



# Progress towards the development of a rapid analytical approach for separation of $^{226}\text{Ra}$ using dibenzo-18-crown-6 ether functionalised silica ( $\text{SiO}_2$ ) disks

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## ABSTRACT

A novel dibenzo-18-crown-6 ether (DB-18CE-6)- functionalised silica ( $\text{SiO}_2$ ) disk was found to be a capable source preparation technique for the rapid analysis of  $^{226}\text{Ra}$  by alpha-spectrometry. DB-18CE-6 was chemically immobilised onto the surface of  $\text{SiO}_2$  disks. It is anticipated that the high levels of selectivity of DB-18CE-6 for radium will allow for an efficient chemical separation of  $^{226}\text{Ra}$  from other elements present in sample matrices.  $^{226}\text{Ra}$  was adsorbed as a monolayer onto the surface of the silica disks, attaching to the functionalised centres of the DB-18CE-6 structure, forming a high resolution counting source for alpha-spectrometry. The chemical recovery of radium from synthetic samples was 2.3% at pH 2, with higher recoveries expected over the pH range of 4–10.

## 1. Introduction

Radium has four naturally occurring radioisotopes,  $^{226}\text{Ra}$  ( $T_{1/2}=1600$  a),  $^{228}\text{Ra}$  ( $T_{1/2}=5.75$  a),  $^{223}\text{Ra}$  ( $T_{1/2}=11.4$  d) and  $^{224}\text{Ra}$  ( $T_{1/2}=3.7$  d) originating from the decay of  $^{235}\text{U}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  primordial isotopes (Jia et al., 2007; Molinari and Snodgrass, 1990). The abundance of each naturally occurring isotope in environmental samples is related to the specific activity concentration and mobility of its parent and its characteristic radioactive decay half-life. Radium itself is highly mobile within the environment and is an important radionuclide to consider in the radiological protection of the environment due to its prevalence, particularly in the isotopic forms of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ . Furthermore, it is highly radiotoxic owing to its chemical similarity to calcium (Maxwell et al., 2016; Wallner and Steininger, 2007).

Worldwide, various regulatory authorities have shown an interest in monitoring and enforcing limits for radium levels in drinking water and industry. The Council of the European Union (CEU) directive applies a limit of  $0.1\text{ mSv a}^{-1}$  for the ingestion of radioactive substances present in water. This is based on an annual consumption of  $730\text{ L a}^{-1}$  which corresponds to  $0.5\text{ Bq L}^{-1}$  of  $^{226}\text{Ra}$  (European Commission Drinking Water Directive, 1998). All EU member states

must comply with this limit, however, individual EU states may set their own specific limits. In the UK, the Department for Environment, Food and Rural Affairs (DEFRA) have enforced a discharge limit on NORM (naturally occurring radioactive material) industries when disposing directly into environmental waters of  $10\text{ mBq L}^{-1}$  (DEFRA, 2011). Also in Germany, the Mineral and Drinking Water Regulation (MTVO) limits the activity of  $^{226}\text{Ra}$  in drinking water, which can be used for the manufacture of baby nutrition products, as  $125\text{ mBq L}^{-1}$  (FNA, 2006). Thus, there is a growing need to develop methods that can achieve rapid and accurate measurement of  $^{226}\text{Ra}$  in drinking water that comply with regulatory limits.

Radium-226 is measured routinely at environmental levels by alpha-spectrometry (Jia et al., 2005; Maxwell, 2006; Bayés et al., 1996; Bergamini et al., 2015). However, current approaches require labour intensive and time-consuming chemical pre-concentration, separation and source preparation steps. Rapid techniques have been developed which combine these steps; by either placing a coated disk in contact with a sample, or passing a sample through impregnated filters. Ra-NucFilm™ disks are comprised of a thin layer of  $\text{MnO}_2$  deposited onto the surface of a polyamide disk (Surbeck, 2000). The disks are contacted with the untreated water samples (pH 4 – 8, typical volume=100 mL) under stirring for 6 h with reported radium chemical

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recoveries of > 90% and uranium adsorption of < 5% (Surbeck, 2000; Eikenberg et al., 2001).

