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Exploratory Methodology for Retrieving Oxidation State Information from X-Ray Resonant Raman Scattering Spectrometry

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ABSTRACT: It has been observed recently that the Resonant Raman Scattering (RRS) peak of an x-ray spectrum contains information about the chemical environment of the irradiated matter. This information is extracted with complex processing of the spectrum data. Principal Component Analysis is a statistical multivariate technique that allows exploring the variance-covariance structure of a set of data, through a few linear combinations of the original variables. This methodology can be applied to obtain information from RRS spectra. To analyze its potentiality several measurements of different oxides in surface nanolayers were measured in total reflection conditions using synchrotron radiation. Multivariate analysis techniques, in particular Principal Component Analysis (PCA), were used to obtain the information encrypted in the RRS peak, and to establish a new methodology, simpler and more accurate. The results show that multivariate analysis techniques are suitable for the analysis of this kind of spectra, foreseeing its application in future researches.

INTRODUCTION

When atoms are irradiated by x-ray photons, different kinds of interactions may take place. These interactions can be classified into two types: first order processes, which have a high probability of occurrence, and second order processes, which have lower probability. However, under resonant conditions, some second order processes turn dominant, and have probability of occurrence as high as first order ones, as is the case of x-ray Resonant Raman Scattering (RRS).

There are several different methods to determine oxidation states in different kinds of materials¹. Alternative methods for determining a sample's chemical environment are needed since they can be crucial for specific experimental conditions. The existence of chemical environment information in the x-ray Resonant Raman Scattering peak has been shown in a previous work by Leani et. al.². This peak has an asymmetric form, with an asymmetry in the low energy side of the peak, so called fine structure, and Leani et. al. have shown that chemical environment information is encrypted in this region. They have compared the oscillations present in the RRS tail with the typical oscillations existent in an EXAFS³ spectrum, and have found important similarities. These oscillation patterns, present in the fine structure of the RRS peak, are attributed to the interaction of the emitted photoelectrons with the neighboring atoms. This interaction modifies the state density and the final state configuration of the excited atom⁴. But one of the problems of the method proposed by Leani et. al. is its high complexity in the processing of the data as to obtain the residuals, in which the oscillations are observable.

The method used involves adjusting Voigt functions for the low energy regimen and Lorentzian functions for the region near the center of the peak, it also takes into account Fast Fourier Transform smoothings and other mathematical methods.

The use of multivariate statistical methods, such as Principal Component Analysis (PCA)⁵, has been suggested recently as an alternative analysis⁶. These methods were applied to samples with a specific oxidation state. Nevertheless, sometimes it is of interest to examine samples, which have a more complex chemical environment, such as nanometric-layered surfaces of layers with different oxidation states. In such cases it is possible to do a depth profile analysis of the chemical environment of the sample exposed to irradiation by combining RRS with Grazing Incidence Analysis⁷. This allows obtaining local structural information of the element of interest with nanometric resolution. In order to accomplish this aim, the use of a radiation source with a tunable beam, sufficiently collimated and of high intensity is imposing. This is why a synchrotron radiation facility was needed.

Principal Component Analysis is a statistical multivariate technique that analyzes the variance-covariance structure of a set of data, through a few linear combinations of the original variables (suppose we have p of them). Its main objectives are (1) dimension reduction, and (2) interpretation in high dimensional data. Although all p components are required to reproduce the total system variability, often a small number, k , of new variables generated through linear combination of the original variables, so called principal components, can account for an important part of the total variability. The k principal

components can then replace the initial p variables reducing the original data set, consisting of n measurements on p variables, to one of n measurements on k principal components. The distinguishing step of this method is how it selects the constants in the linear combinations of the original variables, so as to account for the most important fraction of the total variability⁵. In a brief explanation, Principal Components (PC's) are non-correlated linear combinations of the p original variables, which coefficients are selected in order to maximize the variance that they represent⁸. These new variables allow studying by parts the variability existent in the data set and permit a different interpretation that many times isn't possible from direct observation of the data set. Applied to spectra analysis, PCA allows studying the variability of the energy channels in a set of spectra, and situates all spectra in a new hyperspace, which has the PC's as basis. Analyzing the projection onto two axes of this hyperspace allows interpreting high dimensional data by simple observation. The variability under study will depend on the selection of the two axes, i. e. the PC's one chooses for the projection plane.

The objective of this work is to evaluate the potentiality, of discriminating changes in the chemical environment of superficial nano-metric layers of metallic compounds, using a new method involving PCA in the analysis of data encrypted in RRS peak.

