Calculated response
- Experimental points
Batch A discs were selected at random from nominally 0.4mm thick discs which had undergone normal quality control procedures, i.e. selection by weight and appearance. Batch B were deliberately selected from an experimental batch of discs of widely varying weight, in order to test the validity of equations 8.6 and 8.7 over wider limits, as it was expected that extrinsic variables might conceal any improvement in Batch A discs. The thickness of Batch B discs varied from 0.15 to 0.4mm.

The correlations were made for both $r = 1$ and $r = 0$. The reflectivity of the heating tray was about 0.9 but other experience had suggested that the effective tray reflectivity was nearer zero and this is supported by the results in Table 8.3. For Batch B discs the correlation is much better when $r = 0$. For Batch A discs, the correlation is slightly better when $r = 1$, but the difference is probably not statistically significant. Only a marginal improvement in precision was obtained by correcting Batch A discs for weight alone, but a significant improvement was obtained by correcting for both weight and transmission. This was despite the masking effects of other possible sources of sensitivity variations, and the errors incurred in the measurement of transmission ($\sim 0.5\%$). Individual deviations from the mean weight and coefficient of attenuation of up to 5\% were observed in Batch A, the coefficient of attenuation ($A$) being given by:

$$A_k = b = -\ln\frac{m}{W}$$

i.e. $A \propto -\ln\frac{m}{W}$

For Batch B discs, most of the improvement naturally occurred after correction for the large weight variations, but a further improvement was obtained after correcting for both weight and transmission.

8.2.6. Conclusions

The above results are evidence of the validity of equations 8.4 and 8.5. However, the correlation with transmission observed when discs were corrected for transmission does not show whether or not the optical density of the PTFE is varying from disc to disc, since this effect is not distinguishable from variations in transmission due to variations in phosphor loading. Variations in disc thickness and transmission can be reduced by guarding against foreign bodies during the production process.

8.3. Variations in the amount of phosphor in dosemeters of the same size

Variations in the amount of phosphor in dosemeters of the same size can be due to (a) an inhomogenous mix, or (b) for dosemeters containing a small number
of phosphor grains, statistical fluctuations in the number of grains. The total light emitted by the phosphor grains themselves is proportional to the weight, \( w \), of phosphor. However, the fraction of light reaching the surface of the dosemeter is a function of the dosemeter transmission, \( t_m \), which is dependent on the percentage phosphor loading, \( p \) (section 8.2.2.).

For uniformly irradiated discs, the light, \( L \), reaching the detector is given by:

\[
L = P(\lambda)k_2D_0(1 - \exp \{-bT\})(1+r \exp \{-bT\}) \quad \ldots \quad (\text{cf. section 8.2.3})
\]

\( P(\lambda) \), the light generated per unit absorbed dose, is linearly proportional to \( w \), therefore

\[
P(\lambda) = wP''(\lambda)
\]

where \( P''(\lambda) \) is the light generated per unit absorbed dose and per unit weight of phosphor. If variations in \( P''(\lambda) \), \( k_2 \), \( D_0 \), and \( C \) are insignificant, then

\[
L \propto w \frac{1 - \exp \{-bT\}}{1+r \exp \{-bT\}} \quad \ldots \quad (\text{cf. eqn. 8.5})
\]

\[
L \propto \frac{w}{\ln t_m} (1-t_m)(1+rt_m)
\]

\( w = pAT\rho \), where \( A = \) cross-sectional area of dosemeter

and \( \rho = \) mean density of dosemeter

\[
\ldots \quad \text{For discs of constant cross-sectional area}
\]

\[
L \propto -p\rho T (1-t_m)(1+rt_m) \quad \ldots \quad (8.8)
\]

The density of LiF/PTFE dosemeters varies with the percentage phosphor loading from about 2.15 g cm\(^{-3}\) for pure PTFE to about 2.30 g cm\(^{-3}\) with 30% loading. In figure 8.5, \( L \) is plotted against \( p \) for LiF/PTFE discs 0.4 mm thick, for \( r = 0 \) and 1. The values for transmission were obtained from Table 8.2 and in both curves \( L \) is normalised to 2 for a 2% loaded disc. For 30% loaded discs, and \( r = 0 \), a 1% change in phosphor loading will correspondingly alter the light output by about 0.8%. Again, experimental data agree most closely with the \( r = 0 \) curve.

Assuming an average phosphor grain size of 10 \( \mu m \), and a phosphor density of 2.64 g cm\(^{-3}\), there are about \( 1.4 \times 10^6 \) phosphor grains per mg of LiF, therefore statistical fluctuations in the number of grains are negligible for most dosemeters.
8.4. Variations in phosphor sensitivity

The dosimeter sensitivity will be a function of the average sensitivity of its phosphor grains. The sensitivity of a phosphor grain is dependent on size, and the concentration and distribution of certain activators, thus the sensitivity of individual phosphor grains may vary appreciably, especially if activators were not uniformly distributed in the original crystals. However, if the batch of phosphor is well mixed before incorporation into the dosimeters, and if each dosimeter contains a large number of phosphor grains, then such sensitivity variations should average out. The effect of small variations in activator concentration may be even more noticeable in the supralinear dose-response region. For example, the supralinearity of LiF is dependent on the concentration of Ti (Rossiter et al 1971).

The glow curve structures of LiF/PTFE discs from the same batch show some variation in the height of peaks 4 and 5 relative to peaks 2 and 3, following 'initialisation' (section 9.4.2) to the reader's cooling rate. A typical spread is illustrated in figure 8.6. It would seem that variations in the sensitivity of individual phosphor grains are not always averaged out in the disc production process. This is probably associated with the variation in glow curve structure with grain size, which is discussed in the following section.

8.5. Dependence of the glow curve structure and sensitivity of LiF:Mg,Ti on particle size

8.5.1. Use of fast cooling rate

Spiers and Zanelli (1966) and Zanelli (1968) studied the variations in the thermoluminescence of LiF with particle size, and found a decrease in sensitivity with decreasing particle size (corrected for weight). To explain this, they hypothesised an 'inactive' surface layer in addition to heat conduction and light scattering effects. However, they did not specify the thermal treatment given to LiF. The glow curve structure and sensitivity of LiF:Mg,Ti are greatly dependent on the concentration and state of aggregation of magnesium throughout the crystal lattice, the state of aggregation being a function of previous thermal treatment (sections 4.4.5 and 4.4.6). During a study of the glow curve structure and sensitivity of LiF/PTFE dosimeters, carried out as part of an investigation into the feasibility of annealing dosimeters in the Model 654 reader instead of using an oven, it was found that the glow curve structure of LiF dosimeters cooled fast and reproducibly in the reader yielded information on the variations in glow curve structure with LiF particle size not noticeable with dosimeters cooled somewhat more slowly in an annealing oven. This was because the
Typical spread in glowcurve structures of LiF/PTFE discs (30%, 12.7 x 0.4mm) from the same batch.

Figure 8.6.

Dependence of glowcurve structure of LiF (Harshaw) on grain size

(a) Batch A phosphor (TLD-700), grain size 75-200 μm
(b) Batch A ground down to < 75 μm
(c) Batch B phosphor (TLD-100), grain size 75-200 μm
(d) Batch B, ground down to < 75 μm

Figure 8.7.

Cooling curve of LiF/PTFE discs in Model 654 Reader.

Temperature

Cooling time, seconds

Heating element lowers
migration and aggregation of \([\text{Mg}^{2+}, \text{Li}^+ - \text{vacancy}]\) dipoles into complexes during a slow cool tends to mask these variations.

8.5.2. Experimental procedure

Dosemeters (LiF/PTFE discs or LiF powder) were 'initialised' to the reader's cooling rate by annealing in the reader at 300°C for 36 seconds, followed by a natural cool in the reader. The cooling curve is shown in figure 8.7. The average cooling rate from 300°C to 150°C is about 15°C/sec. It had been found by a separate experiment that 300°C for 36 seconds was sufficient to restabilise the magnesium distribution at that temperature (see also Carlsson, 1967). Dosemeters were irradiated to a dose of about 3 rads with a Sr90/Y90 source, at a dose-rate of about 200 mrad/sec, within 1 hour of being initialised, and stored at room temperature (20-25°C) in the intervening period. All glow curves were obtained by linearly heating up to 300°C, at a rate of 5°C/sec, within 20 minutes of irradiation.

8.5.3. Production of LiF:Mg,Ti

Large single crystals of LiF:Mg,Ti are usually produced by the Stockbarger technique. The crystals are then ground and sieved. The fraction with grain sizes 75-200 μm are normally used for loose powder measurements. The fraction with grain sizes less than 75 μm (LiF 'fines') are used in the production of LiF/PTFE dosemeters, the average grain size being about 12 μm, although this is a function of the grinding method.

Characteristic glow curve structures of two batches (A and B) of LiF (Harshaw) phosphor, grain size 75-200 μm, are shown in figure 8.8 (a and c). The differences between the relative peak heights are typical of different batches of phosphor. The glow curve structure of three batches (C, D, and E) of LiF (TLD-700) phosphor fines are shown in figure 8.9. There is considerable variation between batches, but on average the glow curve structure is degraded (i.e. the dosimetry peaks reduced in comparison with the lower temperature peaks) compared with the glow curve structure of phosphor of grain size 75-200 μm. The degraded glow curve is indicative of an altered concentration or distribution of magnesium (Frank and Edelmann, 1966; section 4.4.6). A possible explanation of this change is related to the hardness of Mg doped LiF. Johnson (1962) found that LiF containing Mg impurity was harder than purer LiF, the hardness being a function of Mg content and distribution. It is therefore reasonable to assume that during the grinding process the original crystal breaks up preferentially where the Mg concentration is lowest. Thus the finer (and softer) grains will have a lower Mg content, accounting for the change in glow curve structure.
Glowcurve structures of representative batches of LiF(TLD-700) fines

Figure 8.0.

Glowcurve structures of LiF/PTE dyes (30% phosphor loading, 12.7 x 0.4 mm) manufactured from the above fines

Figure 8.10.
The above batches of fines (C, D, and E...) were incorporated into batches of LiF/PTFE discs, 12.7mm diameter x 0.4mm thick, loaded 30% with phosphor. Glow curves from these batches of discs are shown in figure 8.10 and it is evident, on comparing figure 8.10 with figure 8.9, that the glow curve structures are again slightly degraded by the disc manufacturing process. The effect of the 300°C anneal on the glow curve structure was tested with batch D discs, samples of which were annealed for 1 hour and 24 hours. Their glow curve structures are shown in figure 8.11. 1 hour at 300°C did not cause any significant degradation but 24 hours at 300°C caused a significant decrease in the heights of peaks 4 and 5.

Evidently the distribution of magnesium throughout the crystal lattice is changed both by the sintering process, during which the phosphor spends about 3½ hours above 300°C, and also by the 300°C anneal. The length of the 300°C anneal should therefore be minimised, but since the glow curve structure is not noticeably degraded by 1 hour at 300°C, repeated anneals in the reader at 300°C for a few seconds will not affect the glow curve structure within the lifetime of the dosemeter.

It is interesting to note that the original post-manufacturing anneal used by Controls for Radiation Inc. (Bjarngard and Jones, 1966) was 17 hours at 300°C. This would have caused appreciable degradation of glow curve structure, more noticeable in dosemeters cooled fairly fast. It is probable that the glow curves obtained by Lin and Cameron (1966) were from LiF/PTFE discs annealed in this way.

8.5.5. Refinements to the LiF hardness hypothesis

If the hypothesis of section 8.5.3 was correct, then LiF phosphor of grain size 75-200 µm which is then ground down further into fine phosphor should contain more Mg than the original 'fines', and thus its glow curve structure would not be so degraded. Samples of phosphor from batches A and B were ground down in an agate pestle and mortar to grain sizes of less than 75 µm. The resultant glow curves are shown in figure 8.8 (b and d). The glow curve structure has degraded (cf figure 8.8.a and c) and is very similar to that of LiF fines. Thus the difference in Mg content must be only marginal, and the hypothesis requires some modification. However, when a batch of LiF/PTFE discs were manufactured from batch A fines, the glow curve structure was not further degraded by the disc manufacturing process (figure 8.12), indicating some improvement (cf. figure 8.8.(b)).

The loss in sensitivity with LiF (PTL 69) and LiF (PTL 70) (obtained from CEC, France) when ground down to a fine powder is even more marked, as illustrated in figure 8.13.
Figure 8.11.

Effect of duration of 300°C anneal on glowcurve structure of LiF/PTFE discs (batch D)

![Glowcurve structure of LiF/PTFE discs, manufactured from batch A powder ground down to <75 μm grain size](image1)

Figure 8.12.

Glowcurve structure of LiF/PTFE discs, manufactured from batch A powder ground down to <75 μm grain size

![Glowcurve structure of LiF/PTFE discs, manufactured from batch A powder ground down to <75 μm grain size](image2)
Figure 8.13.
Dependence of glow curve structure of LiF (CEC) on grain size

(a) PTL 69, grain size 75–200 μm
(b) PTL 69, ground down to <75 μm
(c) PTL 70, grain size 75–200 μm
(d) PTL 70, ground down to <75 μm
It is proposed that the changes in glow curve structure during the grinding process are due to some form of separation of Mg from the portion of the crystal containing the luminescent centre, associated with non-uniform Mg distribution and the relative hardness of LiF on a microscopic scale. This affects the glow curve structure in two ways. Firstly, it results in a lower effective concentration of Mg available to take part in the thermoluminescent process, with corresponding changes in glow curve structure according to the state of aggregation of the remaining Mg. The effect can be most easily seen in LiF that has been cooled fast, since peaks 4 and 5 are restructured by aggregation of dipoles during slower cooling rates. Secondly, the concentration of Ti is relatively increased. The degraded glow curve structure is, in fact, very similar to that obtained by Rossiter et al (1971) with higher concentrations of Ti.

Probably small grains are produced depleted in Mg but enriched in luminescent centres and vice-versa. Also, there may be additional crystal defects preventing charge transfer within a single grain. The original glow curve is not restored by annealing at 400°C for 1 hour, so the separation seems to be fairly permanent. However, the use of higher annealing temperatures may be more successful.

A spark mass spectrographic analysis of a recent batch of LiF (TLD-700) fines has given some support for the above proposal. The concentrations of Ti and Mg by weight were 40ppm and <60ppm respectively, in contrast to the corresponding concentrations of about 15ppm and 80ppm added to the original crystal (British patent specification No.1059518, 1967). It is suggested that the glow curve structure of fine LiF phosphor may be improved, relative to currently available phosphor, by heavier doping with Mg and lighter doping with Ti in the original crystal, to counteract in advance the separation effect which occurs during the grinding process.

8.5.6. The effect of changes in glow curve structure on stability of stored signal

Any differences in glow curve structure lead to different rates of fading and migration and aggregation of traps, and thus affect the stability of stored signal.

When the lower temperature peaks are accentuated, e.g. by (a) the absence of the 80°C pre-irradiation anneal or (b) a fast cooling rate in the reader or (c) the concentrations and distribution of Mg and Ti in fine LiF powder, or any combination of these, their contribution to the total light sum is quite considerable, and consequent trap migration and aggregation causes complex dose storage effects (Booth et al, 1972; Johnson, 1974; Robertson and Gilboy, 1974; section 9.5). Typical changes in glow curve
Changes in glow curve structure of LiF/PTFE discs, with post-dose storage time at room temperature

(a) Lower temperature peaks accentuated by (i) fast cool in reader and (ii) no 80°C pre-irradiation anneal.

(b) Contribution of lower temperature peaks reduced by pre-irradiation anneal of 80°C for 16 hrs.
structure and light output with time are shown in figure 8.14 (a), though these will of course also be a function of the heights of the peaks relative to each other.

The preferred glow curve structure, i.e. peaks 4 and 5 predominating, and peaks 2 and 3 contributing very little to the total light sum, can be restored to fine LiF phosphor by the 80°C pre-irradiation anneal, as was noted by Lin and Cameron (1966) for LiF/PTFE discs. Any further migration and aggregation of traps is thereby minimised, and the change in glow curve structure and light output with time basically reflects the thermal release of stored charge carriers (figure 8.14 (b)).

8.5.7. Applications to other types of dosemeter

The variation of glow curve structure with grain size affects other types of dosemeter, as well as LiF/PTFE dosemeters. More pronounced lower temperature peaks have been found in glass capillary needles filled with LiF (Booth et al, 1972) and also with extruded or hot pressed chips (Johnson, 1974). It is probable that both forms of dosemeter utilise fine LiF powder. The effect may also be found with sintered LiF dosemeters.

8.6. The effect of intrinsic variables on the precision of phosphor/PTFE dosemeters

Following manufacture, a batch of dosemeters is sorted (a) by weight, generally to a 2% coefficient of variation about the mean, and (b) by visual appearance, those with foreign inclusions being rejected. Representative samples are then tested for sensitivity variations. It is not possible to fully exclude extrinsic variables (see chapter 9) when assessing sensitivity variations due to intrinsic variables. However, extrinsic effects can be reduced by measuring the precision under the most favourable readout conditions, in which case the coefficient of variation in the sensitivity of phosphor/PTFE dosemeters relative to the mean sensitivity of the batch is typically 2–4%, depending on the type of dosemeter and the batch. For very thin discs (0.02mm) it can be as high as 20%, due to variations in thickness caused by difficulty in microtoming them reproducibly off of a bar. Typical sensitivity variations in several types of LiF/PTFE dosemeter are shown in Table 8.4.
<table>
<thead>
<tr>
<th>Dosemeter format (dimensions in mm)</th>
<th>Precision of sensitivity (coefficient of variation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc, 30% LiF, 12.7 x 0.4</td>
<td>3-4%</td>
</tr>
<tr>
<td>Disc, 2% LiF, 12.7 x 0.4</td>
<td>2-3%</td>
</tr>
<tr>
<td>Disc, 6% LiF, 8 x 0.4</td>
<td>2-3%</td>
</tr>
<tr>
<td>Disc, 30% LiF, 5 x 0.02</td>
<td>10-20%</td>
</tr>
<tr>
<td>Microrod, 4% LiF, 6 x 1</td>
<td>2-3%</td>
</tr>
</tbody>
</table>

Sources of sensitivity variations in phosphor/PTFE dosemeters containing other than LiF can be expected to be as for LiF/PTFE dosemeters, with the exception of the variation in sensitivity per unit weight of phosphor with grain size.
Extrinsic variables are defined as sources of sensitivity variations apart from those due to manufacturing techniques. In this chapter the extrinsic variables associated with operational procedures followed when using the Model 654 reader are discussed. The method of irradiation, and the reader's light measurement and heating cycle control systems are assumed to be reproducible. Only a plateau-type heating cycle is considered, since it has already been shown (section 5.8.3) that this is superior to the linear ramp for the routine readout of low thermal conductivity dosemeters.

At the end of this chapter, techniques for optimising precision by reducing the effect of both extrinsic and intrinsic variables are discussed.

9.1. Variations in dosemeter shape and surface condition, orientation in tray, and tray reflectivity

9.1.1. Shape and surface condition

The condition of the dosemeter surface is a critical factor in the accuracy and precision attainable, since any change in the surface (e.g. due to contamination, discolouration, scratching, or distortion) can alter the light transmission and scattering and thereby affect the amount of light reaching the detector. The shape and surface condition tend to change with re-use. The discs are initially slightly bowed, as a result of the manufacturing process, but become flatter with repeated readouts or anneals. Handling practices may also cause changes in shape. The surface condition degrades with re-use due to dust and other debris burnt into the surface during readout and annealing.