In order to obtain improved and selective techniques, crown ether-extractant systems, have been developed by the 3 M Company, Empore™ Ra Rad disks (Ďurecová, 1997). The disks consist of 21-crown-7 ether substituents impregnated to the surface of an inert polytetrafluoroethylene (PTFE) matrix. There have been a number of past uses of Empore™ Ra Rad disks (Seely and Osterheim, 1998; Ďurecová et al., 1999); most recently by Purkl and Eisenhauer who successfully used Empore™ Ra Rad disks to rapidly (< 5 h preparation) determine radium in environmental samples with a reported chemical recovery of  $92 \pm 9\%$ . Samples were loaded in 2 M HNO<sub>3</sub>, at flow rates of 50 mL min<sup>-1</sup> resulting in high resolution alpha sources ( $\Delta E_{\alpha}=26-40$  keV) (Purkl and Eisenhauer, 2003).

Extractant systems based on 18-crown-6 ether, such as the Sr-resin and TK100-resin, have been increasingly employed for the separation and extraction of radium and strontium, respectively with reported distribution co-efficient values > 100 mL g<sup>-1</sup> (Surman et al., 2014). The Sr resin, which has various applications for the removal of Fe, Ba, Sr and Pb from radium, contains 4, 4'(5')-di(*tert*-butylcyclohexano) 18-crown-6 ether immersed in 1-octanol as the extractant material (Dietz et al., 1999). McAlister et al., have recently used this particular Sr-resin for the selective separation and recovery of radium from Ca, Ba and Pb. Samples were loaded in 0.5 M perchloric acid and 3 M HNO<sub>3</sub> at flow rates of 2 mL min<sup>-1</sup>, which produced chemical recoveries of 99% for radium (McAlister et al., 2011).

The success of the Sr extraction chromatographic resin indicates selective crown ether structures may be useful in extracting <sup>226</sup>Ra when immobilised to a suitable solid inorganic substrate, such as Fe<sub>3</sub>O<sub>4</sub> or SiO<sub>2</sub> (Mesnic et al., 2013; Awual, 2016). The aim of this preliminary study is therefore to immobilise dibenzo-18-crown-6 ether (DB-18CE-6), an analogous 18-crown-6 ether extractant system used in the Sr resin, onto a flat SiO<sub>2</sub> disk, to produce a chemical separation and source preparation method ideal for the rapid and direct chemical recovery analysis of <sup>226</sup>Ra by alpha-spectrometry.

## 2. Materials and method

All reagents and solvents used were of analytical grade purchased from Sigma-Aldrich (Poole, UK). Standard element solutions at starting concentrations of 10,000 ppm (K) and 1000 ppm (Na) were purchased from Johnson Matthey (Hertfordshire, UK). A standard solution of <sup>226</sup>Ra was prepared from a calibrated solution obtained from the National Physical Laboratory (Teddington, UK). Solutions were diluted with ultrapure water obtained using an ELGA purelabflex water purification system (ELGA, Veolia Water, Marlow, UK, 18 MΩ cm, < 5 ppb Total Organic Carbon). The synthesis of 18-crown-6 ether functionalised silica (SiO<sub>2</sub>) disks followed a modified procedure outlined by Aissaoui et al., involving the surface (monolayer) functionalisation via a silanisation grafting procedure (see Fig. 1a–c) (Aissaoui et al., 2012).

### 2.1. Preparation of the DB-18CE6-functionalised SiO<sub>2</sub> disk

Cleaning (a): a dry SiO<sub>2</sub> wafer (Sigma-Aldrich, Poole, UK) was cut to form squares (10 mm×10 mm) and placed in a freshly prepared piranha solution (H<sub>2</sub>SO<sub>4</sub> (98%):H<sub>2</sub>O<sub>2</sub> (30%), 3:1) for 10 min at room temperature. The disks were washed with deionised water and were air dried.

