

X-ray Photoelectron Spectroscopy Analyses of dicarboxylic acids – Part I - propanedioic acid anhydrous.

SECTION A - Authors

Jose Ferreira (CORRESPONDING AUTHOR, jose.ferreira@surrey.ac.uk), Gustavo F Trindade, Rene Tshulu, John F Watts, Mark A Baker
University of Surrey, The Surface Analysis Laboratory, FEPS mail stop A1, University of Surrey, Guildford, Surrey, GU2 7XH, United Kingdom

SECTION A - Overview

A-3. Abstract: X-ray photoelectron spectroscopy (XPS) was carried out to analyse a commercially available propanedioic acid (malonic acid) powder. XPS spectra were obtained using incident monochromatic Al K α radiation at 1486.6 eV. A survey spectrum together with O 1s and C 1s core level spectra are presented. The presence of characteristic carbon and oxygen photoelectrons peaks allows the use these results as a reference for dicarboxylic acids.

A-3a. Introduction: Propanedioic acid (malonic acid) is used as a chemical building block to produce a number of compounds; its main use being as a polymer precursor [1,2]. It is employed in chemical processes for the manufacture of special materials in a variety of industrial segments, with examples including special solvents, alkyd resins, nutritional, fragrances, electronics and pharmaceutical industries and also the production of surgical adhesives [3-5]. More recently, with the development of the biotechnology industry and the need to replace petrochemical compounds, propanedioic acid has been listed by the US Department of Energy as one of the top 30 chemicals produced from biomass [6].

Research addressing the potential of propanedioic acid for the corrosion protection of metal substrates can be dated back to the late 1950s. Its use as an electrolyte in the anodisation of aluminium suggests that the acid would be suitable for producing anodic coatings with a wide variety of structures and properties. Propanedioic acid has also been employed as a corrosion inhibitor on various metal substrates such as a carbon steel, copper and zinc [7-11].

In order to understand the interaction between dicarboxylic acids and metallic substrates, characterisation of the pure compounds is required. This work presents X-ray photoelectron spectroscopy results of a propanedioic acid standard powder. It is the first part in a series of three papers containing results for dicarboxylic acids with varying chain lengths: propanedioic, butanedioic and pentanedioic.

Dicarboxylic acids and their respective salts are rather unstable and known to undergo damage when exposed to X-rays, hence there was always a compromise between quality of spectra and level of damage, as reported for calcium oxalate by Salvi et. al [12]. The use of a 50 eV pass energy required a lower acquisition time to achieve a reasonable signal-to-noise ratio. For the same reason, the channel width was chosen to be 0.2 eV rather than the typical value of 0.1 eV. The acquisition time was 101 s. In addition to the spectra recorded under standard acquisition conditions, 'snapshot' spectra (acquisition time 1 s) of the C 1s and O 1s peaks are also presented to give an indication of a spectrum expected from an undamaged surface. The molecular structure of propanedioic acid (Figure 1) contains two carboxyl group carbons and one aliphatic carbon, and thus is expected to yield two C 1s photoelectron peaks at binding energies around 289 eV (-COOH) and 285 eV (C-C/C-H) [13] with an intensity ratio of 2:1. The observed (-COOH)/(C-C/C-H) intensity ratio from the C 1s snapshot scan is slightly lower (see Table 1) due to the additional presence of adventitious carbon contamination on the surface at 285 eV. For the results using standard acquisition parameters, two extra peaks were observed at 286.8 eV and 290.5 eV, associated with X-ray beam degradation. These peaks have been labelled as decomposition products (DP1 and DP2). The O 1s scan is expected to have two peaks at around 532 eV (C-O) and 533 (C=O) in equal proportions. Since the adventitious carbon contamination does not affect this O 1s peak intensity, the snapshot data showed two peaks at 532.0 and 533.3 eV with a 1:1 intensity ratio. For the results using standard acquisition parameters, an extra peak was observed at 534.1 eV (DP1), associated with X-ray beam degradation effects.