9.1.2. Orientation in tray

An operational problem with some types of LiF/PTFE disc is a variation in light output depending on the orientation of the disc in the reader. Uniformly irradiated LiF/PTFE discs, 0.4mm thick, loaded 30% with LiF, have approximately 10% higher light output when read concave side up in the Model 654 reader, compared with when they are read convex side up. This effect is not due to the disc being bowed, as the same difference in light output was noted when discs were kept flat during the readout process by means of a quartz disc. With LiF/PTFE discs, 0.4mm thick, and loaded 2% with LiF, the effect is not noticeable, so that it must be due to light scattering effects associated with the surface texture and/or transmission. The surface of the disc is actually a series of spiral ridges and grooves,
rather like a gramophone record, due to the machining process. The amplitude of these ridges and grooves will be a function of phosphor loading, depending on the microscopic vibration pattern of the cutting tool set up as it encounters hard LiF grains, in between its relatively easy progress through the soft PTFE. The surface detail of one side of a disc will be the negative of the other side, and the scattering of the internally generated light will thus be different at each surface. The surface of 2% loaded discs is smoother than 30% loaded discs.

Since the discs flatten out after some use, and it then becomes difficult to identify the original convex and concave sides, reproducible orientation in the reader should be ensured by marking the discs on one side only, i.e. the side normally remote from the light detector.

9.1.3. Tray reflectivity

With 30% or 2% loaded LiF/PTFE discs, 12.7mm diameter x 0.4mm thick, the measured light output is lowered by less than 3% when read out in the Model 654 reader on a tray blackened with colloidal graphite, compared with the usual bright stainless steel surface. This is a rather surprising result in view of the high internal transmission of these dosemeters, but is in agreement with the results of sections 8.2.3. and 8.2.5. It is probable that multiple light scattering at the surface of the disc in contact with the tray, where there is a complex dosemeter/air/tray interface, strongly reduces the effective reflectivity.

For 5mm diameter LiF/PTFE discs, 0.4mm thick, 30% loaded, the corresponding light measurement is lowered by about 8%. These smaller discs do not fully mask the edges of the tray from the PM tube and some of the light is directly reflected without passing through the dosemeter. A similar effect is observed with phosphor/PTFE microrods.

With very thin LiF/PTFE discs, 5mm diameter by 0.02mm thick, the variation in light output with tray reflectivity is a combination of variations in the light reflected back through the disc and also from around the disc. In this case, the light output is reduced by about 35% when a graphited tray is used.

9.2. Variations in sensitivity with heating rate

9.2.1. Non-linearity of light measurement system

A fast heating rate can lead to errors if it results in a luminescent intensity outside the linear capability of the light measurement system. For example, the response of the PM tube or the signal conditioning circuit may be non-linear at high light intensities. The maximum light intensity
from a dosemeter occurs at the glow peak temperature. A useful parameter is the relation between the maximum light intensity and the total light output. This is a function of the heating profile and the type of dosemeter. For example, with LiF/PTFE discs, 30% loaded, 12.7 x 0.4mm, heated in the Model 654 reader through a plateau heating cycle, with heating rates of 30°C/sec, the maximum count rate (per second) is about 0.3 times the total number of counts. Thus the maximum count rate for a full scale reading of 10^6 digits will be 3 x 10^5 cps, and the correction for non-linearity can be estimated from this together with a knowledge of the conversion rate of the CTP convertor, and the current through the PM tube dynode chain (see section 6.5). However, for any given type of dosemeter and heating cycle, direct measurement is preferable.

9.2.2. Thermal quenching in LiF/PTFE dosemeters

For some phosphors there is a thermal quenching effect, in which the probability of a radiationless transition is temperature dependent and increases with temperature, leading to a reduction in light output at fast heating rates. In practice the thermal conductivity of a dosemeter will limit the actual heating rate of the phosphor, but there may be a range of tray heating rates over which the dosemeter sensitivity is altered, hence the rate should be reproducible from one readout cycle to the next.

Gorbics et al (1969) described the thermal quenching effect in LiF powder, mixed with gold grains to promote good heat transfer. Figure 9.1 shows evidence from the present work of thermal quenching effects in three types of LiF/PTFE dosemeters subjected to linear heating from room temperature to 300°C. Gorbic's curve (1) for loose powder is included for comparison. Curve 2 is for 30% loaded, 12.7 x 0.4mm discs. Curve 3 is for a similar shaped disc but containing only 2% phosphor. Curve 4 is for LiF/PTFE microrods with 4% phosphor loading, 6mm long by 1mm diameter.

It can be deduced from figure 9.1 that reproducibility of heating rate is not critical for LiF/PTFE dosemeters heated with a 'plateau' heating profile, in which the heating rate used between the preheat and read plateaux is normally around 30°C/sec. The configuration and thermal conductivity of LiF/PTFE microrods is such that thermal quenching effects were not apparent over the range of heating rates studied. However, reproducibility of the heating rate is more important for LiF/PTFE discs heated at below 20°C/sec, with quenching effects being more noticeable for the disc with higher phosphor loading and hence higher thermal conductivity (the thermal conductivity of LiF is an order of magnitude higher than that for PTFE).
Figure 9.1. Comparison of thermal quenching effects in various types of dosemeter

(1) LiF (TLD-100) powder
(2) LiF/PTFE discs, 30% phosphor loading, 12.7 x 0.4 mm
(3) LiF/PTFE discs, 2% phosphor loading, 12.7 x 0.4 mm
(4) LiF/PTFE microrods, 4% phosphor loading, 6 x 1 mm

Rate of increase of temperature (°C/sec)

Light sum (normalised to 1.0 at 1°C/sec)

1.0
0.9
0.8
0.7

1 10 20 30 40

Figure 9.2. Factors determining selection of read zone temperature for LiF/PTFE discs

(1) Signal from irradiated discs
(2) 2nd reading of irradiated discs
(3) Noise from unirradiated discs

Light output (arbitrary units)

Change of scale

Read zone temperature (°C)

220 240 260 280
9.3. Selection of read zone heating profile

The read zone heating profile should be selected to optimise the overall accuracy in the application. There are two parameters to consider: (a) the reproducibility of heating efficiency, and (b) variations in background signals.

Heat transfer from the heating tray to and through the dosemeter is dependent on such factors as the contact of the dosemeter with the tray, variations in dosemeter shape, and the dosemeter's thermal conductivity. If the read zone temperature is appreciably higher than the glow peak temperature of the dosimetry peaks, then all of the dosemeter is rapidly heated above the glow peak temperature, releasing all the stored energy and rendering negligible the effects of small variations in heat transfer. At somewhat lower read zone temperatures, the cooler portions of the dosemeter may only be at a temperature comparable with the glow peak temperature. The integrated light output during the read zone time may then be less than complete, and will be more susceptible to small variations in heat transfer. However, the background signal, or 'noise', contains several components whose magnitude and variability increase rapidly with temperature (see chapter 10). Consequently, with most dosemeters the highest signal/noise ratio occurs at a less than maximum heating efficiency.

The user is therefore faced with the choice of setting the read zone either to maximise the light output or to minimise background signals, in order to optimise the overall accuracy in various applications. In radiotherapy the doses are usually so high that background effects can be neglected and the overriding concern is to maximise the light output to obtain the best precision. This is in contrast to radiological protection, where the backgrounds may be comparable to the signal being measured, and the overall accuracy may be improved by lowering the read zone temperature to reduce background contributions.

The situation is illustrated by figure 9.2, which shows the relative light output in the read zone as a function of read zone temperature, for LiF/PTFE discs, 12.7 x 0.4mm, 30% phosphor loading. Curves 1 and 2 are the 1st and 2nd readings respectively from irradiated discs. Curve 3 shows the background signal from unirradiated discs. Heating efficiency obviously decreases with decreasing read zone temperature as illustrated by the fall-off in Curve 1 below 240°C and the corresponding increase in the second reading of irradiated discs, shown in Curve 2. The ratio of Curves 1 and 3 gives the signal to background ratio.
It is shown in section 10.4.5 that a read zone temperature of about 240°C is suitable for radiological protection applications, as it gives the highest signal/noise ratio at the expense of a marginal (for this application) effect on reproducibility of readout. However for an application at high dose levels it would be advisable to go to something like 270°C to ensure efficient heating and optimum precision. These results are for a 16 second read zone, which is about the longest tolerable operationally. A shorter read zone would require a higher read zone temperature to achieve the same heating efficiency, with a consequent increase in background signal.

9.4. Variations in sensitivity with re-use

9.4.1. Maximum annealing temperature

Phosphor/PTFE dosemeters soften when heated above 327°C (at which temperature a crystalline transition occurs in PTFE) and have to be carefully supported to avoid distortion. Furthermore, the cooling rate from the anneal temperature should be about 0.6°C/min or less to stress-relieve the PTFE and also achieve uniform optical densities. Annealing at 400°C (the optimum annealing temperature for LiF powder) or thereabouts is thus not recommended as a routine operational procedure, although there could be significant advantages in incorporating such a post-manufacture anneal into the disc production process (see section 12.4.2). The recommended maximum annealing temperature when preparing dosemeters for re-use is 300°C (to leave a margin for safety).

9.4.2. Consistency in sensitivity of LiF/PTFE discs over repeated cycles of use

The consistency in sensitivity of LiF/PTFE dosemeters over repeated cycles of use, with various annealing and readout procedures, has been studied by Wallace (1970), Marshall and Shaw (1971), Webb and Phykit (1971), and Blackman et al, (1974). In general, sensitivity changes are small, providing suitable techniques are used (Blackman et al, 1974), and extreme dose variations are avoided. The re-use of LiF/PTFE discs without an external anneal has been studied in the Model 654 reader at low doses with a view to dispensing with the external anneal in radiological protection applications. The heating cycle profile was similar to that in figure 5.11 and consisted of a preheat of 135°C for 16s, a read zone of 260°C for 16s, and an anneal zone of 300°C for 16s, followed by a fast cool in the reader, the dosemeter temperature dropping to 150°C in about 11s. A feature of these experiments was that they were carried out in a very short time; the average time between cycles for particular discs was about 10 minutes. Discs were irradiated to a dose of about 3 rads at a dose-rate of about 200 mrad/s by a 90Sr/90Y source. The discs had received no thermal treatment since the
The change in sensitivity with repeated readout cycles is illustrated in figure 9.3 for LiF/PTFE discs loaded 30% with LiF. The sensitivity is initially less than optimum, due to the slow cooling rate from the sintering temperature, and increases to a maximum after about 4 read cycles as the disc adjusts to the reader's cooling rate (The term 'initialisation' is sometimes used to described this effect). Thereafter, the sensitivity falls at a rate of about 0.4% per cycle, over the next 30 cycles. This low rate of change of sensitivity (following the initial stabilisation) should not be a problem in either radiological protection or radiotherapy applications, but is a definite trend, in contrast to the findings of Webb and Phykitt (1971), who did not notice any trend in sensitivity up to 100 cycles. The rate of decrease in sensitivity was approximately the same for discs 12.7mm diameter x 0.4mm thick, 5mm diameter x 0.4mm thick, and 5mm diameter x 0.2mm thick. Undoubtedly, changes in surface condition, i.e. debris burnt in during the heating cycle, causing discolouration, are responsible for part of the decrease, and may account for the small variations between discs, but there is little difference in appearance between fresh and cycled discs. The effect was independent of the anneal zone, discs recycled with the anneal zone switched out showing a similar rate of decrease in sensitivity.

It is thought that the effect is due to the traps responsible for the dosimetry peaks (4 and 5) being steadily reduced by the annealing which occurs during each readout cycle. Mason and Linsley (1971b) showed that these traps decrease rapidly during annealing at 100-200°C. The maximum rate of decrease, at 150°C, is of the order of 1% per minute. During the preheat and read zones the dosemeter spends about 20 secs between 100 and 200°C, which implies a decrease of the order of 0.3% per cycle, in reasonable agreement with the observed effect. The effect is obviously not reversed by the anneal zone, but short term changes in sensitivity due to trap migration and aggregation were noticed. For example, the sensitivity decreased by 1-2% after a one hour delay between readout and the next irradiation. Sensitivity changes over longer periods of time are described in section 9.5.

9.4.3. Sensitization

Sensitization (section 4.3.5) in LiF/PTFE discs becomes detectable at doses of about 100 rads and above (Linsley and Mason, 1971a). It cannot be removed economically by a normal 300°C anneal, since the process would take several months. This places a constraint on the repeated use of LiF/PTFE dosemeters at high dose levels since, although dosemeters can
Figure 9.3. Change in sensitivity of LiF/PTFE discs (30% loaded, 12.7 x 0.4mm; no 80°C anneal) with repeated use in Model 654 reader.

Readings (normalised to 1.00 for 4th reading)

'Initialisation'

Read cycle

Figure 9.4. Effect of preheat temperature on variations in signal from LiF/PTFE discs (batch C) with post-dose storage at room temperature.

Readings (normalised to 1.00 for first reading)

0.80 0.85 0.90 0.95 1.00 1.05

Time after irradiation (days)

145°C
135°C
125°C
No preheat
obviously be recalibrated for sensitivity before re-use with a dose low enough not to cause further sensitization, the response vs dose curve may be significantly altered. Additionally, photo-transferred thermoluminescence may under some circumstances lead to significantly higher background signals. The problem of sensitization has encouraged the development of low cost (disposable) LiF/PTFE dosemeters for radiotherapy applications, so that the overall cost per readout is competitive with other types of thermoluminescent dosemeter, in which sensitization can be removed. In radiological protection applications, the frequency of sensitizing doses is so rare that it is economical to discard the few dosemeters that receive particularly high doses.

An attractive solution to the problems of sensitization is to deliberately presensitize LiF/PTFE dosemeters with a high dose followed by a u.v.-anneal, as Mayhugh and Fullerton (1974) have done with LiF powder and chips (section 4.3.5).

9.4.4. The anneal zone in the Model 654 reader

The function of the anneal zone is to further reduce any residual signal remaining after the read zone. The signal/noise ratio in the anneal zone is immaterial since no measurement is made. In some cases operational procedures may thereby be simplified, but at the expense of extending the overall readout time. For example, with LiF/PTFE discs, 12.7mm x 0.4mm, and loaded 30% with phosphor, the standard anneal of 300°C for 16 secs is greater than 99.97% efficient. This is useful in radiological protection applications, since there is less than 2 mrad residual dose for doses of up to 5 rads, i.e. the majority of doses in this application, and a further high temperature anneal is not necessary.

The efficiency of the anneal zone at removing previous doses is dependent on the anneal zone profile and the type of dosemeter. On the standard heating cycle module, the anneal zone time is set to 16 secs, this being about the longest tolerable operationally. There is a choice of two anneal temperatures, 300 or 400°C. The 400°C anneal should not be used with phosphor/PTFE dosemeters. The residual dose remaining after specified anneal zones for some types of dosemeter are given in Table 9.1. It is clear that for thick, low conductivity dosemeters, e.g. LiF/PTFE microrods, the anneal zone may not be adequate, and an external high temperature anneal must be used. Note that the anneal zone is not intended to remove sensitization due to high previous doses; with LiF, this would require an anneal temperature of about 500°C.
Table 9.1. Residual signal remaining after the anneal zone for some types of dosemeter

<table>
<thead>
<tr>
<th>Type of dosemeter</th>
<th>Anneal zone profile</th>
<th>Residual signal (expressed as a percentage of the original dose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF/PTFE disc, 30%, 12.7 x 0.4 mm</td>
<td>300°C, 16s</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>LiF/PTFE disc, 2%, 12.7 x 0.4 mm</td>
<td>300°C, 16s</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>LiF/PTFE microrod, 6 x 1 mm</td>
<td>300°C, 16s</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>LiF chip, 3 x 3 x 0.9 mm</td>
<td>300°C, 16s</td>
<td>&lt;0.004</td>
</tr>
<tr>
<td>LiF chip, 3 x 3 x 0.9 mm</td>
<td>400°C, 16s</td>
<td>&lt;0.0003</td>
</tr>
</tbody>
</table>

9.4.5. The cooling zone in the Model 654 reader

The cooling zone should be considered as an integral part of the overall read cycle, since the sensitivity of some phosphors, e.g. LiF:Mg,Ti, is dependent on the cooling rate from the read or anneal temperature. With the standard heating cycle module the dosemeter is allowed to cool down naturally. On the research module a facility for setting linear cooling rates down to 1°C/sec has been incorporated. Although the cooling rate of the dosemeter itself may be expected to be dependent on factors such as ambient temperature, dosemeter thermal mass and conductivity, contact of the dosemeter with the heating tray, and rate of inert gas flow, it can be inferred from the excellent reproducibility obtained with LiF dosemeters in the Model 654 reader that actual variations in these parameters have a negligible effect on dosemeter sensitivity.

9.5. Use of the preheat zone to minimise variations in sensitivity with time

9.5.1. Purpose of the preheat zone

The preheat zone serves two functions, in the readout of LiF/PTFE discs. Firstly, it can be used as an alternative to the 80°C pre-irradiation anneal, to minimise variations in stored signal with time by removing a portion of the unstable low temperature peaks. Secondly, it is used to reduce the magnitude and variability of background components induced in the discs by ambient light. The preheat zone is thus intended to simplify operational procedures and to facilitate the measurement of low doses; these advantages are achieved at the expense of extending the overall read cycle time. As it was also intended to use an internal high temperature anneal to further simplify operational procedures, investigations into the effects of the preheat zone used discs 'initialised' to the reader's cooling rate.
9.5.2. Initial experiments to determine the most suitable preheat zone for optimum signal stability

LiF/PTFE discs, 12.7mm x 0.4mm with 30% phosphor loading (Batch C, see section 8.5.3), were first initialised to the instrument's cooling rate, and read out immediately before irradiation to standardize the glow curve structure. The discs were then irradiated to a dose of 5 rads at a dose rate of about 200 mrad/sec by a $^{90}$Sr/$^{90}$Y source, and stored in the dark at room temperature (20–25°C) for periods varying from 1 hour to 28 days before readout. Precalibration techniques were used to improve precision. The heating profile during readout was similar to that in figure 5.11. The preheat zone was 16 secs long, followed by a 16 sec read zone at 250°C, and an anneal zone of 300°C, also for 16 secs (The ramp rate in each zone was approximately 35°C/sec). The natural cooling rate was such that discs took about 11 secs to cool from 300°C to 150°C. The preheat time of 16 secs is a compromise between operational convenience and the necessity to minimise the temperature gradient across the thickness of the disc to obtain good resolution of glow peaks.

Figure 9.4 shows the effect of the preheat temperature on variations in signal with time. The experiment was continued over 28 days since this is the normal issue period of dosemeters for personal monitoring. The curves are normalised to unity for the first readings, which were taken approximately 1 hour after irradiation. Intermediate curves were also obtained for preheat temperatures of 120, 130, and 140°C, but these are not shown for the sake of clarity. In all cases an initial fading was later counteracted by a phenomenon consistent with the migration and aggregation of trapping centres as described by Booth, Johnson and Attix (1972). Towards the end of the 28 day period fading again became predominant. It can be seen from figure 9.4 that a preheat temperature of 135°C gives the smallest variation with time.

9.5.3. Variations in the glow curve structure of LiF with time

Variations in glow curve structure, and thus the signal, with time, are due to both fading and trap migration and aggregation. Booth et al (1972) and Johnson (1974) have shown that peaks 4 and 5 grow at the expense of peaks 2 and 3, due to trap migration and aggregation. In LiF cooled slowly, peaks 4 and 5 decrease slowly with time, since the traps responsible for them become less numerous, possibly due to the formation of even larger complexes. In rapidly cooled LiF, the traps giving rise to peaks 2 and 3 provide a supply of new 4 and 5 traps at a more rapid rate than these are destroyed, so that the sensitivity of these glow peaks grows with time.
When the population of lower temperature traps is reduced, e.g. by a slow cool or an 80°C anneal, the losses of 4 and 5 traps cannot be replaced, and the sensitivity continuously decreases with time.

