X-ray Photoelectron Spectroscopy Analyses of dicarboxylic acids – Part III - Pentanedioic acid anhydrous.

SECTION A - Authors

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SECTION A - Overview

A-3. Abstract: X-ray photoelectron spectroscopy (XPS) was carried out to analyse a commercially available pentanedioic 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.

A-3a. Introduction: Pentanedioic acid (glutaric acid) is naturally produced in metabolic pathways of certain aminoacids such as lysine and tryptophan. It can be synthesised via ring-opening of butyrolactone using potassium cyanide, followed by hydrolysis leading to the formation of diacid [1,2]. Glutaric acids's most common use is as a plastifier and a polyester precursor [3,4], mainly for polyols and polyamides. It has been used in the production of cyclohexanone, which is a key intermediate product for the production of adipic acid used in the synthesis of Nylon 66 [5] and has been employed in different industrial sectors as corrosion inhibitor, with a number of patents related to its use being reported [6,7,8].

In order to understand the interaction between dicarboxylic acids and metallic substrates, characterisation of the pure compounds is required. The present work presents X-ray photoelectron spectra of a standard pentanedioic acid powder. It is the third part of a series of three papers presenting results for standard 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 [9]. 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 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 three 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) [10] with an intensity ratio of 2:3. 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](#)

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A-13. Comments on WCF:

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

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Keywords: [pentanedioic acid](#), [glutaric acid](#), [dicarboxylic acids](#), [carboxyl group](#), [organic acids](#)

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

Minor Elements in Spectra:

SECTION A - REFERENCES

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SECTION B - SPECIMEN DESCRIPTION

Specimen #: 1

B-1. Host Material: [H_8C_5O_4 powder](#)

B-2. Chemical Abstract Service (CAS) Registry #: [110-94-1](#)

B-3a. Material Designation Code: [203-817-2](#)

B-3b. Material Designating Organization: [European Community](#)

B-4. Host Composition: [H_8C_5O_4](#)

B-5. Chemical Name: [Pentanedioic acid](#)

B-6. Specimen Manufacturer/Supplier: [Sigma-Aldrich](#)

B-7. Specimen Form: [Powder](#)

B-8. Lot Number: [STBF 1247V](#)

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): 1.2×10^{-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 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	3105	Au	4f_{7/2}	83.69	0.62	566	2.8	100	gold metal	
2	3106	Ag	3d_{5/2}	368.16	0.52	4808	3.1	100	silver metal	
3	3107	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: 221.8

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_8C_5O_4 powder	1 - H_8C_5O_4 powder	1 - H_8C_5O_4 powder	1 - H_8C_5O_4 powder
Suggested Publication Status:	Print in SSS	Print in SSS	Print in SSS	Print in SSS
Spectrum Data File Name	2-Glutaric acid survey data.txt	3-C1s snapshot data.txt	3-O 1s snapshot.txt	3- Glutaric acide C1s peak.txt
Data File Comment:	Shifted data are on "Survey" tab of additional .xls file.	Shifted and peak-fitted data are on "Snapshot 285 eV" tab of additional .xls file.	Shifted and peak-fitted data are on "Snapshot 532 eV" tab of additional .xls file.	Shifted and peak-fitted data are on "C 1s" tab of additional .xls file.
Spectrum Figure Image File Name	Survey.png	C1s snapshot.png	O 1s 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	2016-09-19	2016-09-19	2016-10-24	2016-09-17
Species/ Transitions:	O O1s, C C1s	C C1s	O O 1s	C C1s
Spectral Region Comment:				
Abscissa 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/sec	Counts/sec	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	101.5
Total Elapsed Time (sec):	1025	1	1	287.68
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_8C_5O_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	3- Glutaric acid O1s peak.txt	Au calibration.txt	Ag calibration.txt	Cu calibration.txt
Data File Comment:	Shifted and peak-fitted data are on "O 1s" tab 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	2016-09-17	2014-02-19	2014-02-19	2014-02-19
Species/ Transitions:	O O1s			
Spectral Region Comment:				
Abscissa Label	binding energy	binding energy	binding energy	binding energy
Abcissa Starting Value (eV):	541	89	373	937
Abcissa Increment Value:	0.2	0.02	0.02	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):	101.5	250.5	125.2	200.5
Total Elapsed Time (sec):	300.45	250.5	125.4	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 +1.60 eV

C 1s snapshot +1.68 eV

O 1s snapshot +1.87 eV

C 1s +1.60 eV

O 1s +1.60 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	3108	C	1s	285	2.03	349.55	0.25	60.07	C-C/C-H	
2	3108	C	1s	288.9	2.37	232.1	0.25	39.93	-COOH	
3	3109	O	1s	532.1	2.43	408.49	0.66	50.33	C=O	
4	3109	O	1s	533.2	2.37	402.89	0.66	49.67	C-OH	
5	3104	C	1s	285.0	1.35	5321.81	0.25	59.51	C-C/C-H	
6	3104	C	1s	286.7	1.35	374.54	0.25	4.19	DP1	
7	3104	C	1s	289.1	1.26	2939.54	0.25	32.89	-COOH	
8	3104	C	1s	290.1	1.26	304.71	0.25	3.41	DP2	
9	3103	O	1 s	532.1	1.45	7338.8	0.66	44.21	C=O	
10	3103	O	1s	533.3	1.67	8543.08	0.66	51.48	C-OH	
11	3103	O	1s	534.5	1.73	715.53	0.66	4.31	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: [O 1s snapshot.png](#)

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

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

Survey.png

C1s snapshot.png

O 1s snapshot.png

C 1s.png

O 1s.png