A-6a. # of digitally submitted specimen spectra for SSS publication: 5

A-6b. # of digitally submitted specimen spectra for electronic database only:

A-6c. # of digitally submitted calibration spectra: 3

A-7. Publish Auger Derivative Spectra: -

A-9. Spectra Category: [reference](#)

A-11. Acknowledgements: The authors wish to thank the funding agencies National Counsel of Technological and Scientific Development - CNPq (process 200490/2014-1) and the Coordination for the Improvement of Higher Education Personnel - CAPES (project: 11995-13-0).

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A-13. Comments on WCF:

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Suggested Reviewers

A-15a. Reviewer 1: [Prof. Herman Terryn](#). Delft University of Technology. hterryn@vub.ac.be

A-15b. Reviewer 2: [Dr. Peyman Taheri](#). Delft University of Technology. P.Taheri@tudelft.nl

A-15c. Reviewer 3: [Dr Nick Birbilis](#) Monash University nick.birbilis@monash.edu

Keywords: [propanedioic acid](#), [malonic acid](#), [carboxyl group](#), [XPS](#), [organic acid](#), [dicarboxylic acid](#)

Major Elements in Spectra: [C](#), [O](#)

Minor Elements in Spectra:

SECTION A - REFERENCES

1. E. Seong-il. AATCC Review, 1, 3 (2001).

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SECTION B - SPECIMEN DESCRIPTION

Specimen #: 1

B-1. Host Material: H_4C_3O_4 powder

B-2. Chemical Abstract Service (CAS) Registry #: 141-82-2

B-3a. Material Designation Code: 295-503-0

B-3b. Material Designating Organization: European Community

B-4. Host Composition: H_4C_3O_4

B-5. Chemical Name: propanedioic acid

B-6. Specimen Manufacturer/Supplier: Sigma-Aldrich

B-7. Specimen Form: Powder

B-8. Lot Number: XBB7011V

B-9. Structural Formula: see figure for structural formula

- B-10. Homogeneity: [Homogeneous](#)
- B-11. Phase: [Powder](#)
- B-12. Crystallinity: [Polycrystalline](#)
- B-13. Electrical Characteristics: [Dielectric](#)
- B-14. Material Family: [Organic Compound](#)
- B-15. Special Material Classes: [Powder](#)
- B-16. History and Significance: [see introduction](#)
- B-17. As Received Condition: [Powder form in a plastic container](#)
- B-18. Analyzed Region:
- B-19. Ex Situ Preparation and Mounting: [Four technical repeats of the sample were mounted on pre-cleaned \(isopropanol and acetone\) metal stubs. The stubs contain a small hole \(1mm diameter\). The powder was sprinkled into the stub hole with no pressure applied. No adhesive was used.](#)
- B-20. In Situ Preparation: [Immediately after mounting, the sample was moved to the prep chamber and kept in there for 12 hours in order to achieve optimal working pressure.](#)
- B-21. Specimen Temperature During Analysis (Kelvin): [300](#)
- B-22. Maximum Chamber Pressure During Analysis (in Pa): [1.2x10⁻⁷](#)
- B-23. Pre-Analysis Beam Exposures: [To minimise beam damage, different areas were analysed for each high resolution scan \(C1s and O1s, including snapshots\). In order to guarantee that the different technical repeats and areas were compatible, a quick check with a 1s snapshot of the C1s peak was performed in a neighbour area prior to each measurement.](#)
- B-24. Charge Control Conditions and Procedures: [Flood gun was used for charge neutralisation. Electron energy -2.5 V
Extractor 40 V
Emission 400 uA](#)

The binding energy values were corrected for C 1s at 285.0 eV.

SECTION C - INSTRUMENT DESCRIPTION

- C-1. Spectrometer Manufacturer: [Thermo Scientific](#)
- C-2. Manufacturer Model #: [Theta Probe](#)
- C-2a. Short identifying name for instrument: [Theta Probe](#)
- C-3. Analyzer Type: [SSA](#)
- C-4. Non-Standard Analyzer or Lens:

C-5. Acceptance Angle from Analyzer Axis (degrees): 60

C-6. Analyzer Mode: constant pass energy

C-7. Instrument Throughput Function: other

C-8. Instrument Throughput Function Comment: The transmission function is calculated from a cubic polynomial fit to a plot of LOG (Peak Area * XSF/PE) vs. LOG (RR). RR= KE/PE (Retard Ratio = Kinetic Energy/Pass Energy). XSF is a term to account for the difference in absolute sensitivities at the Ag MNN and Ag 3d peaks.