In the preferred method of use of LiF/PTFE discs, that is when operational procedures are simplified by the use of preheat and anneal zones in the heating cycle, the lower temperature peaks are accentuated by (a) the fast cooling rate in the reader, and (b) the absence of the 80°C pre-irradiation anneal. An additional problem with LiF/PTFE discs and some other forms of dosemeter is that the lower temperature peaks may also be accentuated by the dosemeter manufacturing process (section 8.5). Thus the contribution of the low temperature peaks to the total light sum is quite considerable, and can result in pronounced effects due both to fading and migration and aggregation of traps.

9.5.4. Pre-dose and post-dose storage of LiF/PTFE discs

A consequence of trap migration and aggregation is that growth of peaks 4 and 5 occurs when dosemeters are stored for various periods before irradiation (Booth et al, 1972; Johnson, 1974), in addition to the growth which occurs between irradiation and readout. This in fact indicated that retrapping was not principally responsible for the growth during post-dose storage. A substantial fraction of the filled traps must retain their trapped charge carriers during post-dose migration and aggregation of trapping centres. However, the growth of peaks 4 and 5 with post-dose storage is not as great as with pre-dose storage, indicating a nett loss of trapped charge carriers after irradiation due to thermal activation and/or migration and aggregation. The effects of both pre-dose and post-dose storage at room temperature on the signal from LiF/PTFE discs was studied to determine the optimum preheat temperature. Experimental procedure was similar to that in the initial experiment on post-dose storage. In the pre-dose part of the experiment, initialised discs were readout immediately before storage in the dark at room temperature for various periods before irradiation. Discs were subsequently readout within 1 hour of irradiation. Figures 9.5 and 9.6 show the effect of the preheat temperature on pre-dose and post-dose storage respectively, for storage periods of up to 28 days. The curves are normalised to unity for discs stored for less than 1 hour prior to irradiation, then readout within 1 hour of irradiation.

As expected, the growth of peaks 4 and 5 is greater with pre-dose storage. However, an unforeseen result was the differences in the post-dose curves (figure 9.6) compared with those obtained in the earlier experiment (figure 9.4). The main differences occur about 7 days after irradiation,
Figure 9.5. Effect of preheat temperature on variations in signal from LiF/PTFE discs (Batch D) with pre-dose storage at room temperature.

Figure 9.6. Effect of preheat temperature on variations in signal from LiF/PTFE discs (Batch D) with post-dose storage at room temperature.
when the figure 9.6 curves are reading about 10% higher than the figure 9.4 curves. Although there is always the possibility of some systematic error, it is thought that the reason for these differences is that a different batch of discs (Batch D) was used in the later experiment. The glow curve structures of the two batches of discs (C and D) are shown in figure 8.10; discs had been stored for less than 1 hour prior to irradiation, and read out within 1 hour of irradiation. Peaks 2 and 3 are more predominant in Batch C. Differences in glow curve structure lead to different rates of fading and migration and aggregation of traps, and thus to differences in the stability of signal.

9.5.5. The optimum preheat zone

One of the purposes of the preheat zone was to replace the 80°C pre-irradiation anneal and thus, in conjunction with an internal anneal, simplify operational procedures. However, it is evident that the resulting signal from LiF/PTFE discs may vary considerably over a one month period, depending on the time of irradiation and the phosphor characteristics, whatever the preheat temperature. If the batches of discs investigated to date are representative of future batches, then the optimum preheat temperature for LiF/PTFE discs (30% loaded, 12.7 x 0.4mm) to achieve stability of signal is about 130°C. Even so, the signal may vary by as much as ± 10% about the average, being a complex function of (a) glow curve structure, (b) the time between the last internal anneal and irradiation, and (c) the time between irradiation and readout. Another purpose of the preheat zone is to reduce the sensitivity to ambient light. It is shown in section 10.6.8 that a preheat temperature of about 150°C is optimum for this, and thus some compromise is necessary.

9.5.6. Effect of preheat zone variations on precision

The contribution to the total light sum of the lower temperature peaks can be quite considerable, and consequently small variations in preheat temperature and heat transfer can markedly affect the amount of light recorded in the read zone. Figures 9.7 and 9.8 show the dependence on preheat temperature of readings from LiF/PTFE discs, 30% loaded, 12.7 x 0.4mm (Batch D), for various pre-dose and post-dose storage times respectively. The readings (light sum during the read zone) are expressed as a percentage of the reading obtained from similar dosimeters read with the preheat zone switched out. Considering the slope of the curves, it is seen that a 1°C change in the preheat temperature can cause a change of up to 0.9% in the dosimeter reading, thus the preheat zone and heat transfer must be very repeatable to achieve reproducible results. With the above discs in the Model 654 reader, the
Figure 9.7. Dependence on preheat temperature of readings from LiF/PTFE discs (batch D), for various pre-dose storage times at room temperature.

Figure 9.8. Dependence on preheat temperature of readings from LiF/PTFE discs (batch D), for various post-dose storage times at room temperature.
precision of discs initialised to the reader's cooling rate is improved by about 1% when an 80°C pre-irradiation anneal for 16 hours is used to greatly reduce the lower temperature peaks. This illustrates the excellent reproducibility of the reader's heating cycle and the method of heat transfer, even with low thermal conductivity dosemeters, since unwanted variations in dosemeter temperature must therefore be only about 1°C.

9.5.7. Conclusions

A preheat zone of 130°C for 16 secs will reduce variations in signal with pre- and post-dose storage from 30% loaded, 12.7 x 0.4mm discs to around ±10% about the average over a one month period. It would be interesting to repeat the experiment over a 2 month period, since in practice dosemeters are likely to be stored for up to 1 month before a 1 month issue period, possibly giving rise to even larger variations. For optimum accuracy and precision the 80°C pre-irradiation anneal should be used. This also facilitates low dose measurements, since under these conditions the preheat temperature can be raised to 150°C to remove more of the background component caused by exposure to light.

The preheat zone may be required even when the 80°C pre-irradiation anneal is also used, to reduce variations in background noise due to exposure to light, and possibly also to further improve the stability of stored signal, since the 80°C anneal does not completely remove peaks 2 and 3. The optimum preheat zone temperature may be different for other types of LiF/PTFE disc, since the average temperature of the disc will depend on its size and percentage phosphor loading.

9.6. Techniques for precise measurements with LiF/PTFE dosemeters

9.6.1. Minimising extrinsic variables

It is clear from the above that sensitivity variations due to extrinsic variables can be reduced as follows:

a) Dosemeters should be kept clean and undistorted.

b) Discs should be identified on one surface (the surface furthest from the light detector), so that they can always be orientated the same way up in the reader.

c) Tray reflectivity should not vary appreciably over the duration of the experiment, particularly when using thin discs.

d) For applications where the doses are so high that variations in background signals are generally insignificant, e.g. radiotherapy, the read zone should be selected to extract over 99% of the signal stored in the dosimetry traps; for low dose applications, the read zone should be selected as shown in section 10.4.
e) Dosemeters should be cooled reproducibly from the anneal temperature. An internal anneal is preferred, but is not always practicable.
f) The pre-irradiation anneal of 80°C for 16-24 hours should be used, but a preheat zone may still be required for low dose measurements.

The continued necessity for the 80°C anneal is disappointing from the point of view of simplifying operational procedures. However the errors incurred by not using it (\(\sim \pm 10\%\)) may be just acceptable for radiological protection applications, remembering that other sources of error may add another \(\pm 10\%\).

9.6.2. Batch dependence of dosemeter characteristics

In general, different batches of dosemeters may show significantly different characteristics. It is thus advisable, when planning an experiment, to use dosemeters from only one batch.

9.6.3. Individual calibration of dosemeter sensitivities

General calibration techniques have been described in section 3.3. The coefficient of variation in sensitivity due to intrinsic variables of dosemeters from the same batch may be as high as 5%. In applications where this order of precision is adequate, such as in radiological protection, it is sufficient and convenient to assign the mean sensitivity of the group to all dosemeters. Where better precision is necessary, as in radiotherapy applications, the precision can be improved by individually calibrating dosemeters, i.e. by measuring the sensitivity of each dosemeter relative to the mean sensitivity of the experimental group. It is assumed that the whole group will undergo similar thermal treatment, and that the relative sensitivities between dosemeters will be maintained after the precalibrating dose and the following read cycle (including, if necessary, an anneal). Careful track must be kept of dosemeter identification, either by marking dosemeters or by the use of identification jigs. The calibration procedures which have been developed for the Model 654 reader are described in Appendix 2.

In experiments with the Model 654 reader, the coefficient of variation in sensitivity of groups of 20 discs was generally less than 1% after individual calibration.

9.6.4. A convenient irradiation facility

Some of the problems which may arise when calibrating dosemeters in a known radiation field have already been described (section 3.3). To simplify the operational problem of irradiating dosemeters, an 'automatic irradiator' has been designed which is capable of irradiating a group of dosemeters to the same dose, over a wide dose range, e.g. for improving precision by
individual calibration of sensitivity. The irradiator itself can also be calibrated against a known radiation field, in which case it can be used for
(a) irradiating groups of dosemeters to the same known dose, e.g. for sensitivity calibration dosemeters, and
(b) determining a response vs dose calibration chart for a batch of dosemeters, e.g. to enable the dosemeters to be used to measure doses for which their response is non-linear.

With reference to figure 9, up to about 30 dosemeters can be positioned reproducibly on a radius near the rim of a turntable. Various types of positioning devices can be used to suit and centralise the different types of dosemeter. When the turntable rotates, the dosemeters pass directly under a fixed $^{90}\text{Sr}/^{90}\text{Y}$ source. The turntable is rotated at a constant speed so that dosemeters all receive the same dose per pass under the source. The source views the dosemeter through a wedge-shaped aperture (figure 9), so that each portion of a dosemeter is in view for the same time and is thus uniformly irradiated, provided that the radiation field is uniform along a radius of the irradiator. The number of times that the dosemeters pass under the source can be preset by means of a count-down revolution counter. Dosemeters are loaded whilst the turntable is stationary, and the required number of revolutions is entered. A 'start' button is depressed, and the turntable rotates, stopping automatically after the required number of revolutions. The radiation source has an activity of typically $5\text{mCi}$, and is shielded with perspex, to absorb high energy beta particles without emitting too much bremsstrahlung, and then with lead, to reduce the radiation dose-rate on the surface of the irradiator to a safe level. Materials in the vicinity of the source were selected for resistance to radiation damage, since they can be expected to receive doses of hundreds of megarads over the irradiator's lifetime.

The span of the revolution counter was selected to be greater than 4 decades, for the following reasons. The turntable speed should be as fast as possible to obtain the highest resolution of dose in an operationally convenient time. However, it should not be so fast that dosemeters are displaced by centrifugal forces, and this sets the optimum speed to about 5-10 rpm. Assuming that overnight, i.e. about 16 hours, will normally be the maximum time over which a user will wish to irradiate dosemeters, this gives of the order of $10^4$ revolutions. The activity of the source can be selected to suit the application. For example, in radiotherapy applications a dose of 1 rad per rev allows the dose range 1-$10^4$ rads to be covered.

The excellent reproducibility of the overall system, i.e. reader plus
Figure 9.9. Dosemeter Irradiator

Figure 9.10. Wedge-shaped aperture

- Aperture
- Source holder
- Dosemeter
- Section of turntable
- Centre of turntable
irradiator, can be gauged from Table 9.2, which shows the typical variations in sensitivity obtained over 10 irradiation-read cycles with several types of LiF/PTFE disc. Discs were initialised, then repeatedly irradiated and read out on the Model 654 reader. The heating cycle used had a preheat zone of 135°C for 16 secs, a read zone of 260°C for 16 secs, and an anneal zone of 300°C for 16 secs. Discs were irradiated to a dose of about 10 rads, so that variations in background signal were negligible. Sensitivity is normalised to unity for the first read cycle. The most significant variation is the steady decrease in dosemeter sensitivity with read cycle noted in section 9.4.2. There are also undoubtedly variations due to the fact that the 80°C pre-irradiation anneal was not used (section 9.5.6). Even so, there is rarely more than 1% difference between successive readings. The coefficient of variation obtained with each type of disc is typically 1%, but may vary from about 0.5 to 1.5%.

Table 9.2. Typical repeatability of sensitivity with some types of LiF/PTFE disc (80°C anneal not used)

<table>
<thead>
<tr>
<th>Disc form</th>
<th>30%, 12.7 x 0.4mm</th>
<th>30%, 5 x 0.4mm</th>
<th>30%, 5 x 0.2mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Readout cycle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td>1.002</td>
<td>0.997</td>
<td>0.996</td>
</tr>
<tr>
<td>3</td>
<td>0.994</td>
<td>0.993</td>
<td>0.982</td>
</tr>
<tr>
<td>4</td>
<td>0.994</td>
<td>0.968</td>
<td>0.992</td>
</tr>
<tr>
<td>5</td>
<td>0.994</td>
<td>0.978</td>
<td>1.000</td>
</tr>
<tr>
<td>6</td>
<td>0.988</td>
<td>0.982</td>
<td>0.990</td>
</tr>
<tr>
<td>7</td>
<td>0.996</td>
<td>0.994</td>
<td>0.987</td>
</tr>
<tr>
<td>8</td>
<td>0.993</td>
<td>0.969</td>
<td>0.981</td>
</tr>
<tr>
<td>9</td>
<td>0.979</td>
<td>0.955</td>
<td>0.983</td>
</tr>
<tr>
<td>10</td>
<td>0.986</td>
<td>0.954</td>
<td>0.963</td>
</tr>
<tr>
<td>Coeff. of variation</td>
<td>0.6%</td>
<td>1.5%</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

The Mk.1 irradiator has a disadvantage in that there is a significant dose gradient across the thickness of the dosemeter due both to absorption of the β-rays and also to inverse-square law effects (the source is placed about 15mm above the dosemeters), thus consistent measurements can only be made with dosemeters whose orientation can be maintained between irradiation and readout. With some types of dosemeter, e.g. LiF/PTFE microrods or LiF chips about 1mm thick, errors of up to about 8% can arise from these effects. A Mk.2 version is under construction, which has dual opposed matched sources. It is hoped that this will produce a more uniform
radiation field through dosemeters up to about 2mm thick. Speed control is via a stepping motor, and it is expected that fluctuations in the set speed will be less than 0.1%.

Although the irradiator has been designed for TLD, it is also suitable for other solid-state integrating dosemeter systems, such as TSC, RPL, and TSEE.

9.6.5. The design of LiF/PTFE dosemeters for radiotherapy applications

The problems of (a) changes in supralinearity and (b) photo-transferred thermoluminescence, associated with sensitization (sections 4.3.5 and 9.4.3) limit the number of times that LiF/PTFE dosemeters can be re-used at high dose levels. Thus, for an acceptable cost per readout, they have to be competitively priced, and this necessitates a low phosphor content. The LiF/PTFE microrod, 6 x 1mm, 4% phosphor loading, is most suitable for in vivo applications, but has the disadvantage that it cannot be identified directly. The LiF/PTFE disc is more suitable for applications other than in vivo. The dependence of light output on tray reflectivity is low, and discs with phosphor loadings of greater than about 15% can be directly identified by writing on the disc surface (with lower % phosphor loadings, the disc surface is too slippery to write on). Stability of shape is most easily attained with small diameter, thick discs. Smaller diameter discs are also advantageous for radiotherapy applications, as they allow better spatial resolution of dose gradients. For high precision measurements in the dose range 1 - 10^4 rads, a disc 5 or 6mm in diameter by about 0.4mm thick, and containing 15 - 30% phosphor, is a reasonable compromise for all of the above requirements. Such a dosemeter would only contain 3' - 6mg of phosphor and thus should be attractively priced. Thinner discs, or discs with a lower effective thickness, would be required for skin dosimetry. Preliminary investigations with 5 x 0.4mm and 5 x 0.2mm discs have shown that these shapes are stable and easily and accurately read out on the Model 654 reader (see Table 9.2).

Operational procedures will be greatly simplified if the sensitization/u.v.-anneal technique (see sections 4.3.5 and 9.4.3) can be applied to LiF/PTFE dosemeters. Dosemeters would then have a linear response vs dose characteristic up to about 10^4 rads, and no further sensitization would occur for operational doses totalling 10^4 rads. Accuracy, too, would be improved, since the dosemeter would be more tissue equivalent.

9.7. Concluding remarks

This concludes the description of sources of sensitivity variations in LiF/PTFE dosemeters. It has been shown that with appropriate instrumentation
(e.g. the Model 654 reader) and operational techniques (e.g. individual calibration), the precision of sensitivity obtainable with LiF/PTFE dosemeters is more than adequate for most applications. The problems associated with sensitization at high dose levels still remain, and are at present by-passed by the introduction of low cost 'disposable' dosemeters, which can be economically discarded following exposure to a sensitizing dose. In the next chapter the various components of background signal, and low dose measurements, are discussed.
CHAPTER 10. **LOW DOSE MEASUREMENTS WITH LiF/PTFE DISCS**

10.1. **General**

The lowest dose detectable with a particular type of dosimeter is determined by variations in background signal, or 'noise', i.e. the signals obtained when unexposed dosimeters are read out. The minimum detectable dose may be defined as $1.5\sigma_B$, where $\sigma_B$ is the standard deviation in background signal, expressed as an equivalent radiation dose (EEC, 1974). When the background signal is expressed in this way it is dependent on the sensitivity of the dosimeter and ultimately of the phosphor. The results quoted below are for a representative batch of TLD-700 phosphor fines, incorporated into LiF/PTFE discs. The samples were read out in the Model 654 reader, except where otherwise indicated. Sources of background noise from the reader itself were described in section 6.7, and are not usually limiting factors in low dose measurement.

Discs which had been initialised (see section 9.4) to the reader's cooling rate were used for most of these experiments, since the fast cool in the reader increases the sensitivity of the dosimetry peaks by a factor of about two, compared with an external anneal. Furthermore, this approach was in accordance with complementary experiments (see sections 9.3 - 9.5) on the consistency of sensitivity, with the objective of simplifying operational procedures by dispensing with the external anneal in radiological protection applications. However, a disadvantage of the fast cool is that the lower temperature peaks are accentuated, with an adverse effect on the stability of stored signal if the $80^\circ$C pre-irradiation anneal is not subsequently used.

The background signal contains several components whose magnitude and variability increase rapidly with temperature, and therefore it is very dependent on the heating cycle profile, and heat transfer to the dosimeter. Plateaux type heating profiles were employed, to minimise temperature gradients across the dosimeter, and to allow lower read zone temperatures to be used while still achieving adequate heating efficiencies (see section 5.8.3). Unless otherwise indicated, each result, expressed in millirads equivalent, is the mean of 10 dosimeter readings $\pm$ 1 standard deviation.

10.2. **Background signals associated with radiation history**

It is recommended (EEC, 1974) that any residual signal remaining in the dosimetry traps (4 and 5) after the read zone should be reduced by a high temperature anneal to a level which is less than 50% of the equivalent minimum detectable dose. The Model 654 internal anneal of $300^\circ$C for 16 secs is usually adequate for this task, for doses of up to 5 rads.