EXPERIMENTAL

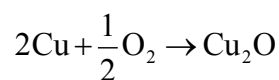
Sample Preparation

Four samples were prepared and irradiated with monochromatic synchrotron radiation. The sample preparation was approached by two different techniques:

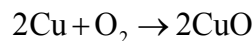
1. *In situ* oxidation of a pure sample of Cr or Cu foil by modifying its temperature through an external heat source during the irradiation period.
2. Prior oxidation of the Cr or Cu substrates before the irradiation period. These samples consisted of two superposed layers (called multilayer) of different oxides of the corresponding metal substrates.

In the first approach the samples were deposited on a silicon wafer via sputtering. Sample (1) consisted of pure Cu foil and sample (2) of pure Cr foil, both with a purity higher than 99.9% and a thickness of (19.8 ± 0.1) nm and (19.9 ± 0.1) nm, respectively. In the second approach, sample (3) consisted of a lower layer of Cu_2O with a thickness of (19.9 ± 0.1) nm and an upper layer of CuO with the same thickness. Sample (4) was made of a lower layer of CrO and an upper layer of Cr_2O_3 , both with a thickness of (20.0 ± 0.1) nm. All layers were deposited over silicon wafers of approximately 1 cm^2 . Samples were prepared in FaMAF's laboratories, at Córdoba National University, Argentina. The thickness of the layers were estimated by the weight of the deposited material, measured with a nanoscale.

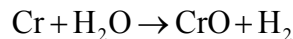
For the assembling of sample (3), a pure Cu foil of (19.9 ± 0.1) nm thickness was deposited via sputtering, followed by a 2 hour thermal treatment at $600 \text{ }^\circ\text{C}$, allowing oxidation of Cu to Cu_2O , represented by the following reaction:



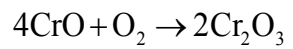
After this thermal treatment, a second layer of pure Cu was deposited on top, and was left at room temperature during 72 hours, allowing it to oxidize to CuO under the following reaction:



In the assembling of Sample (4), a (20.0 ± 0.1) nm thick pure Cr foil was deposited via sputtering, and oxidized to CrO by submerging it in distilled water during 24 hours, allowing the following reaction to take place:



Then another layer of pure Cr, of thickness (20.0 ± 0.1) nm, was deposited on top. This layer was firstly oxidized to CrO in the same way explained above and it was later heated at $100 \text{ }^\circ\text{C}$ in a tubular oven during 12 hours, allowing the following reaction to occur:



in order to obtain Cr_2O_3 .

Measurements

Several spectra were measured for each experimental condition. For the oxidation "in situ" case, spectra were measured at a fixed angle under total reflection and for the multilayer case, spectra were measured at different incident angles, consequently, at different depth positions.

Measurements were carried out in XRF station of the D09B-XRF beamline⁹ at the Brazilian synchrotron facility (LNLS, Campinas)¹⁰. The XRF beamline is equipped with a double crystal "channel-cut" monochromator, the energy resolution of the monochromator is 3 eV at 10 keV using a Si(111) crystal. For the measurements performed in this work, the incident beam was collimated with orthogonal slits to $7 \times 0.5 \text{ mm}^2$ and monitored with ionization chambers, resulting in flux intensity on the sample of approximately 108 ph/s at 10 keV. The detection systems used for these measurements was an energy dispersive type and the detector used was an ultra-LEGe solid-state detector with a Be window of $8 \text{ }\mu\text{m}$ and an energy resolution of 140 eV for de Mn-K α line. The experimental geometry for all samples was a typical total reflection setup in grazing incidence configuration in the orbit's plane so as to minimize effects of Compton Scattering and Rayleigh Scattering¹¹. Samples were placed on a high-resolution goniometric stage, allowing rotations with a precision of 0.0001° and displacements in x, y and z directions of the Cartesian coordinate system with a precision of $1 \text{ }\mu\text{m}$.

Before starting the measurements of prepared samples, fluorescent peak's intensity was measured for different angles of incident beam, so as to calibrate the angle of incidence. The angular scanning performed allowed obtaining the critical angle by comparing it with the theoretical reflectivity curve¹¹. Once obtained the critical angle, all measurements of Cu RRS spectra were performed, for which the incident energy was set to 8964 eV, a few eV below the Cu absorption edge (8989 eV), optimizing RRS production.