C-10. Excitation Source Window or Filter: None

C-11. Detector Description: Multi-channel plate detector

C-12. Number of Detector Elements: 128

C-12a. Was an Ion Gun Used? no

C-13a. Ion Gun Manufacturer:

C-13b. Ion Gun Model #:

C-14. Sputtering Current Measurement Method:

Ion Gun Operating Parameters

C-15a. Energy (in eV):

C-15b. Current Value:

C-15c. Current Units:

C-15d. Sputter Species:

C-15e. Sputter Charge:

C-16. Ion Gun Spot Size (um):

Ion Gun Raster Parameters (normal to source):

C-17a. Was Ion Gun rastered?

C-17b. X-Raster (um):

C-17c. Y-Raster (um):

C-18. Sputtering Comments:

C-19a. Emission Angle (Θ e): 53

C-19b. Incident Angle (Ψ ; i): 30

C-19c. Source-to-Analyzer Angle (Θ ; s): 67.4

C-19d. Specimen Azimuthal Angle (Φ ; sp): 70

C-19e. Sputter Source Incident Angle (Ψ ; ig):

C-19f. Sputter Source Polar Angle (Θ ; ig):

C-19g. Sputter Source Azimuthal Angle (Φ ; ig):

C-20. Angular Geometry Comments:

SECTION D - CALIBRATION INFORMATION

Analyzer Calibration Table

Seq #	Spectrum #	Element	Peak Transition	Peak Energy (eV)	Peak FWHM	Peak Amplitude	Sensitivity Factor	Concentration	Peak Assignment	Peak Assignment Comment
1	3089	Au	4f_{7/2}	83.69	0.62	566	2.8	100	gold metal	
2	3090	Ag	3d_{5/2}	368.16	0.52	4808	3.1	100	silver metal	
3	3091	Cu	2p_{3/2}	932.61	0.81	6827	4.2	100	copper metal	

SECTION E - VARIABLE INSTRUMENT PARAMETERS

E-1. Param Set #: 1

E-1a. Technique: XPS

E-1b. Describe Technique if you selected 'other' above:

Excitation Source Parameters

ES-1. Source Label: Al Ka, monochromated

ES-2. Describe Source if you selected 'other' above:

E-2. Source Energy (eV): 1486.6

E-3a. Strength: 300

E-3b. Strength Unit: watts

Excitation Source Beam

E-4a. Source Beam Size, X Value (um): 50

E-4b. Source Beam Size, Y Value (um): 50

E-5. Was the Source rastered? No

Excitation Source Beam Size at Specimen Surface

E-6a. Source Size at Specimen Surface, X (um): 400

E-6b. Source Size at Specimen Surface, Y (um): 400

E-7. Raster Frame Rate (Hz):

E-8. Analyzer Resolution:

E-8a. Analyzer Resolution Unit: eV (constant pass energy)

E-9 Analyzer Constants: 50

E-9a. Choose eV for pass energy, otherwise blank: eV

Analyzer Widths

E-10a. Analyzer Widths, X Value (um): 800

E-10b. Analyzer Widths, Y Value (um): 800

E-10c. Was the Analyzer Width constant with energy? yes

E-10d. Analyzer Widths, at Energy (eV):

Analyzer Angular Acceptance Widths

E-11a. Analyzer Angular Acceptance Width, X Angle (degrees): 30

E-11b. Analyzer Acceptance Width, Y Angle (degrees): 30

E-11c. Was the Analyzer Angular Acceptance Width constant with energy? yes

E-11d. Analyzer Angular Acceptance Width, at Energy (eV):

E-1. Param Set #: 2

E-1a. Technique: XPS

E-1b. Describe Technique if you selected 'other' above:

Excitation Source Parameters

ES-1. Source Label: Al Ka, monochromated

ES-2. Describe Source if you selected 'other' above:

E-2. Source Energy (eV): 1486.6

E-3a. Strength: 300

E-3b. Strength Unit: watts

Excitation Source Beam

E-4a. Source Beam Size, X Value (um): 50

E-4b. Source Beam Size, Y Value (um): 50

E-5. Was the Source rastered? No

Excitation Source Beam Size at Specimen Surface

E-6a. Source Size at Specimen Surface, X (um): 400

E-6b. Source Size at Specimen Surface, Y (um): 400

E-7. Raster Frame Rate (Hz):

E-8. Analyzer Resolution:

E-8a. Analyzer Resolution Unit: eV (constant pass energy)

E-9 Analyzer Constants: 221.28

E-9a. Choose eV for pass energy, otherwise blank: eV

Analyzer Widths

E-10a. Analyzer Widths, X Value (um): 800

E-10b. Analyzer Widths, Y Value (um): 800

E-10c. Was the Analyzer Width constant with energy? yes

E-10d. Analyzer Widths, at Energy (eV):

Analyzer Angular Acceptance Widths

E-11a. Analyzer Angular Acceptance Width, X Angle (degrees): 30

E-11b. Analyzer Acceptance Width, Y Angle (degrees): 30

E-11c. Was the Analyzer Angular Acceptance Width constant with energy? yes

E-11d. Analyzer Angular Acceptance Width, at Energy (eV):

SECTION F - SPECTRA

Field Name	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
Spectrum #	1	2	3	4
This spectrum is from which Part B Specimen?	1 - H_4C_3O_4 powder	1 - H_4C_3O_4 powder	1 - H_4C_3O_4 powder	1 - H_4C_3O_4 powder
Suggested Publication Status:	Print in SSS	Print in SSS	Print in SSS	Print in SSS
Spectrum Data File Name	1- Malonic acid survey.txt	1- Malonic acid C1s snapshot.tx	1- Malonic acid O1s snapshot.tx	1- Malonic acid C1s peak.txt
Data File Comment:	shifted data are on "Survey" tab of additional .xls file	Shifted and peak-fitted data are on tab "Snapshot C1s snapshot 285 eV" of additional .xls file.	Shifted and peak-fitted data are on tab "Snapshot O1s snapshot 532 eV" of additional .xls file.	Shifted and peak-fitted data are on tab "Snapshot C1s" of additional .xls file.
Spectrum Figure Image File Name	Survey.png	C1s snapshot.png	O1s snapshot.png	C 1s.png
Specimen or Calibration Spectrum:	specimen	specimen	specimen	specimen
Parameter Set # Used	1 - Al Ka, monochromated	2 - Al Ka, monochromated	2 - Al Ka, monochromated	1 - Al Ka, monochromated
Spectrum Date	2016-09-10	2016-09-09	2016-10-10	2016-09-08
Species/ Transitions:	C C1s, O O1s	C C 1s	O O 1s	C C1s
Spectral Region Comment:				
Abcissa Label	binding energy	binding energy	binding energy	binding energy
Abcissa Starting Value (eV):	1350	295.41	542.41	298
Abcissa Increment Value:	0.4	0.188	0.188	0.2
Ordinate Label:	Intensity	intensity	Intensity	Intensity
Ordinate Units:	counts/sec	counts/s	counts/s	counts/sec

Field Name	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
Number of Data Channels:	3401	112	112	101
Number of Scans:	3	1	1	20
Signal Mode:	pulse	pulse	pulse	pulse
Detector Width (eV):	0.4	0.188	0.188	0.2
Total Signal Accumulation Time (sec):	510.15	1	1	101
Total Elapsed Time (sec):	1025	1	1	271.68
Is 'raw data' signal intensity corrected? (Yes/No):	No	No	No	No
Signal Intensity Correction Comment:				
Signal Modulation Method:	none	none	none	none
Peak-to-peak amplitude of Modulation (eV):				
Modulation Frequency of Reference Signal (Hz):				
Time Constant of Lock-in Amplifier Used (sec):				