LiF contains several deep traps which are not emptied by the $300^\circ$C anneal.
(Linsley and Mason, 1971a and b; Mason and Linsley, 1971; Sunta et al, 1971; Sunta et al, 1974; Kathuria et al, 1974; Mayhugh and Fullerton, 1974; Mayhugh, 1974). These can give rise to enhanced background signals when re-using, in daylight, LiF/PTFE discs which have previously been exposed to high radiation doses, due to photo-transferred thermoluminescence from these deep traps to the dosimetry traps. There may also be background signals due to (a) luminescence from the lower temperature tails of the peaks (peaks 6-12) due to deep traps, or (b) transference from deep traps to the dosimetry traps by thermal activation and retrapping. For these reasons, discs which have received doses in excess of about 10 rads should not subsequently be used for low dose measurements.

In the following experiments, only discs with no radiation history apart from natural backgrounds were used. Natural background radiation was at a level of less than 10 μrad/hr, and could be neglected for most of the experiments.

10.3. Chemiluminescence signals

Chemiluminescence is light emitted during the heating process due to chemical reactions. Generally the major part of the chemiluminescent signal is due to the reaction of oxygen with the dosemeter surface, e.g. the oxidation of organic debris and possibly similar effects involving the surface material itself. The chemiluminescence signal from an apparently clean LiF/PTFE disc, 12.7 x 0.4mm, 30% phosphor loading, is typically equivalent to 200 ± 100 mrad when read out in air, and can be as much as several rads if some organic debris has been deposited on the surface. Fortunately, the chemiluminescence signal is greatly reduced by removing oxygen from the dosemeter environment e.g. by flushing the readout volume with an inert gas such as nitrogen or argon (Aitken, 1963; McCall, 1963; Karzmark et al, 1964). Variations in the residual chemiluminescence signal are also considerably reduced. With the above type of dosemeter flushing the readout volume with nitrogen reduces the background signal to typically 8 ± 2 mrad. In all the following experiments, the readout volume was flushed with dry, dust-free nitrogen having an oxygen content of less than 100 ppm, at a flow-rate of 0.4 litre/min.

10.4. Residual background signals

10.4.1. General

Two separate effects were noted in the study of the 'residual' background signal which remains even with nitrogen flow. Firstly, a dependence on the temperature of the read zone. Secondly, the signal is largely diminished by the readout process, and only recovers to its initial value after the
dosemeter has been exposed to air for some time.

10.4.2. Recovery time

It was necessary to determine the recovery time before investigating the temperature dependence. The experiment was performed under darkroom conditions to avoid the known sensitivity to light. The heating cycle used consisted of a preheat zone of 135°C for 16 secs, a read zone of 240°C for 16 secs, and an anneal zone of 300°C for 16 secs, since it was believed that these conditions were close to optimum for low dose measurements (an assumption later proved to be correct). The discs used were 30% loaded, 12.7 x 0.4mm, and had previously been 'initialised' to the reader's cooling rate. Experimental procedure was as follows. Unirradiated discs were read out once to remove the bulk of the residual background signal, then stored in air for various periods before being re-read. The recovery of the signal is illustrated in Table 10.1.

Table 10.1. Recovery of residual background signal

<table>
<thead>
<tr>
<th>Time since last read-out (secs)</th>
<th>Mean reading (mrad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>30</td>
<td>1.8</td>
</tr>
<tr>
<td>100</td>
<td>2.7</td>
</tr>
<tr>
<td>300</td>
<td>3.3</td>
</tr>
<tr>
<td>1000 (~16 mins)</td>
<td>4.5</td>
</tr>
<tr>
<td>1800 (~30 mins)</td>
<td>6.5</td>
</tr>
<tr>
<td>$6 \times 10^5$ (~1 week)</td>
<td>8.0</td>
</tr>
</tbody>
</table>

It can be seen that the signal reaches its maximum level within about 30 minutes of readout. The increased reading after 1 week is expected, being due to natural radiation background of 1 - 2 mrad/week.

It is thought that most of this residual signal is due to chemiluminescence arising from oxygen adsorbed too deeply into the disc surface for the nitrogen purge to displace it. If a disc is re-read immediately, without further exposure to air, the average signal is only about $0.6 \pm 0.2$ mrad. This signal does not decrease significantly with repeated readouts, indicating that most of the adsorbed oxygen is driven out or used up during the first heating cycle. If a disc is stored in nitrogen after readout, the residual signal remains at about 0.6 mrad for at least 5 minutes, supporting the adsorbed oxygen hypothesis. On further exposure to air the signal recovers as shown in the table.
10.4.3. Temperature dependence

The temperature dependence of the residual signal was studied by varying the read zone plateau temperature from 200-300°C, the remainder of the heating cycle being as before. Three types of disc were investigated:

(a) 30% loaded, 12.7mm x 0.4mm  
(b) 30% loaded, 5mm x 0.4mm  
(c) 2% loaded, 12.7mm x 0.4mm

The same sets of 10 discs were used repeatedly, but 30 - 60 minutes were allowed between each readout of a disc, to allow the residual signal to reach equilibrium. The variations in residual signal with read zone temperature for the above dosemeters are shown in figure 10.1. The ordinate is relative light output in arbitrary units, not millirads, but the scale is the same for all three curves.

At lower read zone temperatures, the residual background signal consists mostly of chemiluminescence, which is essentially a surface phenomenon, thus it might be expected that the signals from the different types of dosemeter would be proportional to surface area. Comparing the curves for the 30% and 2% loaded discs, 12.7mm x 0.4mm, which have the same surface area, the signal from the 2% loaded disc is lower, partly because its upper surface temperature is about 15°C lower than the upper surface temperature of the 30% loaded disc, due to the difference in thermal conductivity.

Batch to batch variations in the PTFE may also be important. Comparing the 30% loaded discs, 12.7mm and 5mm diameter, the residual signal from the 5mm diameter disc is only half that from the 12.7mm diameter disc, whereas the effective surface areas are approximately in the ratio 1:4 (the 10mm aperture in the polyimide plate limits the light output from the larger disc). It is possible that an appreciable fraction of the residual signal from the 5mm diameter discs originated from their edges, which were rather ragged since these discs were manufactured by punching them out of larger discs with a ticket punch.

10.4.4. Variations in residual background signal

The dependence of sensitivity (i.e. light output per unit dose) on read zone temperature was also measured, to enable the residual signal, and more particularly, its variations, to be expressed in millirads. As expected, below a critical read zone temperature the sensitivity falls rapidly (cf Curve 1, figure 9.2). The relevant data is summarised in Table 10.2. The notation for Table 10.2 is as follows:

S is the relative sensitivity, normalised to unity for a 240°C read zone temperature. \( \sigma_s \) is the coefficient of variation in S (for a dose of 5 rads).
Figure 10.1. Dependence of residual background signal of several types of LiF/PTFE disc on read zone temperature

(1) 30% LiF, 12.7 x 0.4mm
(2) 2% LiF, 12.7 x 0.4mm
(3) 30% LiF, 5 x 0.4mm

Figure 10.2. Dependence of $\sigma_s$ on read zone temperature

(LiF/PTFE discs, 30% LiF, 12.7 x 0.4mm)

Figure 10.3. Dependence of $\sigma_B$ on read zone temperature

(LiF/PTFE discs, 30% LiF, 12.7 x 0.4mm)
B is the mean residual signal, expressed in millirads (not relative light output).

$\sigma_B$ is one standard deviation in B, in millirads.

Table 10.2. Variations in sensitivity and residual background signal with read zone temperature

<table>
<thead>
<tr>
<th>Type of disc</th>
<th>Parameter</th>
<th>Read zone temperatures, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>30% loaded, 12.7 x 0.4mm</td>
<td>S</td>
<td>.59</td>
</tr>
<tr>
<td></td>
<td>$\sigma_S$</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>$\sigma_B$</td>
<td>2.2</td>
</tr>
<tr>
<td>2% loaded, 12.7 x 0.4mm</td>
<td>S</td>
<td>.78</td>
</tr>
<tr>
<td></td>
<td>$\sigma_S$</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>$\sigma_B$</td>
<td>20</td>
</tr>
<tr>
<td>30% loaded 5 x 0.4mm</td>
<td>S</td>
<td>.59</td>
</tr>
<tr>
<td></td>
<td>$\sigma_S$</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>$\sigma_B$</td>
<td>3.4</td>
</tr>
</tbody>
</table>

10.4.5. Optimising the read zone temperature for low dose measurements

The implications of this data for low dose measurements are discussed with reference to figures 10.2 and 10.3, taking 30% loaded discs, 12.7 x 0.4mm, as an example. Figure 10.2 shows the dependence of $\sigma_S$ on read zone temperature. It can be seen that $\sigma_S$ is substantially independent of read zone temperature, as would be expected from the theory of phosphorescence, since a constant fraction of stored signal should be released for a given dosimeter heating profile. The total uncertainty in a measurement is a combination of $\sigma_S$ and $\sigma_B$ (eqn.7.1). Since $\sigma_S$ is virtually independent of read zone temperature, the optimum temperature for low dose measurements can be determined by reference to $\sigma_S$ alone. Figure 10.3 shows the variations in $\sigma_B$ with read zone temperature. It can be seen that a read zone temperature of about 240°C is optimum for low dose measurements with this type of dosimeter, since $\sigma_B$ is thereby minimised. Below 240°C, the reduction in sensitivity due to poor heating efficiency causes $\sigma_B$ to increase. Above 240°C, the increasing magnitude of the residual signal has the same effect. The optimum read zone temperature for low dose measurements can be determined
in this way for each type of dosemeter.

10.5. **Thermal radiation and triboluminescence**

Considering 30% loaded, 12.7 x 0.4mm discs, the signal of about 0.6 ± 0.2 mrads obtained (240°C read zone) when a disc is re-read immediately, without further exposure to air, could be due to a combination of (a) thermal radiation from the hot dosemeter and its environment, (b) chemiluminescence due to oxygen impurities (< 100 vpm) in the nitrogen supply, and (c) triboluminescence caused by thermal stress during cooling.

As the read zone temperature is increased the component of residual background signal due to thermal radiation will also increase, but in practice thermal radiation will generally be negligible if the read zone temperature is selected to minimise variations in residual background signal. Triboluminescence which may occur due to mechanical stress and shock during operational use is minimised by the PTFE matrix, but significant signals can be caused by extreme conditions, e.g. severe vibration (Bjarnard and Jones, 1967).

10.6. **Intrinsic sensitivity to light**

10.6.1. **General**

In considering the response of LiF/PTFE discs to ambient lighting, it is important to distinguish between (a) the 'intrinsic' response, which is independent of radiation history, and (b) the response due to photo-transferred thermoluminescence, which is a function of radiation history (see section 10.2). For a disc which has received a total previous dose of less than about 10 rads, it is only necessary to consider the intrinsic response (providing the disc is never exposed to intense uv light).

Ambient lighting conditions vary considerably, and so it is difficult to make comparisons or to define precisely the expected response. The dependence of the sensitivity of the intrinsic response on wavelength has not been systematically studied. Instead, an attempt has been made to gauge the extent of the operational problem by experiments in daylight, exposure to a uv lamp, and exposure to typical laboratory fluorescent lighting.

Mason (1971) found that the intrinsic response of LiF (TLD-700) powder to uv light was mostly in a low temperature peak at about 90°C. The response at saturation was equivalent to a radiation dose of about 220 mrads. Marshall et al (1971) studied the behaviour of LiF/PTFE discs handled in normal lighting conditions and attributed most of the light sensitivity to the PTFE. Webb & Phykit (1971) have also investigated the response of LiF/PTFE discs to uv light.

The intrinsic response may more correctly be termed 'light-induced thermoluminescence', but the former description has been preferred to avoid confusion with photo-transferred thermoluminescence, which is sometimes referred to as the 'induced' response (section 4.1.6).
10.6.2. Room temperature phosphorescence

LiF/PTFE discs phosphoresce at room temperature after exposure to daylight. The effect was studied by utilizing the CAL mode facility on the Model 654 reader. Discs were exposed to daylight, and placed in the drawer (still exposed to daylight). The drawer was then closed and the light output from the disc was integrated (no heating) for 16 secs from the time when the drawer was closed. Signals equivalent to 200 ± 200 mrad were observed from 30% loaded, 12.7 x 0.4mm discs, depending on the intensity of light and the period of exposure. After removal from daylight, the signal decays approximately exponentially, and takes up to 10 secs to decay to a negligible level. This 'prompt' phosphorescence is thus a potential source of error, unless a preheat zone or some other form of delay is used prior to the read zone. A similar signal was observed from pure PTFE discs of the same physical size, thus the effect is probably associated only with the PTFE.

10.6.3. Growth of intrinsic light signal in daylight

When discs are exposed to daylight, there is a rapid initial build-up in background signal over the first few seconds. In experiments with 30% loaded, 12.7 x 0.4mm discs, the discs were first read out to minimise the background signal (to about 0.6 mrads), then exposed in air to daylight through a plate glass window for various periods. Discs were laid side by side on a sheet of white paper during the exposure period, then read out with no preheat, but with a read zone of 240°C for 16 secs. The start of the heating cycle was delayed by 10 seconds to remove prompt phosphorescence. A typical graph of the growth in background signal with time is shown in figure 10.4. Note that the signal includes a small component from the residual chemiluminescence signal, which is also building up. The saturated background signal due to light is typically equivalent to about 30 mrads, although it has been observed to vary from 10 to 50 mrads, depending on the ambient light intensity. For standard lighting conditions, the saturated light signal is quite uniform from one disc to the next in a given batch, with a standard deviation of typically 3 mrads. If discs are exposed directly to bright sunlight, with no intervening plate glass window, background signals of up to 150 mrads equivalent have been observed. The 80°C pre-irradiation anneal has no significant effect on the magnitude or the growth-rate of the light signal.

10.6.4. Intrinsic light signal due to daylight ± glow curve structure and dependence on volume of dosemeter

Several types of LiF/PTFE disc were read out to minimise the background signal before being exposed to daylight for 5 minutes, and then read out with a linear ramp of 5°C/sec from ambient to 300°C. Figure 10.6 shows the resultant glow curves from the following types of disc: (a) Pure PTFE,
Figure 10.4. Growth of background signal due to intrinsic light effect (daylight) and air in LiF/PTFE discs (30% LiF, 12.7 x 0.4mm)

![Graph showing growth of background signal due to intrinsic light effect and air exposure over time.]

Figure 10.5. Effect of preheat zone on reducing the intrinsic light signal due to daylight in LiF/PTFE discs (30% LiF, 12.7 x 0.4mm)

![Graph showing the effect of preheat zone temperature on reducing the residual background signal.]
12.7 x 0.4mm, (b) 30% LiF, 12.7 x 0.4mm, (c) 30% LiF, 12.7 x 0.2mm. All figures are on the same relative scale. The light-induced glow peaks appear at tray temperatures of 130 - 140°C, but the disc temperatures are nearer 100°C when allowance is made for the poor thermal conductivity of PTFE. Comparing curves (a) and (b) it is apparent that the greater part of the light signal originates from the PTFE. Further, comparing curves (b) and (c), the light signals originate from the same effective surface area, but the signal from the 0.4mm thick disc is about twice that of the 0.2mm thick disc. Therefore, the light signal appears to be directly dependent upon dosemeter volume.

The peaks from the LiF loaded discs are broader and shifted slightly to higher temperatures, but it is difficult to tell whether this is due to a separate light signal from the LiF content or due to the higher residual background signals (compare the high temperature ends of the curves). This increase in the residual background signals reflects the differences in the average disc temperatures, due to the different thicknesses and thermal conductivities. The 0.2mm thick disc is hottest, and the pure PTFE disc coolest, relative to the indicated tray temperature.

Subsequent investigations with 5mm diameter discs have further confirmed that the light signal is roughly proportional to volume.

10.6.5. Intrinsic light signal due to intense uv light (365nm)

The previous experiment was repeated with exposure to intense uv light. Discs were placed 30 cm from a mercury vapour lamp (Philips HPR, 125W) for five minutes, and also briefly exposed to daylight during transit to and from the reader. The corresponding glow curves are shown in figure 10.7. It can be seen that a second peak appears in pure PTFE at a temperature about 60°C higher than the lower temperature peak, and the loaded dosemeters show a broad peak at about 170°C.

10.6.6. Intrinsic light signal due to fluorescent tubes

The growth of intrinsic light signal was studied for 30% loaded, 12.7 x 0.4mm discs exposed at bench level only to the normal artificial lighting of a laboratory. This was provided by fluorescent tubes suspended from the ceiling. The response was not significantly different from the residual background signal without light exposure, for exposure times of up to 30 mins. Readings were obtained with a preheat zone of 130°C for 16secs.

10.6.7. Fading of intrinsic light signal

Since the light signal due to daylight peaks at a true temperature of about 100°C, it can be expected to fade fairly rapidly in the absence of further excitation. To test this, 30% loaded, 12.7 x 0.4mm discs were initially read out before being saturated with daylight, and then kept in darkness at
Figure 10.6. 
Glowcurve structure of intrinsic light signal due to daylight

(a) Pure PTFE disc, 12.7 x 0.4mm

(b) LiF/PTFE disc, 30% LiF, 12.7 x 0.4mm

(c) LiF/PTFE disc, 30% LiF, 12.7 x 0.2mm

Figure 10.7. 
Glowcurve structure of intrinsic light signal due to UV light (+ some daylight)
(predominant UV wavelength = 365 nm)

(a) Pure PTFE disc, 12.7 x 0.4mm

(b) LiF/PTFE disc, 30% LiF, 12.7 x 0.4mm

(c) LiF/PTFE disc, 30% LiF, 12.7 x 0.2mm
room temperature (20–25°C) for 96 hours. Following this, they were read out without further exposure to light. The average signal was 10 mrad, which is slightly higher than the residual background signal obtained without exposure to light. Thus the total background signal will be a function not only of the degree of exposure, but also of the time since removal from daylight.

10.6.8. Reduction of intrinsic light signal by a preheat zone

Since the bulk of the intrinsic light signal due to daylight is in a low temperature peak at about 100°C, most of it can be removed by a suitable preheat zone. The preheat zone should not cause appreciable fading of the dosimetry peaks, and the preheat temperature is thus limited to a maximum of about 150°C (Webb and Phykit, 1971). This is not sufficient to remove the higher temperature peak from discs exposed to intense uv light. Since daylight may contain a uv component, it might be expected that the intrinsic light signal due to daylight may not be completely removed by a preheat zone (in figure 10.6 any such higher temperature peak is masked by the other components), and this has been confirmed by experiment. The effect of the preheat zone temperature on removing the intrinsic light signal due to daylight is illustrated in figure 10.5. Discs (30%, 12.7 x 0.4mm) were initially "zeroed", and then exposed to daylight for 5 minutes, before being read out with a 16 sec preheat zone, followed by a read zone of 240°C for 16 secs. It can be seen that even with a preheat temperature of 150°C the background signal is not completely reduced to the residual signal obtained without exposure to light. The mean signal from 20 discs read out as above, at a preheat temperature of 150°C, was $12.5 \pm 2.8$ mrad.