30 RRS spectra of sample (1) were measured in the same experimental configuration. Each spectrum was measured during 3 s. During this stage the sample was allowed to oxidize "in situ" by putting it in contact with an external heat source (approximately $400 \text{ }^\circ\text{C}$). The angle of incidence was fixed at 0.3200° allowing total reflection to occur.

A total of 150 spectra of sample (3) were measured in Total Reflection (TR) conditions. These spectra consisted of measurements of 10 spectra at 15 different incident angles. The grazing incident angle was modified in steps of 0.0679° . Exposure time to the beam was of 300 seconds in each spectrum.

For the Cr-sample experiments, the energy of the incident beam was set to 5971 eV, also a few eV below de Cr absorption edge (5989 eV). Pure Cr sample (sample (2)) was exposed to monochromatic beam while in contact with the same external heat source as in measurements mentioned before, allowing it also to oxidize "in situ". On the other hand, 20 spectra were measured, each with 2 seconds of exposure, fixing the grazing incident angle at 0.5000° . Finally, spectra of sample (4) (Cr multilayer) were measured. The incident angle was modified 10 times in steps of 0.0433° , fixing the first TR angle at 0.3280° . In this case, 10 spectra were collected for each angle, resulting in 100 spectra. Each spectrum was exposed to the beam during 300s.

DATA ANALYSIS

Spectra were processed as to identify the RRS peak. Origin 8¹³, Mathcad¹⁴ and InfoStat¹⁵ were the programs used for spectra manipulation, preprocessing of data and statistical analysis. Preprocessing of data consisted first of all in obtaining the average spectrum of spectra measured in each experimental condition. Then, channels corresponding to RRS peak "tail" were selected, identifying them in the average spectrum. This selection consisted in those beneath the channel with maximum count of the peak and those larger than a channel not identifiable in the peak or belonging to an adjacent peak. Preprocessing concluded with the normalization of the selected data to the maximum intensity of the peak.

Before applying PCA, a Hierarchical Cluster Analysis (HCA) was performed to data of channels selected from spectra of the "in situ" oxidation experiments. An Euclidean distance matrix was processed with Ward's clustering method¹⁶ to quantify differences between pairs of spectra and to identify as much clusters as oxidation states expected in each experiment. Spectra were also visualized in the PC1-PC2 plane obtained from a PCA applied on the correlation matrix between energy channels; observations were discriminated in the above mentioned PCA plane obtained in function of the cluster assigned by the previous clustering algorithm.

Spectra of the multilayer measurements were also visualized in a PC1-PC2 plane. These PC's were obtained from a PCA applied to the correlation matrix between energy channels of the multilayer spectra. Since the depth penetration of the beam was known (from the angle of incidence) in each measurement, observations were discriminated in the mentioned PCA plane with different symbols depending on the layer to which it belonged in the multilayer compound.

RESULTS

Spectra corresponding to the low-energy side of the RRS peak are shown in Fig. 1. They belong to the pure Cu sample (sample 1) that was oxidized "in situ" through contact with an external heat source and are normalized to unity.

From the calculated average lectures and variation coefficients (shown in Table 1) it can be seen that the largest relative variation in a channel is present in those energies most

distant from the maximum of the peak. Two clusters can be evidenced clearly in the dendrogram of Fig. 2, obtained with hierarchical clustering algorithm. The numbering of the spectra in this graph represents ordering in time, being n° 1 the first spectrum measured, consisting of the counts in 3 seconds of exposure to the beam and to the heat source, and n° 30 the last, also of 3 seconds of exposure to the beam and heat source, but with 87 seconds previous of exposure to the heat source. From the observation of Fig. 2 it can be concluded that the first 13 spectra do not have substantial differences between themselves, and belong to the group of spectra of pure Cu. The remainders of the measurements are also very similar to each other and different from the first 13 spectra; they correspond to a new group of oxidized Cu.

After applying PCA to the data set and observing the eigenvalues of the PC's (Table 2), a score plot of the spectra in the PC1-PC2 plane was made (Fig. 3). Though the first two PC's explain only 39% of the total variance in the data set (Table 2), it can be seen in Fig. 3 that the plane that they conform is sufficient to discriminate both groups of spectra suggested by the HCA (Fig. 2). Since PC's are orthogonal, the variability explained by one PC differs from the variability explained by any other PC. Since the variability covered by PC1 and PC2 with respect to the total variability is sufficient for a successful discrimination of the oxides, the PC1-PC2 plane is the most interesting plane of PC's and hence the plane observed. The separation of the two clusters suggested by the HCA in the PC1-PC2 plane supports their existence. It should be noticed that the clustering method used did not utilize any additional information about the oxidation state. Only the measured data were used.