Silane-grafting (b): SiO<sub>2</sub> disks were immersed in 3-triethoxysilylpropyl isocyanate (TESPI, 50 mmol), with anhydrous ethanol as the solvent, for 24 h. The TESPI-treated SiO<sub>2</sub> disks were washed with anhydrous ethanol and dried.

Crown ether-immobilisation (c): the crown ether structure, 4'-amino-dibenzo-18-crown 6 ether (NH<sub>2</sub>-DB-18CE6) (0.02 g, 0.05 mmol) was immobilised onto the surface of each TESPI-treated

SiO<sub>2</sub> disk, with anhydrous DMF as the solvent and left to incubate for 24 h. The DB-18CE6-functionalised (f) silica (SiO<sub>2</sub>) disk was then washed with anhydrous DMF and dried.

### 2.2. Adsorption and recovery studies

The adsorption behaviour of the DB-18CE6-f SiO<sub>2</sub> disks was studied by placing them into a glass liquid scintillation vial (20 mL, see Fig. 1d). Individual solutions were added containing either <sup>23</sup>Na or <sup>39</sup>K (10 ppm) in both deionised water (pH 7) and 0.1 M HNO<sub>3</sub> (pH 1). Samples were left for 24 h to equilibrate and aliquots were taken and measured using an Agilent 8800 triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS) (B. Russell et al., 2015). The instrument was fitted with quartz double-pass spray chamber and a MicroMist nebuliser (Glass Expansion, Melbourne, Australia) and nickel sample and skimmer cones (Crawford Scientific, South Lanarkshire, UK). The instrument was tuned daily using a mixed 1 ppb standard solution.

The recovery of radium using the DB-18CE6-f SiO<sub>2</sub> disks was studied by placing the disks into glass liquid scintillation vials. Solutions containing <sup>226</sup>Ra (0.1 Bq) were prepared in 0.01 M HNO<sub>3</sub> and added to each of the vials for recovery analysis at pH 2. Samples were left to incubate for 24 h. The DB-18CE6-f SiO<sub>2</sub> disks were removed from solution and air dried. They were then mounted on planchets (dia. 25 mm) in preparation for measurement. Measurements of <sup>226</sup>Ra were performed using an ORTEC Octete Plus alpha-particle spectrometer with passivated implanted planar silicon (PIPS) detectors, which had an estimated geometrical counting efficiency of 21% (Larijani et al., 2016). The energy calibration of the detectors was performed with a mixed calibration source containing <sup>241</sup>Am, <sup>244</sup>Cm and <sup>237</sup>Np (Teddington, UK).

## 3. Results and discussion

In the current work we present the adsorption and recovery studies obtained with the DB-18CE6-f SiO<sub>2</sub> disks. The adsorption of <sup>23</sup>Na or <sup>39</sup>K was calculated by comparing the initial counts per second (*CPS<sub>i</sub>*) attained prior to the addition of the DB-18CE6-f SiO<sub>2</sub> disks with the final counts per second (*CPS<sub>f</sub>*) obtained post equilibration (see Table 1). The equation used to determine the % adsorption capability (*A*) for each of the metals studied is shown in Eq. (1).