10.6.9. Implications for low dose measurements

Discs can readily be sealed in light-proof containers during their issue period, but can only be fully protected from light during readout if discs are unsealed, read out, and re-sealed in the container under darkroom conditions. This is not operationally convenient, and generally discs are likely to be exposed to light of some kind during readout, in which case a preheat zone should be employed to reduce the intrinsic light signal. Both background calibration and issued dosimeters should be exposed to similar amounts of light. Exposure to light containing a uv component should be minimised, to avoid (a) build-up of signal in the 170°C peak, and (b) photo-transferred thermoluminescence. The preheat temperature also affects the stability of stored signal(section 9.5) and in practice should be set to 130°C if the 80°C pre-irradiation anneal has not been used. If this anneal has been used, then the preheat temperature can be increased to up to 150°C.
A practicable solution to the light problem, and one that can readily be achieved operationally, is to unseal dosemeters from their light-proof containers, read them out, and re-seal them in the containers, in a room lit only by suitable artificial lighting. Some types of artificial light, e.g. fluorescent tubes, are much less intense than daylight, and appear to emit a much lower UV component. Discs can be exposed to such lighting for operationally feasible periods (e.g. of the order of tens of minutes) before and after readout, without affecting the ability of the preheat zone, at either 130 or 150°C, to reduce the intrinsic light signal to an undetectable level. If discs are read out in daylight, some build-up in background signal is inevitable for preheat temperatures of up to 150°C, although the higher the preheat temperature, the better. Variations in background signal can be minimised by exposing all discs to similar amounts of light.

10.7. Surface condition and contamination

10.7.1. Chemiluminescence not reduced by inert gas flow

It has been observed that some types of surface contamination, e.g. debris burnt into the dosemeter surface during readout or anneal, can give rise to background signals which are not appreciably reduced by nitrogen flow. The effect of changes in surface condition on sensitivity have already been discussed in section 9.1.

The dosemeter will normally be sealed in a plastic container during use, thus protecting its surface from both chemical contamination and light. The chances of contamination can be reduced by dispensing with the external high temperature anneal, since annealing ovens can be a source of contamination (section 10.7.2). The frequency of contamination is thereby reduced to accidental deposition of debris on the surface of the dosemeter during its application, or in transit to and from the reader, or in the reader (e.g. the tray). This may manifest itself, when reading a batch of zero dose dosemeters under conditions favourable to low dose measurements, as an occasional high reading outside the normal distribution. A problem with phosphor/PTFE dosemeters is that their surfaces can become electrostatically charged, and may attract debris to them. Dosemeters should be handled with tweezers (manual or vacuum) since even apparently clean hands leave a layer of finger oils on the dosemeter surface, and the reader tray must be cleaned regularly.

The following cleaning procedures have been devised as a result of several years experience. However, it should be remembered that cleaning procedures themselves can quite easily become a source of contamination. It is recommended that a clean working surface be provided close to the reader, on which the dosemeters can be placed. For example, the working surface
could be a large smooth sheet of white paper, which can readily be changed as required. Whilst it is accepted that the best procedure is not to let the dosemeters get dirty, some dirt collection is inevitable. Before readout or annealing the state of the dosemeter surface should be assessed and cleaned by the most appropriate of the methods described below.

(a) Loose surface dust or debris: Brush off with a soft brush or suck off with vacuum tweezers.

(b) If dosemeters have been mishandled, and are contaminated with finger oils, grease, or other substances, or are appreciably dirty: Rinse in pure methyl or ethyl alcohol followed by a rinse in distilled water. Allow to dry on a clean, smooth, lint-free surface.

(c) To remove ingrained or severe contamination: Soak for up to a few hours in chloroform, then rinse in pure methyl alcohol for at least 10 minutes, and finally in distilled water for at least 10 minutes (see also section 10.7.2). Allow to dry on a clean, smooth, lint-free surface.

10.7.2 Contamination by the annealing oven and the use of chloroform

The reduction of abnormal background levels in LiF/PTFE discs by chloroform has previously been reported by Robertson and Gilboy (1972). The experiments concerned contamination occurring in the annealing oven. Extremely high and variable background signals had been reported by some radiation workers using LiF/PTFE discs, 30% loaded, 12.7mm in diameter by 0.4mm in thickness, for personnel monitoring. Three separate batches of 20 such discs (Batches 1, 2 and 3) were obtained from institutions reporting these effects, and were put through a standard cleaning and annealing procedure before being read out on a Pitman Model 205C TLD Reader. The standard anneal used in all experiments was 300°C for 4 hours, followed by a slow cool (approx. 2°C/min) to 80°C and maintenance at this temperature for 24 hours. The high background signals were confirmed, and repeated ultrasonic cleaning with Arkline P(R), followed by soaking and rinsing in pure ethyl alcohol and distilled water showed little or no improvement, as can be seen from Table 10.3, which shows the background levels at various stages of such cleaning procedures.

Previous experience within our own laboratories had shown typical background levels equivalent to 15 ± 2 mrad for 100 discs (Batch 4) over seven anneal-read cycles. However, following a further anneal, the Batch 4 discs developed high and erratic backgrounds of 80 ± 30 mrad. It was discovered that the annealing oven, normally set aside for dosemeters only, had inadvertently been used for setting Araldite(R), an epoxy resin. The

(R) - registered trade name
distinctive aroma of burnt Araldite was apparent when the oven was reheated, and it was suspected that the discs had been coated with a layer of epoxy resin. In order to clean the oven, it was run continuously for 3 days at 330°C with the vent hole open. It would have been impractical to clean the aluminium annealing stand sufficiently, so it was replaced. The dosemeter cleaning procedures described above were found to be ineffective, and as an alternative the discs were soaked for 5 days in pure chloroform, which breaks down Araldite, before being finally rinsed in ethyl alcohol. The 5 day period was to some extent arbitrarily chosen, and is not necessarily an optimum. The discs were then annealed (standard cycle) in a lidded vitreous silica crucible and read out as before. The average background was found to be reduced to $20 \pm 2$ mrad. Irradiated controls showed that the TL sensitivity had not changed appreciably. Batches 1, 2 and 3 were then similarly treated with chloroform, with equal success (see Table 10.3). The nature of the contamination for these discs was not known, but it is effectively removed or suppressed by soaking in chloroform.

Table 10.3. Summary of variations in background signals with cleaning procedure

<table>
<thead>
<tr>
<th>Dosemeter condition</th>
<th>Batch 1</th>
<th>Batch 2</th>
<th>Batch 3</th>
<th>Batch 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before surface contamination. Cleaned in ethyl alcohol</td>
<td></td>
<td></td>
<td></td>
<td>15 ± 2</td>
</tr>
<tr>
<td>After surface contamination. Cleaned ultrasonically in ethyl alcohol and distilled water</td>
<td>114 ± 25</td>
<td>82 ± 20</td>
<td>50 ± 10</td>
<td>80 ± 30</td>
</tr>
<tr>
<td></td>
<td>88 ± 22</td>
<td>71 ± 19</td>
<td>100 ± 24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>187 ± 31</td>
<td>86 ± 23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>143 ± 19</td>
<td>77 ± 18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After cleaning in chloroform</td>
<td>10 ± 3</td>
<td>15 ± 3</td>
<td>10 ± 2</td>
<td>20 ± 2</td>
</tr>
</tbody>
</table>

* Each result is given in millirads as the mean of 10 dosemeter readings ± 1 standard deviation. One millirad is the equivalent of a radiation dose of one tissue millirad to discs of the same batch which have undergone the standard annealing cycle.

No particular precautions were taken to shield discs from light during these investigations, and this accounts for most of the residual signal and its variations. Clearly, the chances of severe contamination can be reduced by using an internal anneal instead of an annealing oven. If an annealing oven is used, it should be set aside exclusively for dosemeters.
It was subsequently found that the use of chloroform has a drawback, in that if the chloroform is not allowed to evaporate thoroughly from the disc surface, the remaining traces of chloroform will stain the surface brown during the next heating process. The problem is solved by following the soak in chloroform with a rinse in methyl alcohol, since chloroform is soluble in methyl alcohol.

10.7.3. Other surface phenomena

Two effects require further investigation. Firstly, there is some evidence that the residual chemiluminescence signal, which is due to oxygen adsorbed into the PTFE surface (see section 10.4)*, is dependent on thermal treatment, in particular the cooling rate from the anneal temperature. The effect is probably a function of the porosity of the PTFE surface. Preliminary results indicate that the residual chemiluminescence signal decreases with slower cooling rates, thus the signal to noise ratio of LiF/PTFE discs might be improved by slower cooling rates, despite the consequent decrease in sensitivity of the LiF.

Secondly, as mentioned in section 10.7.1*, the surfaces of phosphor/PTFE discs can become electrostatically charged and may attract debris, resulting in abnormal chemiluminescence signals. There is also the possibility of electroluminescence as electrostatic charges recombine.

10.8. The design of dosemeters for low dose applications

10.8.1. The dependence of minimum detectable dose on the residual background signal

The disc is a convenient form of dosemeter both from the point of view of ease of manufacture and also its suitability for low dose applications. In considering the various components contributing to the background signal it can be seen that generally the minimum dose detectable with a specific type of dosemeter will be governed only by the intrinsic light signal and the residual (chemiluminescence) background signal, providing that background noise arising in the reader itself is negligible. These signals are approximately independent of the % phosphor loading, whereas the thermoluminescent signal is roughly proportional to the % phosphor loading, which should therefore be maximised (30%) to obtain the highest signal/noise ratio. The intrinsic light signal is a function of the dosemeter's volume and its optical transmission. The ratio of radiation induced thermoluminescence to intrinsic light signal is approximately independent of disc diameter and thickness, thus the intrinsic light signal can only be reduced by appropriate operational techniques, not by altering dosemeter dimensions. If the intrinsic light signal can be made negligible, the minimum detectable dose is determined by variations in the residual background signal, which is essentially a surface-
dependent chemiluminescent effect.

10.8.2. Dependence of the residual background signal on dosemeter format

As shown in section 10.4.5, the read zone can be optimised for each type of dosemeter to minimise variations in residual background signal. The minimum detectable dose, defined as $1.5\sigma_B$, where $\sigma_B$ is the standard deviation in residual background signal, from 3 types of LiF/PTFE disc, measured under the most favourable readout conditions, are shown in Table 10.4.

Table 10.4. Minimum detectable doses for some types of LiF/PTFE disc

<table>
<thead>
<tr>
<th>Disc format</th>
<th>Min. detectable dose $(1.5\sigma_B)$, in mrad.</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% LiF, 12.7 x 0.4mm</td>
<td>2</td>
</tr>
<tr>
<td>30% LiF, 5 x 0.4mm</td>
<td>5</td>
</tr>
<tr>
<td>30% LiF, 5 x 0.02mm</td>
<td>$\sim$ 50</td>
</tr>
</tbody>
</table>

The residual background signal is probably almost totally due to chemiluminescence from adsorbed oxygen, and will be some function of the total disc surface area.

The signal/noise ratio for a given weight of phosphor is higher with thinner discs, due to lower self-attenuation of light output. Thus the minimum dose detectable with a 5 x 0.02mm disc is only about 10 times higher than that detected by a 5 x 0.4mm disc, i.e. a disc containing 20 times more phosphor.

The above results are for discs of normal optical transmission, and would be modified if colourants are used to decrease the transmission e.g. to reduce the effective thickness.

10.8.3. Phosphors other than LiF

The factors determining the minimum dose detectable with LiF/PTFE discs can be expected to apply to other phosphor/PTFE discs, since they are mainly associated with the PTFE rather than the phosphor. For example, CaSO$_4$:Dy has a sensitivity approximately 30 times that of LiF, so that CaSO$_4$:Dy/PTFE discs should be able to detect doses 30 times smaller than those detectable with LiF/PTFE discs having the same format, provided this phosphor does not strongly modify the chemiluminescence behaviour.

10.8.4. The design of LiF/PTFE dosemeters for personnel dosimetry

The optimum effective thickness of discs may vary from about 0.02 - 0.4mm (5 - 100mg cm$^{-2}$), depending both on the nature of the radiation of interest (penetrating or non-penetrating), and also on the body organ that the dosemeter is required to simulate (EEC, 1974). The minimum detectable dose will thus vary from 2 mrad to as high as about 50 mrad (Table 10.4), with present techniques and using currently available LiF.
Regarding the choice of disc diameter, there are advantages in using the larger diameter discs, loaded to the maximum practicable extent, in addition to their greater sensitivity. Background noise from the reader itself, in particular dark current, will be less significant. Furthermore, the contribution of any accidental surface contamination will be minimised, from the point of view of both sensitivity and background perturbations. The 12.7mm diameter disc at present widely used is a convenient size for a two element non-discriminating (skin dose and whole body dose only) personal badge (EEC, 1974). The NRPB automatic TLD system is based on a coded aluminium plaque containing two 12.7mm diameter discs (Dennis et al, 1974). A 0.4mm thick disc is used for the measurement of penetrating radiations, and a 0.2mm thick disc for non-penetrating radiations. For manual systems, a plastic badge employing the same disc format is currently marketed by D. A. Pitman Ltd. A badge design containing more than two elements is likely to be excessively bulky if based on the 12.7mm diameter disc, and a smaller diameter would then be more suitable. The 12.7mm diameter disc is also inconveniently large for extremity monitoring. A preferred diameter for this application would be in the range 5 - 10mm, to arrive at a compromise between operational convenience and minimum detectable dose.

A further factor to consider is that the cost of a LiF/PTFE dosemeter is dominated by its phosphor content, which may safely be reduced in some applications.

10.8.5. Possible ways of improving low dose measurements with LiF/PTFE discs

There may still be scope for improving the sensitivity of the LiF in LiF/PTFE discs by doping the LiF with a higher concentration of Mg and/or a lower concentration of Ti than presently used to counteract the separation effect which occurs during the grinding process (section 8.5.5). However, the most significant improvement in sensitivity may be obtained with the sensitizing technique (section 4.3.5) developed by Mayhugh and Fullerton (1974).

Apart from the sensitivity of the phosphor, the basic limitation to low dose measurements is variations in the residual background signal. This signal is temperature dependent, and it is probable that some of the observed variations are due to variations in the temperature of the top surfaces of the discs. The design of the polyimide aperture on the Model 654 reader is a compromise in order to enable different types of dosemeter to be read, and this may give rise to some variation in the top surface temperature of large LiF/PTFE discs, depending on their degree of contact with the tray. If the reader is to be used only with this type of dosemeter, a more suitable design of top support would have a crosspiece in the polyimide aperture to hold the
disc more firmly against the tray, and thereby improve the reproducibility of heat transfer. This may in turn decrease the variability in residual background signal. Another avenue of research would be to investigate the effect of inert gases other than nitrogen in reducing the chemiluminescence signal. A gas such as helium should be more successful in displacing the adsorbed oxygen.

A significant improvement in low dose measurement may be gained by individually calibrating discs for both sensitivity and residual background signal. This is rather tedious with a manual system, and is probably unnecessary in most applications, but may be useful in reducing the minimum dose measurable with very thin discs.

Although the short-term reproducibility of dark current in the Model 654 reader is very good, the dark current does vary with ambient temperature and the work-load, and in some circumstances frequent correction may be required, e.g. when reading out the lower sensitivity 5 x 0.02mm discs. There is thus a case for offering a version with a cooled PM tube, maintained at a constant temperature of about 10°C. The potential user would have to balance the convenience of not making corrections for dark current against the extra cost. This concludes the discussion on low dose measurements with LiF/PTFE discs.
CHAPTER 11

THE DESIGN OF LiF/PTFE DISCS FOR SKIN DOSIMETRY

11.1. Definition of skin dose

A major problem in radiological protection is to adequately measure the dose, generally referred to as the skin dose, to cells in the basal layer of the epidermis. The thickness of the epidermis varies over the surface of the body from person to person (Whitton, 1973), but for many practical purposes can be taken to be 5 to 10 mg cm\(^{-2}\). New ICRP recommendations are in preparation, which will recommend that skin dose be taken as the average dose to tissue at a depth of between 5 and 10 mg cm\(^{-2}\). Thus, an 'ideal' skin dosemeter would be optically transparent, tissue equivalent, 5 mg cm\(^{-2}\) thick, and covered by a radiation filter of tissue equivalent material also 5 mg cm\(^{-2}\) thick.

11.2. The design of LiF/PTFE discs, of normal optical transmission, for skin dosimetry

The fabrication, and readout on a routine basis, of 5 mg cm\(^{-2}\) thick dosemeters is not easily achieved. Stability of shape of phosphor/PTFE discs is a function of both diameter and thickness, but thin dosemeters of any diameter tend to crinkle and curl, making reproducible readout difficult. LiF/PTFE discs 5 mg cm\(^{-2}\) thick can be manufactured but, in addition to the above problem, are extremely fragile and have a coefficient of variation in sensitivity of typically 20%, due primarily to variations in thickness.

It has been found experimentally that the thinnest dosemeter of diameter 12.7mm which does not crinkle or curl under laboratory conditions is about 50 mg cm\(^{-2}\) thick. This is for a disc containing 30% by weight of LiF, and is equivalent to a physical thickness of 0.22mm, since the density of LiF is 2.64 g cm\(^{-3}\), and the density of PTFE in this application is about 2.15 g cm\(^{-3}\). The above configuration is of particular interest for automatic read out systems since a disc diameter of 12.7mm is believed to be about optimum in the design of a simple, inexpensive, coded, multi-element dosemeter. However, this large diameter in turn sets the lower limit on the thickness of the disc at about 0.2mm. Thinner discs would be prone to damage, either during use or read out. For these reasons, a disc 12.7mm diameter by 0.2mm thickness will be used by NRPB for skin dosimetry in the NRPB automatic TLD system (Dennis et al, 1974). Decreasing the diameter of discs to about 5mm has several advantages for manual read out systems, one of which is greater stability of shape. Discs of this diameter might be stable down to about 25 mg cm\(^{-2}\) thick (~0.11mm), under operational conditions.

The evaluation of a practical skin dosemeter is obviously best carried out
by comparison with the 'ideal' skin dosemeter, which is defined as a
dosemeter whose light output is proportional to the average dose in tissue
at a depth of between 5 and 10 mg cm\(^{-2}\). For comparison purposes, all
dosemeters are assumed to be covered by a 5 mg cm\(^{-2}\) tissue equivalent
filter. In practice, the filter is generally an opaque plastic which also
serves to protect the dosemeter against light and surface contamination.
Note that any filter of thickness \(d\) g cm\(^{-2}\) reduces the surface dose to a
dosemeter by a factor \(\exp\{-\nu d\}\), but this does not affect comparisons, so
long as all dosemeters are covered by the same type of filter. It is
possible to enhance the response of a practical dosemeter relative to the
'ideal' dosemeter by decreasing the thickness of the filter covering the
practical dosemeter, as Marshall and Docherty (1971) have done. However,
5 mg cm\(^{-2}\) of a typical filter material, e.g. polyethylene, is fairly
fragile, and a thinner filter might not be suitable for routine applications.

Figure 11.1 shows the theoretical response of 30% loaded LiF/PTFE discs,
25 and 50 mg cm\(^{-2}\) (0.11 and 0.22mm) thick, relative to the ideal skin
dosemeter. The discs are assumed to have normal optical transmission, i.e.
their effective coefficient of attenuation, \(b = 9.38\) cm\(^2\) g\(^{-1}\) (section 8.2).
The curves are calculated from equations 3.6 and 3.7\*, assuming identical
irradiation conditions and optimum readout conditions for the LiF/PTFE discs,
i.e. from section 3.3.4\*, best results would be obtained when the surface
of the disc nearest the radiation source is also the surface nearest the
light detector during read out, and when tray reflectivity is low or zero.
It can be seen that the LiF/PTFE discs appreciably underestimate the tissue
dose from beta particles of end point energy less than about 1 MeV.

11.3. The use of colourants to effectively reduce disc thickness

An alternative approach to the design of LiF/PTFE discs for skin dosimetry
is to manufacture thicker, less transparent dosemeters with a lower effective
thickness, by incorporating colourants.