Now focusing on the Cu multilayer experiment, 15 average spectra were measured for different incident angles. The correspondence between incident angle and depth penetration ($Z_{1/e}$) was established theoretically by the following equation:

$$Z_{1/e} = \frac{\lambda}{4\pi B}$$

being $B = \frac{1}{\sqrt{2}} \{[(\theta^2 - \theta_c^2) + 4\beta^2]^{1/2} - (\theta^2 - \theta_c^2)\}$, θ the incident angle, θ_c the critical angle of the media, $\beta = \mu\lambda/4\pi$ the imaginary part of the refraction index, λ the incident photon wavelength and μ the linear absorption coefficient.

PCA was applied to spectra and no discrimination was possible in any plane conformed by any principal components. The analysis seems to indicate the existence of only one oxidation state in the sample. A similar situation appeared in the Cr "in situ" oxidation experiment, where the dendrogram obtained with HCA to the data did not evidence any clustering in the data set (Fig 4). The existing variability between spectra is not useful for the discrimination of the expected groups. This seems to suggest that all spectra correspond to the same oxidation state; i. e. the sample never changed its oxidation state.

Studying now the case of the Cr multilayer sample, ten spectra were measured for ten different incident angles. An average spectrum was calculated for each angle, resulting in ten final spectra, each one associated with a different penetration depth. Again, normalization to the maximum of the RRS peak was performed in each spectrum (Fig. 5). Penetration depth was calculated theoretically for each angle of incidence as mentioned before, allowing the separation of spectra into two groups through comparison with the thickness of the layers: the first 5 spectra belonging to the external layer

(Cr₂O₃) and the rest (also 5 spectra) corresponding to the lower layer (CrO).

Once established the classification based on the theoretical depth, PCA was performed to the energies of interest and spectra were plotted in PC1-PC2 plane, and differentiation (by circles or triangles) was based on this classification (Fig. 6). Table 3 shows the constants of the linear combination that constitutes PC1. This principal component contains the information that allows the discrimination of different regions. It can be seen that the values of the constants in Table 3 change in sign for different energy ranges. This allows concluding that the region in the spectrum that characterizes one oxide is disjoint from the region that characterizes the other oxide.

Table 4 shows that PC1 and PC2 explain 55% of total variance existent in the set of spectra. It can be seen in Fig. 6 that this variability is sufficient for the discrimination of both oxidation states.

FINAL COMMENTS

Reviewing the results obtained from the multivariate analysis performed on the Cu “in situ” oxidized sample, it can be concluded that two oxidation states were differentiated at a specific temporal instant (between spectrum n° 13 and n°14, i. e. after 39 seconds of exposure to the beam and to the external heat source). This indicates that spectra information changed drastically after n°13 rather than gradually in time. This conclusion is supported by the HCA performed. All spectra in one cluster are those measured in the first 39 seconds, and all spectra measured afterwards are grouped in a second cluster, very different from the first cluster. Since we were expecting two oxidation states, this allows to associate the first cluster to the non-oxidized Cu and the second cluster to Cu in an oxidized state, confirming that the pure Cu sample was oxidized during the experiment. Another important fact that this analysis allowed to observe is that oxidation was very abrupt in time, i. e. it happened in less than 3 seconds, between one measurement and another. Similar behaviors have been observed in other works, such as the study of Cu surface oxidation by grazing angle x-ray excitation¹². Given the conditions of the experiment, the expected final oxidation state was copper (I) oxide. Summarizing, PCA allowed establishing PC's, formed by linear combination of the channels of the low energy regimen of RRS peak, that discriminate pure copper from copper (I) oxide, validating the objectives of this work.

The results of multivariate analysis applied to the Cu multilayer measurements evidenced problems in sample preparation. In the preparation, a layer of copper (II) oxide was deposited on a layer of copper (I) oxide. But compounds of copper (I) oxide can shift to copper (II) oxide with time¹⁷. Since time between the preparation of samples and performing the experiment was long (4 days), it is probable that the copper (I) oxide layer changed to copper (II) oxide. PCA showed that the spectra measured for all depths did not evidence substantial differences. This result shows that PCA supports the possibility of a transition from copper (I) oxide to copper (II) oxide.