Field Name	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8
Spectrum #	5	6	7	8
This spectrum is from which Part B Specimen?	1 - H_4C_3O_4 powder	*** No Section B - Specimens selected! ***	*** No Section B - Specimens selected! ***	*** No Section B - Specimens selected! ***
Suggested Publication Status:	Print in SSS	Database Only	Database Only	Database Only
Spectrum Data File Name	1- Malonic acid O1s peak.txt	Au calibration.txt	Ag calibration.txt	Cu calibration.txt
Data File Comment:	Shifted and peak-fitted data are on tab "Snapshot O1s " of additional .xls file.			
Spectrum Figure Image File Name	O 1s.png			
Specimen or Calibration Spectrum:	specimen	calibration	calibration	calibration
Parameter Set # Used	1 - Al Ka, monochromated	1 - Al Ka, monochromated	1 - Al Ka, monochromated	1 - Al Ka, monochromated
Spectrum Date	2016-09-09	2014-02-19	2014-02-19	2014-02-19
Species/ Transitions:	O O 1s			
Spectral Region Comment:				
Abscissa Label	binding energy	binding energy	binding energy	binding energy
Abscissa Starting Value (eV):	541	89	373	937
Abscissa Increment Value:	0.2	0.02	0.03	0.02
Ordinate Label:	Intensity	Intensity	Intensity	Intensity
Ordinate Units:	counts/sec	Counts/sec	Counts/sec	Counts/sec
Number of Data Channels:	101	501	501	401
Number of Scans:	20	10	10	10

Field Name	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8
Signal Mode:	pulse	pulse	pulse	pulse
Detector Width (eV):	0.2	0.02	0.02	0.02
Total Signal Accumulation Time (sec):	101	250.5	125.2	200.5
Total Elapsed Time (sec):	286.85	250.5	125.2	200.5
Is 'raw data' signal intensity corrected? (Yes/No):	No	No	No	No
Signal Intensity Correction Comment:				
Signal Modulation Method:	none	none	none	none
Peak-to-peak amplitude of Modulation (eV):				
Modulation Frequency of Reference Signal (Hz):				
Time Constant of Lock-in Amplifier Used (sec):				

SECTION H - ANALYSIS METHODS

H-1. Energy Scale Correction: The binding energy values were corrected for C 1s at 285.0 eV.

H-2. Recommended Energy-Scale Shift: Survey +1.0 eV

C 1s snapshot +0.81 eV

O 1s snapshot +1.41 eV

C 1s +0.8 eV

O 1s +0.8 eV

H-3. Intensity Scale Correction:

H-4. Peak Shape and Background Methods: The Smart background is derived from the Shirley background but iteratively adjusts the background position so that the background does not go above the data curve.

H-5. Quantitation Method: Relative % intensities (using respective sensitivity factors) on Avantage software.

SECTION I - Units for Spectral Features Quantitative fields

I-1. Peak Amplitude Method: peak area

I-2. Peak Amplitude Units: eV x counts/sec

I-3. Concentration Units: atomic percent

I-4. Comments to Spectral Features Table:

Table of Spectral Features

Seq #	Spectrum #	Element	Peak Transition	Peak Energy (eV)	Peak FWHM	Peak Amplitude	Sensitivity Factor	Concentration	Peak Assignment	Peak Assignment Comment
1	3092	C	1s	285	1.98	189.1	0.25	38.16	C-C/C-H	
2	3092	C	1s	288.9	1.98	306.2	0.25	61.84	COOH	
3	3093	O	1s	532	2.37	852.2	0.66	49.14	C=O	
4	3093	O	1s	533.3	2.55	881.7	0.66	50.86	C-OH	
5	3087	C	1 s	285	2.0	3031	0.25	40.06	C-C/C-H	
6	3087	C	1s	286.8	1.5	375	0.25	4.96	DP1	
7	3087	C	1s	288.9	1.6	3877.7	0.25	51.28	-COOH	
8	3087	C	1s	290.5	1.7	279.8	0.25	3.7	DP2	
9	3088	O	1s	532	1.63	12711.1	0.66	51	C=O	
10	3088	O	1s	533.1	1.49	8942.7	0.66	35.89	C-OH	
11	3088	O	1s	534.1	1.75	3264.0	0.66	13.1	DP2	

FIGURE IMAGE FILES

This submission has 5 spectrum records with associated image files.