The applicability of phosphor/PTFE dosemeters containing colourants to
surface dose measurements was noted by the author in 1971, during some
manufacturing trials with lithium borate/PTFE discs. Discs containing 30%
and 5% by weight of lithium borate turned dark grey and light grey,
respectively, during the sintering process. It was obvious that the effective
light output from the 30% loaded discs was coming from a thin surface layer,
and their application to surface dosimetry was immediately apparent.
However, the sensitivity of the discs was such that the minimum detectable
dose was about 5 rads, which was too high for radiological protection
applications, but useful for radiotherapy. The reason for the darkening of
the discs was traced to the activator in the lithium borate, MnCl\(_2\). Some
of this was not incorporated into the crystal lattice, and during the
Figure 11.1.
Theoretical response of LiF/PTFE discs (normal optical transmission) relative to 'ideal' skin dosemeter

(1) $T = 25 \text{mg cm}^{-2}$ (0.11mm)
(2) $T = 50 \text{mg cm}^{-2}$ (0.22mm)

Notes: (a) 30% phosphor loading
(b) Response normalised to 1.00 as $v \to 0$
(c) Optimum read out conditions ($r = o$, and surface 1 nearest PM tube)
(d) $b = 9.38 \text{ cm}^2 \text{g}^{-1}$
(e) Calculated from eqns. 3.6 and 3.7
sintering process was converted to $\text{MnO}_2$, which is black. In fact, it is suspected that that particular batch of lithium borate by accident contained too much $\text{MnCl}_2$.

It was clearly necessary to turn to other phosphors, e.g. LiF, to develop a skin dosemeter of adequate sensitivity for radiological protection. The theory described in Chapter 3 was developed to facilitate the design of such a dosemeter, and experiments have recently been initiated into the production of LiF/PTFE dosemeters containing various colourants to alter their effective transmission (a LiF/PTFE disc, 100 mg cm$^{-2}$ thick, and containing 30% LiF, has an effective transmission, $t_m$, of about 0.45).

It was found that 'carbon black' is an extremely sensitive colourant, so sensitive in fact that it is difficult to weigh reproducibly the small amounts required. Hence attention has also turned to metal oxides, which are stable in PTFE and easier to weigh reproducibly, since a greater weight is required to produce the same colouring effect as carbon black. Good results have been obtained with $\text{MnO}_2$. One factor that has to be borne in mind is any change in the effective atomic number due to the colourant, and for this reason it may in the end be worthwhile to persist with carbon black, which is more tissue equivalent than $\text{MnO}_2$.

The use of semi-transparent dosemeters is often accompanied by the operational problem of ensuring correct orientation, but this is facilitated with phosphor/PTFE discs since identification numbers or marks can be written on the surface of the disc.

The question now is, to what extent would the performance of a LiF/PTFE disc be improved by decreasing its effective transmission, and what loss in sensitivity would result? Figure 11.2 shows the theoretical response of a dosemeter, 50 mg cm$^{-2}$ thick, relative to the 'ideal' skin dosemeter, for a range of effective transmissions, $t_m$ (see section 3.2.6). This figure assumes identical irradiation conditions, and optimum readout conditions for the semi-transparent dosemeter, i.e. surface 1 nearest detector and $r = 0$. In fact, the dependence on $r$ is not significant for $t_m \leq 0.1$. It can be seen that a very low effective transmission, $t_m = 0.000001$, is required to produce a good match to the 'ideal' dosemeter. This would not be measurable by the method described in section 3.2.6, thus optimum colourant concentration would have to be determined by a radiation method.

The effect on sensitivity of variations in $t_m$ can be best considered as $v \to 0$. To simplify matters assume optimum readout conditions as before.

For the 'ideal' skin dosemeter ($b=0$),

$$k_1 (v \to 0) = C$$

(see equation 3.9)
Figure 11.2.

Theoretical response of 50mg cm\(^{-2}\) thick LiF/PTFE disc relative to the ideal skin dosimeter.

Notes:
1. Response normalised to 1.00 as $y \rightarrow 0$
2. Optimum readout conditions ($r = a$, and surface 1 nearest PM tube)
3. Calculated from eqns. 3.6 and 3.7.

- (1) $t_m = 1.0$
- (2) $t_m = 0.1$
- (3) $t_m = 0.01$
- (4) $t_m = 0.001$
- (5) $t_m = 0.0001$
- (6) $t_m = 0.00001$
- (7) $t_m = 0.000001$

Mass absorption coefficient, $\gamma$ (cm\(^{-1}\) g\(^{-1}\) MeV\(^{-1}\)) assuming media is tissue.
For semi-transparent dosemeters,

\[ k_1 (v \to 0) = G \left( \frac{1 - \exp \{-bT\}}{bT} \right) \]  

(see equation 3.7)

The sensitivity of a semi-transparent dosemeter relative to the ideal skin dosemeter is thus given by

\[ \frac{T}{T'} \left( \frac{1 - \exp \{-bT\}}{bT} \right) = \frac{1 - \exp \{-bT\}}{bT'} \]

where \( T' \) (= 5 mg cm\(^{-2}\)) is the thickness of the ideal skin dosemeter. The factor \( T/T' \) accounts for the differences in phosphor content. The dependence on \( t_m = \exp\{-bT\} \) of the sensitivity of a 50 mg cm\(^{-2}\) thick semi-transparent dosemeter is illustrated in Table 11.1.

Table 11.1. Dependence on \( t_m \) of the sensitivity of a 50 mg cm\(^{-2}\) thick semi-transparent dosemeter

<table>
<thead>
<tr>
<th>Effective transmission, ( t_m )</th>
<th>Sensitivity ( (v \to 0) ) (relative to the ideal skin dosemeter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>0.1</td>
<td>3.9</td>
</tr>
<tr>
<td>0.01</td>
<td>2.14</td>
</tr>
<tr>
<td>0.001</td>
<td>1.44</td>
</tr>
<tr>
<td>0.0001</td>
<td>1.09</td>
</tr>
<tr>
<td>0.00001</td>
<td>0.87</td>
</tr>
<tr>
<td>0.000001</td>
<td>0.72</td>
</tr>
</tbody>
</table>

It can be seen that in the cases when a good match with the ideal dosemeter is obtained, the sensitivity of the practical dosemeter is about 0.72 of the sensitivity of the ideal dosemeter. However, this does not necessarily mean that the minimum detectable dose is correspondingly increased, since, if this is determined by the signal/noise ratio of the dosemeter, as is generally the case with good instrumentation, the ratio of the noise signals from the practical and ideal dosemeters must also be considered.

11.4. Relation of photon or beta-ray energy to mass absorption coefficient

The mass absorption coefficient scale in figures 3.8, 11.1, and 11.2 can readily be converted to photon or beta ray energies for a given media, from standard tables. For example, for the important case of \( \beta \)-rays in tissue, the \( \beta \)-ray end point energy \( E_o \) (in MeV) can be calculated (Loevinger et al, 1956) from the formula

\[ \nu = 18.6 (E_o - 0.036)^{-1.37} \text{ cm}^2 \text{ g}^{-1} \]
where \( \nu \) is the \( \beta \)–ray apparent mass absorption coefficient in tissue. As an illustration, the figures are also scaled in \( E_0 \), assuming \( \nu \) as above.

11.5. The further development of LiF/PTFE skin dosemeters

The theoretical basis and experimental techniques required have been developed. The optimum configuration (shape and transmission) will depend on the application. For extremity and personnel monitoring a small disc (\( \sim 5 \text{mm diameter} \)) would be very convenient, but in automatic systems the diameter of the disc is governed by other considerations. Three possible designs of LiF/PTFE disc for skin dosimetry are summarised in Table 11.2.

Apart from the diameter, the choice is basically between (Type 1) discs of thickness 25-50 mg cm\(^{-2}\) and normal optical transmission, with good sensitivity as \( \nu \rightarrow 0 \) but a fall-off in response as \( \nu \) becomes appreciable, and (Types 2 and 3) discs having an actual or effective thickness of 5-10 mg cm\(^{-2}\) with a somewhat lower sensitivity but a response reasonably independent of \( \nu \) over the range of interest.

The minimum detectable doses given in Table 11.2 are those obtainable with currently available LiF. The sensitivity of the Type 1 disc probably outweighs the better energy response of the Type 2 disc. However, it may be possible to reduce minimum detectable doses by a factor of 5 by sensitization followed by a uv anneal (sections 4.3.5 and 10.8.4), in which case Type 2 would become more acceptable. The Type 3 dosemeter is rarely used for routine skin dosimetry on account of its extreme fragility and the requirement for individual calibration.

Table 11.2. Characteristics relevant to skin dosimetry of different types of 30% loaded LiF/PTFE discs

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Type</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mg cm(^{-2}))</td>
<td></td>
<td>25–50</td>
<td>25–50</td>
<td>5–10</td>
</tr>
<tr>
<td>Diameter (mm)</td>
<td></td>
<td>5–13</td>
<td>5–13</td>
<td>5</td>
</tr>
<tr>
<td>Optical transmission, ( t_m )</td>
<td></td>
<td>0.6</td>
<td>(10^{-4})–(10^{-6})</td>
<td>0.8</td>
</tr>
<tr>
<td>Minimum detectable dose, mrads (( ^{60})Co)</td>
<td></td>
<td>5–20</td>
<td>50–200</td>
<td>50–100</td>
</tr>
<tr>
<td>Response to low energy ( \beta ) particles</td>
<td></td>
<td>Poor (fig.11.1)</td>
<td>Good (fig.11.2)</td>
<td>Good</td>
</tr>
<tr>
<td>Mechanical stability</td>
<td></td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>
CHAPTER 12. RECOMMENDATIONS FOR FUTURE WORK AND FINAL CONCLUSIONS

In this chapter the extent and limitations of some aspects of the research are discussed, and suggestions given for future work.

12.1. \textit{LiF:Mg,Ti}

\textit{LiF:Mg,Ti} is the phosphor at present most widely used in radiological protection and radiotherapy. Its properties and thermoluminescence mechanism are described in detail in chapter 3. Some studies of the thermoluminescence of \textit{LiF} doped with various activators were carried out, but were hampered by the unavoidable presence of low concentrations of Ti in the starting material. The concentrations of Mg and Ti in currently available \textit{LiF} phosphors have been selected to optimise the performance of \textit{LiF} of grain size 75-200 \(\mu\text{m}\). It is possible that the degradation in glow curve structure which occurs when large \textit{LiF} crystals are ground down to the fine powder used in \textit{LiF/PTFE} dosemeters (see section 8.5) may be partially counteracted by varying the concentrations of Mg and Ti, e.g. by heavier doping with Mg and/or lighter doping with Ti. There is thus scope for further research into the preparation and properties of \textit{LiF:Mg,Ti}, to study the dependence of sensitivity, glow curve structure, and sensitization on grain size and Mg and Ti concentrations, with a view to optimising the characteristics of fine (<75\(\mu\text{m}\)) \textit{LiF} phosphor. It may be possible to dispense with the 80°C anneal if peaks 2 and 3 can be significantly reduced in comparison with peaks 4 and 5.

12.2. \textit{Instrumentation}

The development of the manual TLD reader (the 'Toledo' Model 654) has been very successful, and no major problems have been encountered with it during two years operational experience. The desirability of a different type of polyimide aperture if only large diameter phosphor/PTFE discs are to be read has been discussed in section 10.8.5. There is also scope for improvement in the design of dosemeter trays and accessories. In particular, it has been found that the light output from powder read out in the type P tray may vary from tray to tray by as much as 10\%, implying that there is some variation in the shape of these trays. This is not critical for repeated readings in one tray, but does require the trays to be individually identified. The problem is thought to be associated with variations in the angle of the sides of the depression in the tray. Another matter requiring further investigation is the readout of very thin discs. In section 5.7.4 it was noted that an electroformed mesh may be more suitable than a quartz disc when reading out 0.02\text{mm} discs.

The long-term stability of the light sources should be checked by comparison of a reference light source with a low intensity photometric standard at
regular intervals (6.6). Facey (1966) found no change in the light output, of the type of light source used, within experimental error ($\pm 2\%$) over a 13 month period, but with the Toledo there is the additional possibility of changes in the aluminium reflective coating. From a dosimetric point of view, TLD is a comparative technique and the only requirement is that the reader should be stable between the readout of unknown and calibration dosemeters. In most applications this is rarely more than a day, and over this period there should be negligible drift in the output from the light source. The only problem which would occur if the light output drifted significantly over a period of years is that the range of the light measurement system would correspondingly vary, and might need adjustment if an experiment required a sensitivity setting near the upper or lower limits.

A significant advantage of the Toledo over other manual readers is that the system of removeable trays and the smooth drawer action are conducive to automation, and an automatic sample changer capable of handling up to 30 dosemeters of any type at one loading is currently being constructed. Also under development are two fully automatic TLD readers for the NRPB dosemeter, which consists of two LiF/PTFE discs in an aluminium alloy plaque (Dennis et al, 1974). The light measurement and heating systems of these readers are similar to those developed for the 'Toledo'. One of the readers is being developed, in conjunction with Frazer-Nash Ltd., for the NRPB personal thermoluminescent dosemeter processing system, which will largely replace the present film badge system in 1976.

12.3. LiF/PTFE dosemeters

12.3.1. Dosemeter form

Sources of sensitivity and background variations in LiF/PTFE discs have been investigated (chapters 8, 9, and 10), enabling the design of dosemeters and operational techniques for precise measurements at both radiological protection and radiotherapy dose levels to be optimised. The most suitable effective thickness of disc will be determined by the application; the effective thickness being a function of both the true thickness and the optical transmission.

Considering disc diameter, the 12.7mm diameter disc (30% phosphor loading) at present widely used in non-discriminating two-element personnel dosemeter badges seems to be well suited for this application. The same diameter disc, but with only 2% phosphor loading, is finding acceptance as an inexpensive criticality dosemeter. However, a smaller diameter disc would be more convenient for other applications, such as extremity monitoring and radiotherapy (see sections 10.8.4 and 9.8.5 respectively) and to meet this requirement it is proposed to produce discs 5.5mm in diameter, this also being a convenient
size for the existing Tray M supplied with the Toledo reader. These discs could be supplied in different phosphor loadings, for example, 30% for extremity monitoring, and 15% for radiotherapy. The selection of phosphor loading must be made with regard to such factors as sensitivity, cost of phosphor, ease of heating, optical density, surface condition, and uniformity of dosemeters within a batch.

12.3.2. Sensitization plus uv anneal

A promising line of research, which should be investigated immediately, is to try to improve the characteristics of LiF/PTFE dosemeters by applying the techniques of radiation sensitization, followed by a uv anneal (see section 4.3.5). The success or failure of this venture will depend on whether PTFE is sufficiently transparent to uv light of the critical wavelengths (Mayhugh and Fullerton (1974) used 254nm light).

12.3.3. Semi-transparent LiF/PTFE dosemeters

A theory of thermoluminescent dose measurement has been developed (sections 3.1 and 3.2) with special reference to the use of semi-transparent dosemeters for the measurement of penetrating and non-penetrating radiations. The theory has been successful in explaining the dependence of the sensitivity of LiF/PTFE discs on their thickness and optical transmission (8.2 - 8.3). The theory still has to be verified for the case of LiF/PTFE discs containing colourants in order to reduce their optical transmission and thereby alter their effective thickness. Suitable experimental techniques have been developed, and the next step will be to produce LiF/PTFE discs of physical thickness 0.1 - 0.2mm, but possessing optical transmissions in the range $10^{-3} - 10^{-4}$, for use in skin dosimetry (chapter 11).

12.3.4. The design of LiF/PTFE discs for diagnostic radiology

The specification of a dosemeter for the monitoring of the dose to patients during diagnostic radiology can be summarised as follows:

(a) A minimum detectable dose of the order of 10 mrad.
(b) Response reasonable independent of photon energy over the range 10 - 100 keV.

and (c) Dosemeter shape and composition should be such that it does not leave a concealing shadow on the radiograph.

The suitability of 0.2mm thick LiF/PTFE discs (for this application) should be investigated. Errors due to photon energy dependence could be reduced by calibrating at a photon energy within the range of interest. Furthermore, dosemeters which have been sensitized with a high radiation dose (plus uv anneal) might have a more suitable photon energy dependence (see section 4.3.5).
12.3.5. Neutron dosimetry with LiF/PTFE discs

The response of LiF to neutrons was discussed in general terms in section 4.2.10. There are two promising methods of neutron dosimetry which are suited to LiF/PTFE discs and should be investigated further. Firstly, Ayyanger et al (1974) have shown that a suitable mixture of the isotopes of Li can give a rem equivalent response to a mixed field of photons and thermal and intermediate energy neutrons. Secondly, Busuoli et al (1970), and Endres and Lucas (1974), have suggested the use of the ratio of the '210' and '280°C' peaks in LiF for simultaneous measurements of photons and neutrons. The 'plateaux' heating cycle on the Toledo reader is especially suited to the separation of different peaks, and the '280°C' peak could be measured by arranging to integrate the light output during an internal anneal at a temperature of ~300°C.

12.4. Annealing procedures with LiF/PTFE dosemeters

12.4.1. Limitations of the internal anneal

The advantages of the internal anneal (i.e. in the reader) over the external anneal (i.e. in an oven) have been discussed in section 4.3.2. Briefly, the advantages of the internal anneal are:

- (a) Simplification of operational procedures.
- (b) No necessity for the user to buy a high temperature annealing oven.
- (c) The fast cool in the reader increases the sensitivity by a factor of about two, compared with a typical oven cool.
- (d) Less chance of surface contamination or damage, which might cause high background signals or decrease sensitivity.
- (e) Less chance of sensitivity variations due to changes in the distribution of impurities.

For these reasons, parameters such as dependence of sensitivity on re-use and storage time, and components of background signal, were studied with discs which had received only an internal anneal (see chapters 9 and 10). At the start of the experiments, it was already realised that the internal anneal had the disadvantages of a longer readout cycle and incomplete erasure of previous signals, and that an external anneal might therefore be preferred in some operational situations. Two further disadvantages have emerged during the course of this research.

Firstly, there is the problem of 'initialisation', in which 3 or 4 readout cycles are required to fully stabilise the dosemeter's sensitivity as it adjusts from the cooling rate during manufacture to the reader's cooling rate. From an operational point of view, it should only be necessary to read out dosemeters (as received from the manufacturer) once prior to use, to
stabilise the sensitivity and zero the background signal. With the Toledo reader it is possible to achieve initialisation in 1 cycle by increasing the anneal zone to 36 secs at 300°C (somewhat shorter times may also be adequate). However, the overall cycle time is then excessively long for manual operation, and the automatic sample changer (see section 6.8) would be required to place this technique on an operational basis. An alternative and more practicable solution is for the disc manufacturer to fast-cool the dosemeters, before the customer receives them, as part of a post-manufacture anneal. For example, Webb (private communication) has cooled large numbers of discs fast and uniformly from 300°C by placing them in a rotating mesh basket in an oven cooled by CO₂ gas. Following this anneal, the discs required only 1 cycle in the reader to stabilise their sensitivity.

The second problem encountered with the internal anneal is the variation in sensitivity with pre- and post-dose storage time at room temperature, due to trap migration and aggregation effects. The stability of the stored signal can be improved by a pre-irradiation anneal at 80°C for about 16 hours. However, further research is required into (a) the dependence of sensitivity on the storage time from the last read cycle to the pre-irradiation anneal, and (b) variations in sensitivity with re-use, when using the pre-irradiation anneal.

12.4.2. Annealing LiF/PTFE discs above 327°C

In section 9.4.1 it was mentioned that LiF/PTFE discs can be annealed above 327°C, at which temperature a crystalline transition occurs in PTFE, but that this was not generally recommended because of the special care required. Dosemeters must be cooled evenly through the crystalline transition to obtain uniform optical densities, and temperature programming equipment is required since the cooling rate through the transition should be about 0.6°C/min or less (to stress-relieve the PTFE), whereas the natural cooling rates of most ovens are faster than this.