$$\% A = 1 - \frac{CPS_f}{CPS_i} \times 100 \quad (1)$$

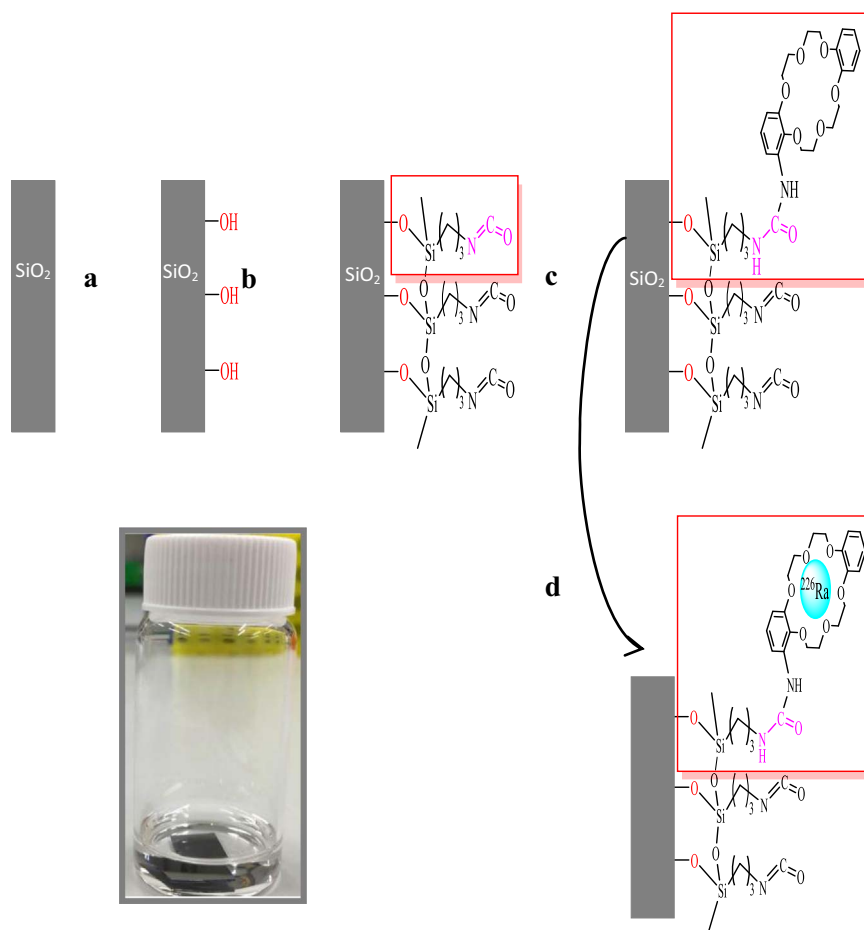
No adsorption of <sup>23</sup>Na was observable at pH 1. While at pH 7% adsorption of <sup>23</sup>Na (10%) was less than <sup>39</sup>K (18%), which demonstrates the selectivity of the dibenzo-18-crown-6 ether cavity toward ions of different ionic radii.

The chemical recovery of <sup>226</sup>Ra was measured by alpha-spectrometry at the following characteristic energies: 4601 keV (5.95%) and 4784 keV (94.03%) (Fig. 2). The percentage chemical recovery (% *R*) of <sup>226</sup>Ra was determined using Eq. (2):

$$\% R = 1 - \frac{A_f}{A_i} \times 100 \quad (2)$$

Where, *A<sub>f</sub>* refers to the measured activity i.e. the net decays per second (net counts/count time) and *A<sub>i</sub>* refers to the initial activity of solution prior to the addition of DB-18CE6-f SiO<sub>2</sub> disk. The chemical recovery of <sup>226</sup>Ra at pH 2 was determined to be 2.3%. To ensure the adsorption observed could be attributed to the treated dibenzo-18-crown-6 ether disk, a control experiment was performed containing the <sup>226</sup>Ra standard solution and an untreated SiO<sub>2</sub> disk. No adsorption was observed under these conditions.

The low recoveries at pH 2 could be attributed to the high affinity of dibenzo-18-crown-6 ether for hydronium ions (H<sub>3</sub>O<sup>+</sup>) (Gaikwad,



**Fig. 1. a–d** Reaction scheme for silica ( $\text{SiO}_2$ ) surface modification by the silane coupling agent, 3-triethoxysilylpropyl isocyanate (TESPI) and the crown ether structure, 4'-aminodibenzo-18-crown-6 ether ( $\text{NH}_2$ -DB-18CE6) to form DB-18CE6-functionalised  $\text{SiO}_2$  disks.