Spectrum No 1: [Survey.png](#)

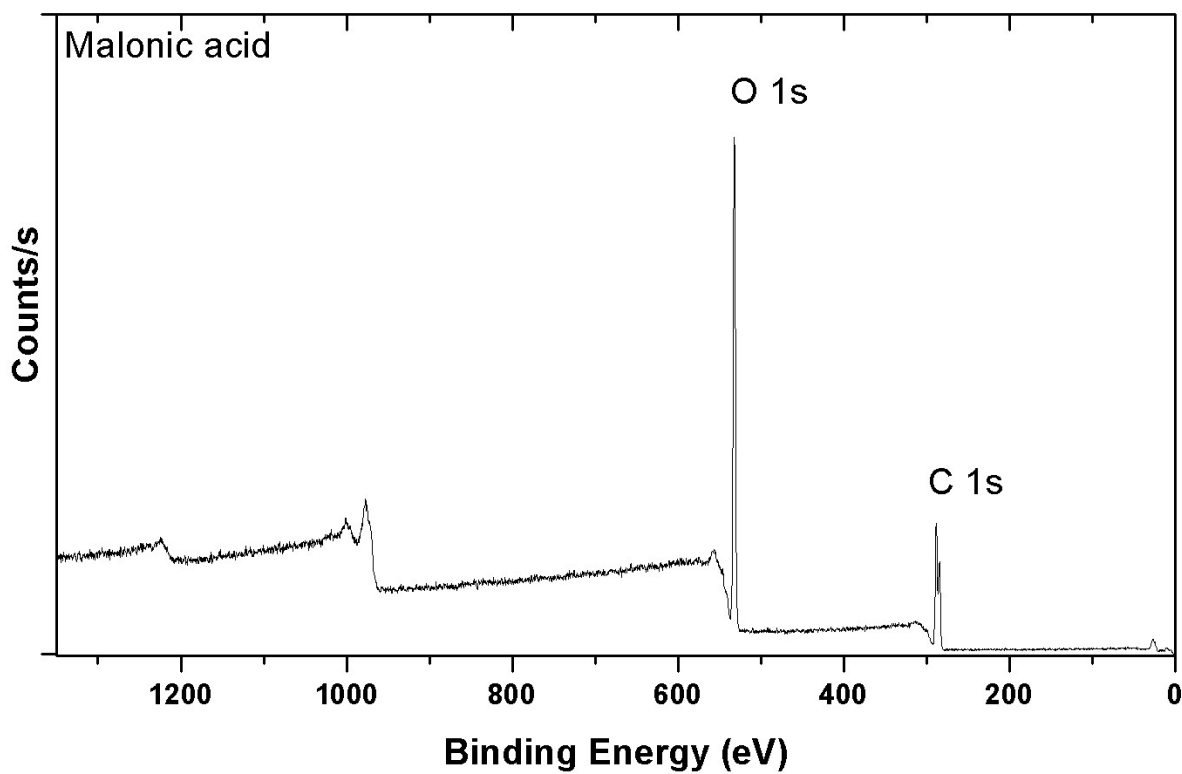
Spectrum No 2: [C1s snapshot.png](#)

Spectrum No 3: [O1s snapshot.png](#)