It was shown in section 8.2 that the apparent opaqueness of LiF/PTFE discs is due to light scattering at their surfaces, and that they are actually quite transparent. When discs are passed through a temperature cycle similar to that used in the sintering process (e.g. a slow ramp to 365°C, and maintenance at that temperature for 1 hour, followed by a slow cool at a rate of 0.6°C/min down to at least 250°C) they appear to be more transparent than before. The increased transparency seems to be due to a change in the surface texture, which is much smoother than the comparatively coarse surface produced during manufacture by the action of veneering the disc off a bar (see section 8.1).
Another interesting effect of the 'sintering cycle' is that the discs are completely stress-relieved of the distortion incurred during veneering. This is due to a memory effect in PTFE, which causes the disc to revert to the shape it would have been during its last sintering process. The characteristic 'bowing' disappears, and the discs become quite flat. In the manufacture of 0.2mm thick (or thinner) discs, significant stretching can occur as the discs are veneered off, which causes them to be 'saddle-shaped' and slightly larger in diameter and thinner than expected. However they become flat and return to the required dimensions after being passed through the sintering cycle.

Experiments with annealing above 327°C should be pursued further, for the following reasons:-

(a) The problems with changes in disc shape, and orientation in tray, noted in section 9.1 may be alleviated by the flatness and smooth surface of re-sintered discs. Furthermore, heat transfer should be improved.

(b) The increased transparency implies a somewhat higher sensitivity. Initial experiments have confirmed this, but show that the glow curve structure is slightly degraded, as would be expected from the results in section 8.5.

(c) Sensitization and attendant problems can be removed by an anneal of 400°C for 1 hour (see section 4.3.5).

(d) The smoother surface may reduce the adsorption of oxygen and thereby lower the residual background signal, resulting in lower minimum detectable doses (section 10.4).

12.4.3. Dependence of background signals on annealing procedure

The components of background signal described in chapter 10 were studied with dosemeters which had received only an internal anneal. Many of the experiments should be repeated with different annealing procedures, to determine the dependence of signal to noise ratio on factors such as annealing temperature (up to 400°C) and the cooling rate from the anneal temperature. In particular, the crystallinity of PTFE is known to depend on the cooling rate through a crystalline transition at 327°C, and this will probably affect the residual background signal, which is due to oxygen adsorbed into the dosemeter surface.

12.4.4. The use of metal block baths as annealing ovens

Currently, forced circulation air ovens are recommended for annealing (section 4.3.2). However, the use of metal block baths for this purpose should also be investigated. They have the advantages of relatively low cost, small size, and low temperature gradients, and the metal blocks can
be drilled in different configurations to suit different types of dosemeter and applications. For example, a metal block could be supplied with numbered depressions, each capable of accepting at least one dosemeter, so that the block acts both as an annealing stand and also as an identification jig, for keeping track of individual dosemeters.

12.4.5. **Recommended annealing procedures**

Clearly, more information is required before dosemeter annealing procedures (for both initial use and re-use) can be optimised for specific applications. On the basis of available data, the recommended annealing procedure for LiF/PTFE dosemeters is as follows:

If means for 'initialising' dosemeters are available, use the internal anneal wherever possible, plus an external 80°C pre-irradiation anneal for 16 hours. Otherwise use an external anneal of 300°C for 1 hour, followed by a natural cool in the oven, and then the 80°C anneal.

12.5. **Other phosphor/PTFE dosemeters**

Lithium borate/PTFE dosemeters may eventually be more suitable than LiF/PTFE dosemeters for radiotherapy applications, due to their simpler glow curve structure and better tissue equivalence. As noted in section 11.3, previous attempts to manufacture lithium borate/PTFE discs have been complicated by discolouration due to excess MnCl₂ activator, which oxidised to MnO₂ during the sintering process. There were also indications that this discolouration worsened with re-use of the discs, leading to sensitivity variations from one read cycle to the next. However, the excess MnCl₂ may have been atypical, and it is possible that better results may be obtained with future batches of lithium borate from the same or other manufacturers. With currently available lithium borate, the sensitivity of lithium borate/PTFE discs is too low for use in radiological protection.

CaSO₄·Dy is a high sensitivity phosphor which is finding acceptance in some applications. An interesting challenge is to produce CaSO₄·Dy/PTFE discs in which the average grain size of the CaSO₄·Dy is less than 1 μm, thus reducing the photon energy response to about that of the PTFE (section 7.3.5).

12.6. **A new type of thermoluminescent dosemeter**

In diagnostic radiology, even small departures from tissue equivalence can lead to greater or lesser absorption of radiation in the dosemeter than in surrounding tissue, which can cause confusing shadows on X-ray photographs of patients wearing dosemeters. To overcome this problem, a dosemeter has been developed very recently which is barely perceptible on a mammography radiograph. This dosemeter is fully described in British Patent Application 54465/73, but a brief description is given below. The dosemeter consists of
a layer of lithium borate powder sandwiched between two layers of thermoplastic Kapton Type F (registered trade name of Du Pont de Nemours Inc). A dosemeter is made by applying a measured quantity of \( \text{Li}_2\text{B}_4\text{O}_7\text{Mn} \) to a predetermined area of a plate of Kapton Type F film. In the samples made the Kapton Type F film consisted of a Kapton base 0.05mm thick and a layer of Teflon FEP, also 0.05mm thick. 15mg of phosphor, grain size 75-200 \( \mu \text{m} \), were evenly spread over a circular area of 8mm diameter. A second Kapton Type F plate is positioned over the first plate and is thermally bonded to it, trapping the phosphor in between. Thermal bonding is carried out under pressure at about \( 310^\circ\text{C} \) and the phosphor grains become embedded in the layers of Teflon FEP.

The dosemeter is stable for temperatures up to at least \( 300^\circ\text{C} \). Kapton and lithium borate are near tissue equivalent, and the thin layer of Teflon FEP does not cause a significant shadow on the radiograph. The peak of the emission spectrum of \( \text{Li}_2\text{B}_4\text{O}_7\text{Mn} \) is at about 600 nm and at this wavelength a Kapton film 0.05mm thick has a transmission of about 75\%, thus most of the light emitted by the phosphor reaches the surface of the dosemeter. The standard deviation in sensitivity of 20 hand-made samples was 3.7\%. Further work is required to determine the lowest measurable dose. The dosemeter should not be sensitive to uv light since the Kapton film effectively filters this out.

12.7. Application aids

Grouped under this title are such ancillaries as dosemeter badges, fingertip sachets, phantoms for treatment planning in radiotherapy, dosemeter identification and handling jigs, etc. More effort should be put into the development of these very essential items, which have so far been accorded much lower a priority than the reader and dosemeters.

12.8. Concluding remarks

A collaborative research project of this nature should satisfy both academic and commercial criteria for success. On the academic front, the various sources of error in a thermoluminescent dosimetry system based on LiF/PTFE dosemeters have been identified, and means described for reducing them both by appropriate design of instrumentation and dosemeters, and also by suitable calibration procedure and other operational techniques. From the commercial viewpoint, the research has been justified by the success of the 'Toledo' TLD system. Sales of this system and derivatives are currently (1975) valued at about £250,000 per annum, and are expected to increase over the next few years, as the automatic systems come into operation. The development of LiF/PTFE dosemeters for specific applications is well advanced, and operational procedures have been made more specific.
Concerning the recommendations for future work, priority should be given to the following projects:

(a) Production of 5.5mm diameter discs.
(b) Annealing using metal block baths.
(c) Sensitization plus uv anneal.
(d) Application aids.
(e) The automatic sample changer for the Toledo reader.

Thermoluminescence dosimetry has now reached the stage where it is already accepted as a suitable technique for radiotherapy and extremity and environmental monitoring, and is beginning to displace the film badge in personal monitoring. It is envisaged that the Toledo system and corresponding automatic readers will have a useful life-time of about 10-20 years. Beyond that is difficult to predict, but quite likely TLD will in turn be superseded by another technique, possibly TSC (see Table 1.2), in which the state of the dosemeter surface is not so critical for precise measurements.
Detailed description of Model 654 thermocouple amplifier and cold junction compensation circuit (see section 5.8.7)

The action of the cold junction compensation circuit is illustrated in figure A1-1. A compensating voltage \( V_{023} \) derived from a silicon resistor (which has a positive temperature coefficient) at the cold junction temperature is added to the amplified thermocouple signal \( V_{01} \) to render the combined voltage \( V_0 \) essentially independent of the cold junction temperature. The compensation is achieved by matching the first and second derivatives (with respect to temperature) of \( V_{01} \) and \( V_{023} \) at 25°C, i.e. the middle of the temperature range of interest (0 - 50°C). It is shown that the maximum errors, at 0 and 50°C, are only of the order of 0.1°C.

The combined thermocouple amplifier and cold junction compensation circuit is shown in figure A1-2. To understand the circuit, consider the voltages \( V_1, V_2 \) and \( V_3 \) (with respect to 0 volts) at points A, B, and C respectively. These voltages are the inputs to the 709A operational amplifier, which is here used as a summing amplifier. The 709A was selected because of its low input offset voltage and low coefficient of input offset voltage with temperature.

\( V_1 \) is the output from the thermocouple due to the temperature difference between the heating element and the terminal block and is applied to the non-inverting input of the operational amplifier. It can be shown that the output signal \( V_{01} \) at point D due to \( V_1 \), is given by:

\[
V_{01} = \frac{R_6 + R_7 + R_0}{R_0} V_1 , 
\]

\[ \text{(1)} \]

where \( \frac{1}{R_0} = \frac{1}{R_4} + \frac{1}{R_5} + \frac{1}{R_9} \).

\( R_7 \) is adjusted so that \( V_{01} = 500V_1 \).

The cold junction compensation and the zeroing of the input offset voltage of the operational amplifier is accomplished by means of \( V_2 \) and \( V_3 \), which are fed to the inverting input of the operational amplifier. \( V_2 \) is a voltage dependent on the temperature sensitive silicon resistor, \( R_1 \). The temperature of the terminal block is sensed by this resistor (Texas Instruments TM4 10K n° sensistor), which is in thermal contact with the terminal block, in close proximity to the thermocouple cold junction. It can be shown that the output signal \( V_{023} \) at point D due to \( V_2 \) and \( V_3 \) is given by:

\[
V_{023} = - \left( \frac{R_6 + R_7}{R_4} \right) V_2 - \left( \frac{R_6 + R_7}{R_5} \right) V_3
\]

\[ \text{(2)} \]
Figure A1.1. **Action of cold junction compensation circuit**

\[ V_0 = V_{01} + V_{023} \]

\[ V_{01} = A_1 \left[ \frac{V_x - k \exp(BT)}{\exp(BT) - 1} \right] \]

\[ V_{023} = A_3 V_3 - \frac{12R_F A_2}{(R_1 + R_F)} \]

\[ V_0 = V_{01} + V_{023} = \text{a constant (± 0.12°C) for a given temperature of the heating element.} \]

At 25°C,

\[ \frac{dV_{01}}{dT} = -\frac{dV_{023}}{dT} \]

and

\[ \frac{d^2V_{01}}{dT^2} = -\frac{d^2V_{023}}{dT^2} \]
The term containing $V_3$ is actually positive, since $V_3$ is negative, and $V_3$ is adjusted via $R_{13}$ so that $V_{023}$ is positive and equivalent to 500 times the output of a similar thermocouple with its hot junction at the temperature of the terminal block and its cold junction at 0°C. It is assumed when making this adjustment that $R_1$ is at precisely the same temperature as the terminal block. Note that this adjustment also compensates for the input offset voltage of the operational amplifier. The total output voltage at $D$, $V_0$, is thus equivalent to 500 times the EMF of the thermocouple with its hot junction at the temperature of the heating element and its cold junction at 0°C.

i.e. $V_0 = V_{01} + V_{023}$ ...........................(3)

or, $V$ (heating element : 0°C) = $V$ (heating element : terminal block) + $V$ (terminal block : 0°C)

If the temperature of the terminal block changes, $V_{01}$ will be altered. For a reproducible heating cycle $V_0$ must be independent of the temperature of the terminal block hence $R_1$ correspondingly alters and changes $V_2$, in a manner to be described below, to maintain $V_0$ practically constant for a given temperature of the heating element. The temperature coefficient of other components and the input offset voltage of the operational amplifier are assumed to be insignificant over the temperature range of interest, that is 0 - 50°C.

Differentiating eqn (3) with respect to $T$, the temperature of the terminal block : 
$$\frac{dV_0}{dT} = \frac{dV_{01}}{dT} + \frac{dV_{023}}{dT}$$ ...........................(4)

If $V_0$ is independent of the temperature of the terminal block, $\frac{dV_0}{dT} = 0$, and from eqn (4) : 
$$\frac{dV_{01}}{dT} = -\frac{dV_{023}}{dT}$$ ...........................(5)

Similarly,
$$\frac{d^2V_{01}}{dT^2} = -\frac{d^2V_{023}}{dT^2}$$ ...........................(6)

Equations (5) and (6) are key equations in the following argument. Both must be satisfied if $V_0$ is to be independent of the temperature of the terminal block. They are restated in terms of the input voltages, in equations (9) and (10), and finally combined and expressed in terms of circuit components, in equation (19).

Restating equations (5) and (6) in terms of the input voltages :-

Let 
$$\frac{R_6 + R_7 + R_0}{R_0} = A_1$$

(the amplification of the signal in the op.amp)
Similarly, let \( \frac{(R_6 + R_7)}{R_4} = -A_2 \) and \( \frac{(R_6 + R_7)}{R_5} = -A_3 \)

\[ \therefore \text{From eqn (2), } V_{O23} = A_2V_2 + A_3V_3 \] \( \ldots (8) \)

Substituting eqns (7) and (8) into (5) and (6) :-

\[ A_1\frac{dV_1(T)}{dT} = -A_2\frac{dV_2(T)}{dT} \] \( \ldots (9) \)

\[ \left( \frac{dV_3(T)}{dT} \right) = 0, \text{ since } V_3 \text{ is maintained constant } \]

and

\[ A_1\frac{d^2V_1(T)}{dT^2} = -A_2\frac{d^2V_2(T)}{dT^2} \] \( \ldots (10) \)

For thermocouples, the EMF \( (V_{TC}) \) is usually expressed as a function \( V_{TC}(T') \) where the cold junction is at 0°C and the hot junction at \( T' \) °C. If the cold junction is at a temperature \( T \), the EMF \( = V_{TC}(T') - V_{TC}(T) \). For a chromel-alumel thermocouple, it has been found that the function of EMF \( (V_{TC}) \) versus temperature \( (T') \) between 0 and 50°C is accurately described by an equation of the form :-

\[ V_{TC}(T') = k\left[ \exp(BT') - 1 \right] \], \( \text{cf. eqn. 5.2} \)

where \( k \) and \( B \) are constants.

On the Model 654 the cold junction is not at 0°C, but at the temperature \( T \) of the terminal block, therefore the output of the thermocouple \( (V_1) \) is given by :-

\[ V_1(T) = k\left[ \exp(BT') - 1 \right] - k\left[ \exp(BT) - 1 \right] \]

At a given temperature \( T' \) of the heating element,

\[ k\left[ \exp(BT') - 1 \right] = \text{a constant, } V_x \]

\[ \therefore V_1(T) = V_x - k\left[ \exp(BT) - 1 \right] \] \( \ldots (11) \)

\[ \therefore \frac{d^2V_1(T)}{dT^2} = \frac{B}{A_1} \frac{dV_x(T)}{dT} \] \( \ldots (12) \)

Eliminating \( dV_1(T) \) from equations (9) and (12) :-

\[ \frac{d^2V_1(T)}{dT^2} = -\frac{B}{A_2} \frac{dV_2(T)}{dT} \] \( \ldots (13) \)

Eliminating \( d^2V_1(T) \) from equations (10) and (13) :-
\[ \frac{d^2V_2(T)}{dT^2} = \frac{B}{dV_2(T)} \] ..............(14)

From the circuit it can be seen that \( V_2(T) \) is set by a potential divider network (between +12 volts and 0 volts) consisting of \( R_1(T), R_2, R_3 \), and resistors in parallel with \( (R_2 + R_3) \), namely \( R_4, R_5, R_6, R_{12} \), and part of the potentiometer \( R_{13}^* \):

\[ V_2(T) = \frac{12R_F}{R_1(T) + R_F} \text{ volts} \] ..............(15)

where \( R_F \) is constant and given by

\[ \frac{1}{R_F} = \frac{1}{R_2 + R_3} + \frac{1}{R_4 + R_5 + R_{12} + \text{part of } R_{13}} \]

\[ dV_2(T) = -\frac{12R_F}{(R_1 + R_F)^2} \frac{dR_1}{dT} \] ..............(16)

and

\[ \frac{d^2V_2(T)}{dT^2} = -12R_F \left[ \frac{(R_1 + R_F)d^2R_1 - 2\left(\frac{dR_1}{dT}\right)^2}{(R_1 + R_F)^2} \right] \] ..............(17)

Substituting for \( dV_2(T) \) (eqn.16) and \( d^2V_2(T) \) (eqn.17) in eqn.14:

\[ 12R_F \left[ \frac{(R_1 + R_F)d^2R_1 - 2\left(\frac{dR_1}{dT}\right)^2}{(R_1 + R_F)^2} \right] = B \frac{12R_F}{(R_1 + R_F)^2} \frac{dR_1}{dT} \]

i.e.

\[ (R_1 + R_F)d^2R_1 - 2\left(\frac{dR_1}{dT}\right)^2 = B (R_1 + R_F) \frac{dR_1}{dT} \]

i.e.

\[ R_F = \frac{2\left(\frac{dR_1}{dT}\right)^2}{\frac{d^2R_1}{dT^2} - B \frac{dR_1}{dT}} \]

The sensor \( R_1 \) was chosen to be 10 KΩ (at 25°C), the highest available value, to minimise the current through it and thus power dissipation and self-heating effects. From experiments on 10 such silicon resistors, temperature cycled between 0 and 50°C, it was determined that the function of resistance \( R_1 \) versus temperature \( T \) between 0 and 50°C for Texas Instruments Ltd. TM4 10 KΩ sensors is accurately described by an equation of the form:

\[ R_1(T) = R_0 \exp\{\alpha(T-T_0)\} \]
where \( R_0 \) is the resistance at a temperature \( T_0 \) and \( \alpha = 0.0078 \pm 0.0002 \text{°C}^{-1} \). This value for \( \alpha \) is in good agreement with a value of \( 0.0079 \pm 0.0002 \) obtained by interpretation of data supplied by Texas Instruments Ltd.

Now \( \frac{dR_1}{dT} = \alpha R_1 \), and \( \frac{d^2R_1}{dT^2} = \alpha^2 R_1 \)

:. Equation (18) becomes

\[
R_F = R_0 \left( \frac{2\alpha}{(\alpha - B)} - 1 \right) \exp \left( \alpha (T - T_0) \right)
\]  

Equation (19) must be satisfied over the temperature range of interest if \( V_0 \) is to be constant. However, this is clearly impossible since the equation contains a temperature dependent term, whereas \( R_F \) is constant. Hence \( R_F \) is evaluated at the mid-range temperature of 25°C. It is shown later that the errors incurred by this non-compliance over the temperature range are very small.