**Table 1**

Percentage adsorption capabilities (%A) for  $^{23}\text{Na}$  and  $^{39}\text{K}$  attained with a control sample (CPS<sub>i</sub>) and DB-18CE6-f  $\text{SiO}_2$  disks (CPS<sub>f</sub>) at pH 7 and pH 1, respectively.

Target Species	pH	CPS <sub>i</sub>	CPS <sub>f</sub>	%A
$^{23}\text{Na}$	7	6.99E+5	6.32E+5	10 (1)
$^{39}\text{K}$	1	1.20E+5	1.09E+5	9 (1)
$^{39}\text{K}$	7	1.30E+5	1.06E+5	18 (1)

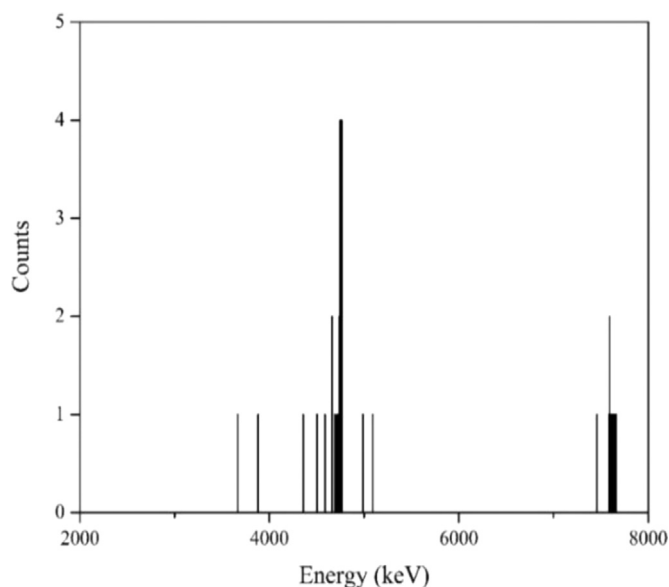
1987). The high concentration of  $\text{H}_3\text{O}^+$  present at pH 2 would compete with the trace amount of  $\text{Ra}^{2+}$  ions when binding to the cavity of the dibenzo-18-crown-6 ether extractant in place of  $^{226}\text{Ra}$ .

Future work will aim to improve the chemical recoveries of the DB-18CE6-f  $\text{SiO}_2$  disks, with literature suggesting that a pH range of 4–10 will substantially increase the chemical recovery (Mesnic et al., 2013).

#### 4. Conclusion

There is particular interest from industry in the development of novel and rapid analytical methods suitable for the determination of mBq levels of radium in a wide-range of environmental sample matrices. Present research indicates that the dibenzo-18-crown-6 ether-functionalised silica ( $\text{SiO}_2$ ) disks are capable of discriminating between cations of differing sizes such as  $^{23}\text{Na}$  and  $^{39}\text{K}$ . Moreover, the disks are potentially applicable to the separation and quantification of  $^{226}\text{Ra}$  in order to comply with the need for high selectivity and low limits of detection.

The application of  $\text{SiO}_2$  disks functionalised with crown ethers enables for rapid chemical separation and radiometric alpha-counting,



**Fig. 2.** Alpha spectrum of the DB-18CE6-f  $\text{SiO}_2$  disk exposed to 0.1 Bq of  $^{226}\text{Ra}$  at pH 2, collected for 36,000 s. The main  $^{226}\text{Ra}$  peak at  $E_\alpha=4.78$  MeV is apparent; the higher energy peak at 7.69 MeV is associated with the alpha decay of  $^{214}\text{Po}$  which is a daughter decay of  $^{226}\text{Ra}$ .

thus facilitating environmental monitoring and increasing the sample throughput for analysis. The method resulted in high-quality alpha-spectra of  $^{226}\text{Ra}$ , which confirms the feasibility of the proposed

analytical procedure.

Furthermore, increasing the chemical recovery of radium will help improve the efficiency of the method, therefore additional studies on pH dependency for the affinity of  $^{226}\text{Ra}$  to dibenzo-18CE6-SiO<sub>2</sub> disks is to be investigated especially in the neutral pH range.

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