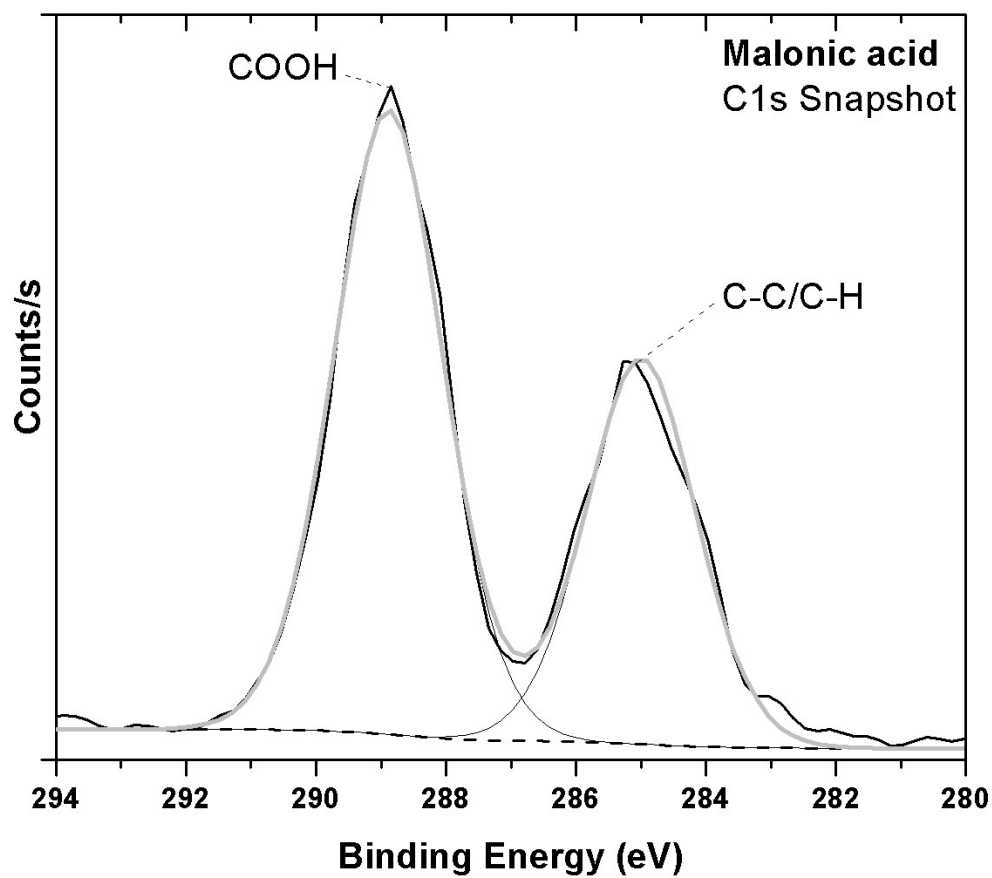
Spectrum No 4: [C 1s.png](#)

Spectrum No 5: [O 1s.png](#)