\( R_0 \) is nominally 10 kΩ at 25°C. \( B \) is determined from standard thermocouple tables as follows:

\[
V_{TC}(T') = k \left[ \exp(BT') - 1 \right]
\]  

At 50°C, \( V_{TC}(T') = 2.022 \text{mV} \)

\[
2.022 = k \left[ \exp(50B) - 1 \right]
\]  

At 25°C, \( V_{TC}(T') = 1.000 \text{mV} \)

\[
1.000 = k \left[ \exp(25B) - 1 \right]
\]

Putting \( \exp(25B) = x \), and dividing (20) by (21):

\[
\frac{2.022}{1.000} = \frac{x^2 - 1}{x - 1}
\]

:. \( x^2 - 2.022x + 1.022 = 0 \)

\( (x - 1.022)(x - 1) = 0 \)

:. \( x = 1.022 \) or 1

\( = \exp(25B) \)

The value \( x = 1 \) is trivial, as then \( B = 0 \)

Putting \( \exp(25B) = 1.022 \),

\[
25B = 0.02175
\]

\[
B = 0.00087
\]

Solving for \( k \) in eqn 20, we find that \( k = 45.45 \)

:. the complete law for the thermocouple from 0 to 50°C is:

\[
V_{TC}(T') = 45.45 \left[ \exp(0.00087 T') - 1 \right]
\]  

:. from eqn (11), \( V_1(T) = V_x - 45.45 \left[ \exp(0.00087 T) - 1 \right] \)

Table A1-1 compares the values for \( V_{TC}(T') \) obtained from eqn (22) with the values from standard thermocouple tables over a range of temperatures between 0 and 50°C.
It can be seen that they compare well and the value of B is therefore justified.

Table A1-1  

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>EMF, standard thermocouple tables (mV)</th>
<th>$V_{TC}(T')$ * (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.397</td>
<td>0.395</td>
</tr>
<tr>
<td>20</td>
<td>0.798</td>
<td>0.795</td>
</tr>
<tr>
<td>25</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>30</td>
<td>1.203</td>
<td>1.204</td>
</tr>
<tr>
<td>40</td>
<td>1.611</td>
<td>1.609</td>
</tr>
<tr>
<td>50</td>
<td>2.022</td>
<td>2.022</td>
</tr>
</tbody>
</table>

* $V_{TC}(T') = 45.45 \left[ \exp(0.00087T) - 1 \right]$

Substituting the values for $R_0, \alpha, B,$ and $T(T_0=25^\circ C)$ in eqn (19), we find that $R_F = 12.53 K/\alpha$. We now have sufficient information to determine the circuit components to satisfy eqn.(9):

\[
\frac{dV_2(T)}{dT} = - \frac{12R_F}{(R_1+R_F)^2} \frac{dR_1}{dT}
\]

Solving this equation at $25^\circ C$:

\[
\left( \frac{dV_2(T)}{dT} \right)_{T=25^\circ C} = -23.1 \text{ mV/°C}
\]

To find

\[
\left( \frac{dV_1(T)}{dT} \right)_{T=25^\circ C} \quad : -
\]

\[V_1(T) = V_x - k \left[ \exp(BT) - 1 \right]
\]

\[
\frac{dV_1(T)}{dT} = - B k \exp(BT)
\]

\[
\left( \frac{dV_1(T)}{dT} \right)_{T=25^\circ C} = -0.0404 \text{ mV/°C}
\]

$A_1$, (see eqn.7), the amplification of the thermocouple signal, is set to 500 for a suitable comparison of the thermocouple signal with the voltage output from the heating cycle generator. To give an idea of the scaling, 8 volts on the amplifier output corresponds to a heating element temperature of about $400^\circ C$. 

Rearranging eqn. 9:

\[
A_2 = \frac{\frac{\mathrm{d}V_1(T)}{\mathrm{d}T}}{\frac{\mathrm{d}V_2(T)}{\mathrm{d}T}}
\]

The values of \( A_1 \), \( \frac{\mathrm{d}V_1(T)}{\mathrm{d}T} \), and \( \frac{\mathrm{d}V_2(T)}{\mathrm{d}T} \) are now known at \( 25^\circ\text{C} \),

and

\[
A_2 = -\frac{500 \times 0.0404}{23.1} = -0.8747
\]

Now

\[
A_2 = -\frac{(R_6 + R_7)}{R_4}
\]

\( (R_6 + R_7) \) is set to 135 k\( \Omega \) by the requirement that \( A_1 = 500 \) and the value of 270 \( \Omega \) chosen for \( R_9 \).

\[ R_4 = \frac{135}{0.8747} = 154 \text{k}\Omega \]

In practice, \( A_2 \) will vary with the tolerances on \( R_9 \), since \( R_7 \) is adjusted to compensate for these (\( R_5 \) and \( R_4 \) being relatively insignificant in determining \( R_0 \)); hence \( R_9 \) must be specified to close tolerances to minimise variations in \( A_2 \). \( R_5 \), \( R_{12} \), \( R_{13} \) and \( R_{14} \) are selected to obtain the correct DC bias at the output of the amplifier, \( R_5 \) being chosen to be \( \gg R_9 \). \( R_2 \) and \( R_3 \) are now selected so that the required value of \( R_F \) can be obtained. \( R_3 \) has to be able to compensate for component tolerances; for example, \( R_1 \) can be \( \pm 10\% \) from the nominal value of 10 k\( \Omega \) at \( 25^\circ\text{C} \). In practice \( R_3 \) is adjusted on test until \( V_2 \) reaches the value given by eqn (15), with \( R_F = 12.53 \text{k}\Omega \) and \( R_1(T) \) calculated from the sensistor temperature and a value of 10 k\( \Omega \) at \( 25^\circ\text{C} \). At \( 25^\circ\text{C} \), \( V_2 = 6.674 \) volts. \( R_8 \) is set equal to \( R_9 \) to reduce input offset voltage and drift. Capacitor \( C_1 \) eliminating any AC pickup from the heating waveform.

The action of the circuit is illustrated in figure A1-1 by plotting \( V_{01} \) (for a given temperature of the heating element) and \( V_{023} \) versus the temperature of the terminal block over the range 0 - 50°C.

In figure A1-1, \( V_{01} = A_1 \left[ V_x + k \left( \exp(BT) - 1 \right) \right] \)

\( \cdots \) cf. eqns. (7) and (11)

and \( V_{023} = -\frac{12 A_2 R_F + A_3 V_3}{(R_1 + R_F)} \)

\( \cdots \) cf. eqns. (8) and (15)

\( V_0 = V_{01} + V_{023} \), and is practically independent of \( T \), the temperature of the terminal block (i.e. the cold junction), as can be seen from Table A1-2, in which \( V_0 \) is tabulated against \( T \).
Table A1-2. Output voltage ($V_0$) versus temperature ($T$) of terminal block

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$V_0^*$ (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$A_1 V_x + A_3 V_3$ - 6.335</td>
</tr>
<tr>
<td>10</td>
<td>$A_1 V_x + A_3 V_3$ - 6.335</td>
</tr>
<tr>
<td>20</td>
<td>$A_1 V_x + A_3 V_3$ - 6.336</td>
</tr>
<tr>
<td>25</td>
<td>$A_1 V_x + A_3 V_3$ - 6.338</td>
</tr>
<tr>
<td>30</td>
<td>$A_1 V_x + A_3 V_3$ - 6.338</td>
</tr>
<tr>
<td>40</td>
<td>$A_1 V_x + A_3 V_3$ - 6.338</td>
</tr>
<tr>
<td>50</td>
<td>$A_1 V_x + A_3 V_3$ - 6.340</td>
</tr>
</tbody>
</table>

$V_0^* = A_1 V_x + A_3 V_3 - A_1 k \left[ \exp(BT) - 1 \right] - \frac{12 R_F A_2}{(R_1 + R_F)}$

The variation in $V_0$ is equivalent to $\pm 0.12^\circ\text{C}$ (i.e., $\pm 2.5\text{mV}$) from 0 to 50°C, assuming $B$ to be constant at 0.0078 over this temperature range. A change in $B$ of 0.0002 will lead to an error of about 0.6°C at 0 or 50°C.

The output of the amplifier drives an analogue temperature meter on the front panel and is stepped down to provide a $\times 100$ (± 0.2%) output on the instrument back panel. A heating element temperature of 400°C will give an output at the back panel of about 1.6V, thus by reference to standard thermocouple tables the temperature can be readily and accurately measured by a 0–2V digital panel meter.

Similar cold junction compensation circuits can be derived for other types of thermocouple by determining a law for the thermocouple from standard tables, as for chromel–alumel in eqn (23), and inserting the value for $B$ so obtained in eqn (19). The cold junction compensation circuit consisted basically of a constant voltage maintained across the temperature sensitive resistor ($R_1$) and the constant resistor ($R_F$) connected in series. An equivalent circuit, also resulting in eqn (19), consists of a constant current flowing through $R_1$ and $R_F$ connected in parallel.

Similar circuits can be constructed around temperature sensitive resistors with negative $\alpha$. In this event $R_F$ also becomes negative (see eqn.19), but can be generated electronically. The technique of matching 1st and 2nd derivatives at a mid-range temperature has also been successfully applied to linearising circuits for thermocouples and platinum resistances.
Figure A1-2. Circuit of Model 654 thermocouple amplifier and cold junction compensation.
Appendix 2: Calibration procedures

The following calibration procedures were developed for use with the 'Toledo' Model 654 reader. The readings from unknown dosemeters can be evaluated simply by comparison with calibration dosemeters, as described in A2.1. However, for ease of interpretation the reader can be adjusted to give a direct reading of dose in suitable units, and this is described in A2.2. In each case, procedures are described for (i) obtaining measurements by assigning the mean sensitivity of the batch to all dosemeters in that batch, and (ii) improving accuracy by the calibration of individual dosemeters.

A2.1. Reading unknown dosemeters by reference to calibration dosemeters

A2.1.1. Readings obtained by assigning the mean sensitivity of the batch to all dosemeters

Unknown doses are found by comparison with the readings of sensitivity and background calibration dosemeters.

1. Subject all dosemeters to a thermal treatment (readout and/or anneal) sufficient to standardise their sensitivity and background levels.
2. Irradiate the sensitivity calibration dosemeters to a dose very much greater than the expected standard deviation of the mean equivalent dose of the background calibration dosemeters.
3. Set 'Sensitivity' to give sufficient resolution of dose on the display. Set 'Background' to zero.
4. Read out all the dosemeters, interspersing the unknown dosemeters with calibration dosemeters at regular intervals.
5. Let the mean reading of the sensitivity calibration dosemeters be $M$. Let the mean reading of the background calibration dosemeters be $B$. If an unknown dosemeter reads $x$, its dose ($D$) is given by

$$D = \frac{(x - B)C}{(M - B)}$$

where $D$, $x$, $B$, $M$ and $C$ are all expressed in the units selected.

Notes: (a) If the background signal is insignificant, i.e., if $x$ and $M \gg B$, then the dose is given by

$$D = \frac{xC}{M}$$

(b) The standard error in $M$ or $B$ can be reduced by taking larger numbers of calibration dosemeters.

(c) Adjustments in $B$ may be required at intervals to compensate for variations in PMT dark current.
A2.1.2. Improving accuracy by precalibration of individual dosemeters

The procedure described in A2.1.1 does not make any allowance for differences in sensitivity between dosemeters of the same batch. Corrections can be made for these differences, if it is assumed that the relative sensitivities between dosemeters are maintained after a read cycle (including, if necessary, an anneal cycle). Careful track must be kept of dosemeter identification.

1. Subject all dosemeters to a thermal treatment (readout and/or anneal) sufficient to standardise their sensitivity and background levels.

2. Arrange for the identity of each dosemeter to be known. Select some of the dosemeters to be sensitivity and background calibration dosemeters. Two sets of background calibration dosemeters are required.

3. Irradiate all dosemeters except the second set of background calibration dosemeters to a dose very much greater than the expected standard deviation of the mean equivalent dose of background calibration dosemeters.

4. Set 'Sensitivity' to give sufficient resolution of dose on the display. Set 'Background' to zero.

5. Read out all dosemeters, interspersing the dosemeters to be used for sensitivity calibration with the other dosemeters.

6. Let the mean reading of the sensitivity calibration dosemeters be \( N \). Let the mean reading of the 2nd set of background calibration dosemeters be \( b \).

Let \( R \) be the reading of an individual dosemeter.

Assign a sensitivity correction factor \( k \), to each dosemeter (except the background calibration dosemeters), where \( k \) is given by:

\[
(R - b) = k(N - b)
\]

where \( R, N, \) and \( b \) are all expressed in the same units.

7. The 2nd set of background calibration dosemeters are not used in the subsequent experimental work. Anneal, if necessary, the remaining dosemeters and for the experimental work proceed as in A2.1.1, using the sensitivity calibration dosemeters and the 1st set of background calibration dosemeters from the precalibration experiment as calibration dosemeters. If an unknown dosemeter reads \( x \), its dose \( D \) is given by:

\[
D = \frac{(x - B)C}{(N - B)k}
\]

where \( k \) is the correction factor for that particular dosemeter, as determined by the precalibration experiment, \( C \) is the dose to which the sensitivity calibration controls are irradiated and \( M \) and \( B \) are...
the mean readings of the sensitivity and background calibration
dosemeters respectively.

A2.2. \textbf{Calibrating the instrument to give a direct reading of dose}
in suitable units

A2.2.1. \textbf{Calibrating the instrument to the mean sensitivity of a}
batch of dosemeters

Two sets each of sensitivity and background calibration dosemeters are
required to calibrate the instrument for direct reading. The first sets
of sensitivity and background calibration dosemeters are read out before
the unknown dosemeters, to determine the appropriate settings of the
Sensitivity, Background, and Dec.Pt. switches. The second sets are
interspersed with unknown dosemeters during readout to check instrument
stability. Note that the accuracy of instrument calibration will be a
function of the numbers of dosemeters in the 1st sets.

1. Subject all dosemeters to a thermal cycle (read out and/or anneal)
sufficient to standardise their sensitivity and background levels.

2. Irradiate the sensitivity calibration dosemeters to a dose \( C \) very
much greater than the expected standard deviation in the mean
equivalent dose of the background calibration dosemeters.

3. Set 'Sensitivity' to give sufficient resolution of dose on the
display. Let the relative sensitivity be given by \( S_{A} \). Set
'Background' to zero.

4. Read out the 1st sets of sensitivity and background calibration
dosemeters. Let their mean readings be \( M \) and \( B \) respectively.

5. Change 'Sensitivity' to set a new relative sensitivity \( S_{B} \), where
\[ S_{B} = \frac{C}{(M-B)} \]
and \( C \), \( M \) and \( B \) are expressed in the units selected.
Set 'Background' to \( \frac{B \cdot C}{(M-B)} \). Set 'Dec.Pt.' to the appropriate
position for the units selected.

6. Read out the unknown dosemeters, interspersed with the second set
of calibration dosemeters at regular intervals.

Note: Although the instrument has been set to the mean sensitivity of the
batch, the precalibration of dosemeters as described in A2.1.2. can
still be applied. First, find a correction factor \( k \) for each unknown
dosemeter, as described in A2.1.2. Then follow A2.2.1, and finally
divide a particular dosemeter's reading by its correction factor \( k 
\) to obtain a more accurate result.

A2.2.2. \textbf{Calibrating the instrument to the sensitivity of an individual}
dosemeter

1. Determine a correction factor \( k \) for each unknown dosemeter as
described in A2.1.2.
2. Follow A2.2.1. (1-4).

3. Change 'Sensitivity' to set a new relative sensitivity $S_c$, 
   \[ S_c = \frac{S_A}{C} \frac{C}{k(M-B)} \]
   where $S_c = \frac{S_A}{C}$ and $C$, $M$ and $B$ are expressed in the units selected.

   Set 'Background' to $\frac{B.C}{k(M-B)}$.

   Set 'Dec.Pt.' to the appropriate position for the units selected.

4. Read out the dosemeter.

Note that the above procedure can apply to sensitivity calibration dosemeters used in checking instrument stability as well as unknown dosemeters. This is useful in that a quicker and more accurate assessment of instrument stability is obtained, since each sensitivity calibration dosemeter should read the same, within experimental error.
Appendix 3. References to manufacturers.

Acheson Colloids Company,
P.O.Box 12, Prince Rock, Plymouth, Devon, England.

Alfa Inorganics, Inc.,
8, Congress St., Beverly, Massachusetts, U.S.A.

B.D.H. Chemicals Ltd.
Poole, England. BH12 4NN
Tel: Parkstone 5520, Telex: 41186, Telegrams: Tetradome Poole.

British Nuclear Fuels Limited,
Risley, Warrington, Lancashire, England WA3 6AS
Tel: Warrington 35953, Telex: 627581, Telegrams: NUFUEL Warrington.

CEC (Carbonisation Enterprise et Ceramique),
B.P.60-92 Montrouge, France.
Tel: 253 78-10.

Chance-Pilkington (Pilkington Brothers Ltd.)
St.Asaph, Flintshire, U.K.
Tel: St.Asaph 3301, Telex: 61291.

Controls for Radiation, Inc: see Teledyne Isotopes.

Dow Corning Corporation,
Electronic Materials Dept., Midland, Michigan, U.S.A.

Du Pont de Nemours International, S.A.
P O Box CH-1211, Geneva 24, Switzerland.
Tel: (022) 43 98 11, Telex: 22 512, Geneva.

E.M.I. Electronics Ltd.,
Tel: 01 573 3888 ext:2542, Telex: London 22417, Telegrams: Emidata, London.

The Harshaw Chemical Company,
Crystal and Electronic Products Dept., 6801 Cochran Road, Salon, Ohio 44139, U.S.A. Tel: (216) 248-7400.

Madison Research Inc., No information available.

Omega Engineering Inc.,
Box 4047, Stanford, Conn.06907, U.S.A.
Tel: (203) 359-1660.

Nuclear Enterprises Ltd. Sighthill, Edinburgh, Scotland, EH11 4EY.
Tel: 031-443-4060. Telex: 72333.
D. A. Pitman Ltd.,
Mill Works, Jessamy Road, Weybridge, Surrey, England. KT13 8LE
Tel: Weybridge 46327, Telex: 929823, Telegrams: Pitway, Weybridge.

The Radiochemical Centre, Amersham, Buckingham, England. HP7 977.
Tel: Little Chalfont 4444.

Teledyne Isotopes,
50 Van Buren Avenue, Westwood, New Jersey, 07675, U.S.A.
Tel: 201-64-7070, Telex: 134-474.

Texas Instruments Ltd.,
Manton Lane,
Bedford, England. Tel: Bedford 67466 Telex: 82178

20th Century Electronics Ltd.
King Henry's Drive, New Addington, Croydon, Surrey, England.
Tel: Lodge Hill 2121-6.

Manufacturers of temperature indicating devices (T.I.D.'s):

1. A. Levermore & Co. Ltd.,
40-44 Broadway, Wimbledon,
London SW19 ISQ
Tel: 01-540-7186

2. Synthetic & Industrial Finishes Ltd.
Imperial Works, Imperial Way,
Tel: Watford 28363.
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TL:- thermoluminescence or thermoluminescent.
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Atari, N.A. & Ettinger, K.V., 1974; Krakow, 395-416, "Lyoluminescence in inorganic solids".


Attix, F.H., 1970; SM-143/25; "Luminescence and exoelectron dosimetry in personnel monitoring".

Attix, F.H., 1974; Krakow, 31-60; "Further consideration of the track interaction model for thermoluminescence in LiF (TLD-100)".

Attix, F.H. et al; 1968(a); Gatlinburg, 389-395, "Variations of electron-induced radioluminescence in Lithium Fluoride as a function of total dose".

Attix, F.H. et al; 1968(b); From report of NRL progress presented at Congress on Nuclear Electronics and Radioprotection, Toulouse, France, (March); "Thermoluminescent dosemeters for personnel monitoring".

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