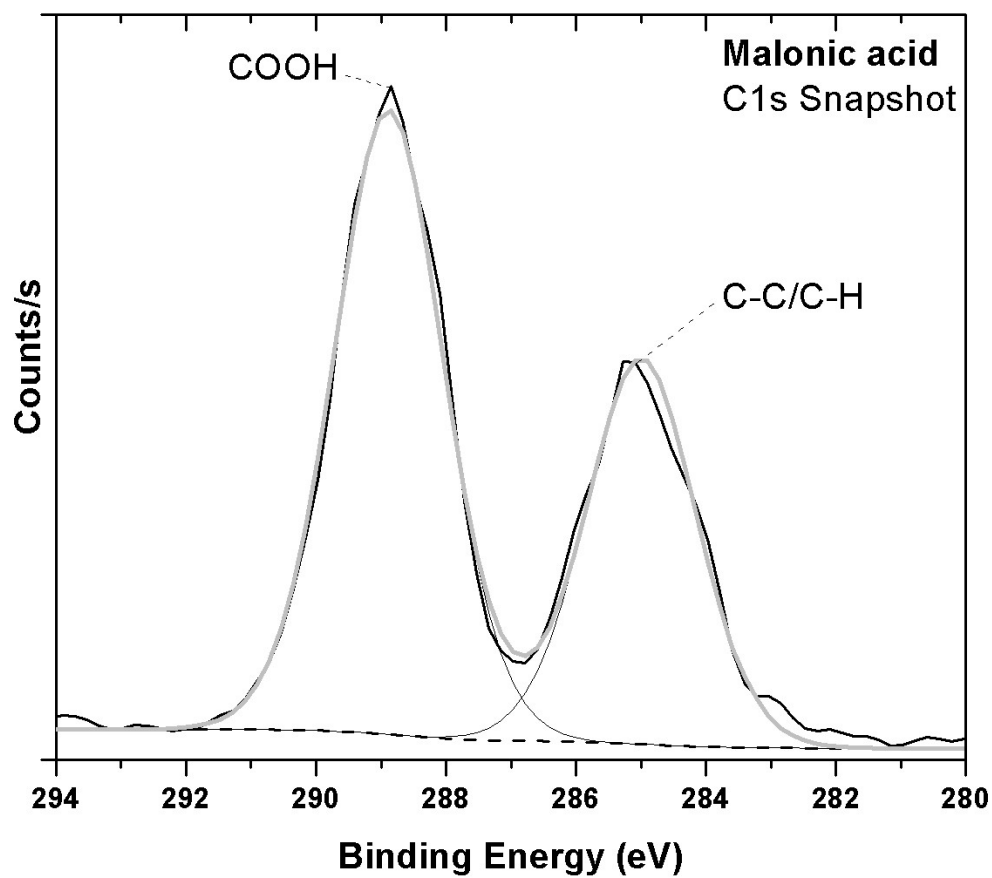
Survey.png



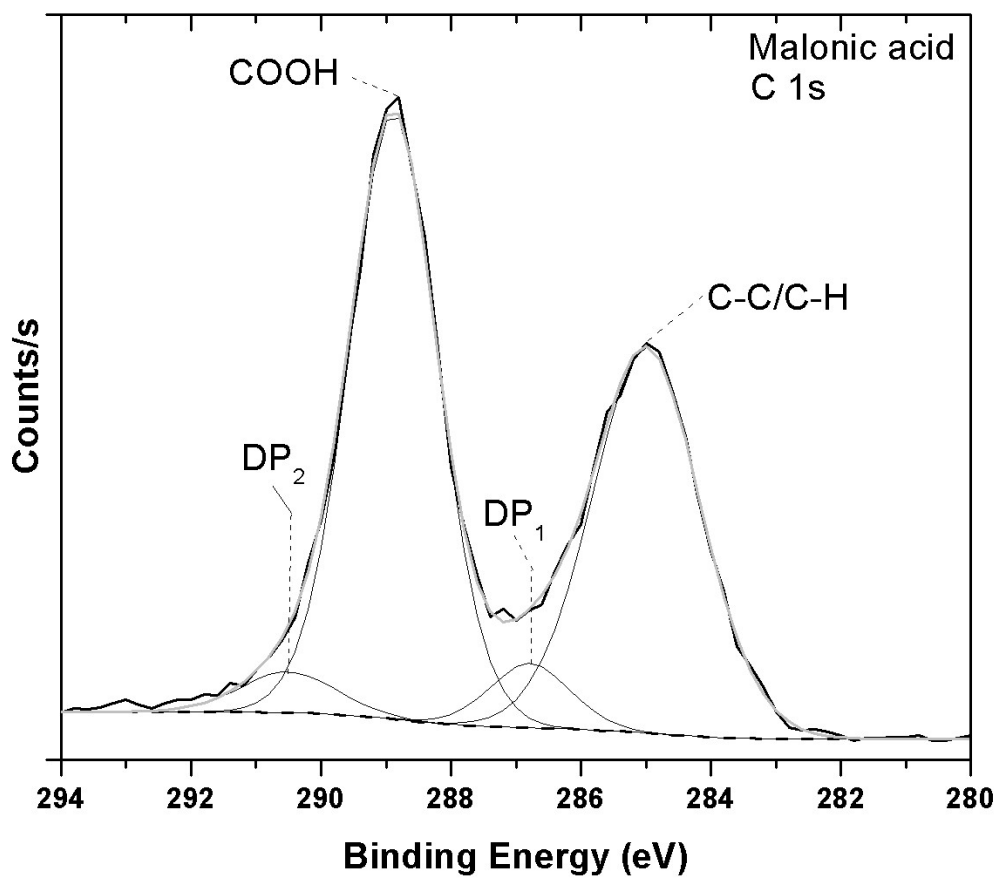
C1s snapshot.png



O1s snapshot.png



C 1s.png



O 1s.png