HCA and PCA applied to data obtained in Cr “in situ” oxidation measurements didn't show any change in the analyzed sample's oxidation state. An interesting fact is that problems surged during these measurements: approximately after a minute of irradiation, the external heat source stopped heating, preventing the continuity of the experiment. Because of this,

measurements were restarted with a different external heat source, but using the same sample. During the measurements, this fact was considered irrelevant since the whole incident lasted less than a minute of exposure to the heat source. Nevertheless, comparing the time of exposure in this experiment with the time that the pure Cu sample was oxidized in the Cu “in situ” oxidation measurement (39 seconds), it results evident that the sample oxidized during this elapsed measuring time (Cr oxidizes faster than Cu at the temperature it was exposed to). Besides, chromium oxidizes easily with air, and since samples were transported from Córdoba (Argentina) to Campinas (Brazil) in a common receptacle in which atmosphere was not controlled, there exists a possibility that they could have oxidized completely during the trip. Taking into account this observation, it seems that in our measurements, all collected spectra were of an already oxidized sample. Due to this, no changes were observed in its chemical environment while in contact with the new external heat source. However, the development of the experiment and the concluding results in the Cu “in situ” oxidation measurements supports the results obtained with PCA. PCA not only was successful in finding spectra of different oxidation states, but also was able to alert problems in the experimental procedure, that would not have been taken into account without the use of this technique.

Finally, the Cr multilayer experiment showed the outcomes expected at the beginning of the work. By means of the PCA, applied to Cr multilayer spectra, PC1-PC2 plane allowed the discrimination of the oxides in the multilayer (Fig. 6). Principal component 1 is the fictitious variable necessary and sufficient to achieve this discrimination. According to the theoretical calculation of depth penetration as a function of the incident angle, the first 5 spectra could be identified with the chromium (III) oxide layer and the other 5 spectra to the chromium (II) oxide layer. PC1 gives negative values for all spectra of chromium (III) oxide and positive values for those of chromium (II) oxide. Summarizing, existing oxide layers in a sample of (40.0±0.2) nm thick were differentiated applying multivariate analysis techniques at x-ray RRS spectra obtained in TR conditions.

CONCLUSIONS

This work showed the potentiality of Principal Component Analysis to study x-ray RRS spectra. Variability between spectra measured at different depths of a sample with different Cr oxides was successfully analyzed, allowing the discrimination of the existing oxide layers at different nanometric depths. Besides, the identification of oxidation time and final oxidation state of a pure Cu sample was achieved with a hierarchical clustering analysis and a PCA. Finally, PCA applied to RRS spectra obtained from Cu multilayer sample and Cr “in situ” oxidation sample gave clues of existing complications during experimental development, alerting problems in measurements.

At present state of development, RRS spectroscopy is a qualitative technique and some prior knowledge of the sample, or standards, are needed for the characterization of materials. However the potentiality of the technique together with the help of Multivariate Methods represents a useful tool, complementary of other spectrometric techniques. Further developments of the theoretical frame of RRS will provide the possibility of a quantitative methodology.

1 In conclusion, an alternative methodology for the
2 analysis of oxidation states from RRS spectra in diverse mate-
3 rials has been presented and proved, mainly using Principal
4 Component Analysis. The application of this method to this
5 kind of spectra results very simple and allows exploring effi-
6 ciently the information encrypted in RRS peaks.

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TABLES

Energy	Mean Value	VC	Energy	Mean Value	VC
7807	0.07	22.56	7952	0.44	9.88
7818	0.08	23.05	7963	0.50	7.88
7829	0.10	15.48	7975	0.58	10.71
7840	0.11	21.61	7986	0.63	9.54
7852	0.12	16.82	7997	0.69	5.77
7863	0.14	15.41	8008	0.76	6.98
7874	0.15	16.61	8019	0.83	7.96
7885	0.18	14.87	8030	0.87	6.93
7896	0.21	10.02	8042	0.91	6.11
7907	0.25	13.84	8053	0.96	4.57
7919	0.29	11.51	8064	0.96	4.99
7930	0.34	11.15	8075	0.96	4.52
7941	0.38	11.70			

Table 1. Mean value and variation coefficient (VC) calculated for energies belonging to RRS tail of pure Cu sample. By mean value we refer to the sum in all measured spectra of the same energy channel, divided by the total number of measured spectra. VC allows understanding the dispersion of data around the mean value.

λ	Value	Proportion of total variance explained	Accumulated Proportion
1	7.65	0.29	0.29
2	2.59	0.10	0.39
3	2.01	0.08	0.47
4	1.75	0.07	0.54
5	1.61	0.06	0.60
6	1.48	0.06	0.66
7	1.33	0.05	0.71
8	1.24	0.05	0.76
9	1.05	0.04	0.80
10	0.98	0.04	0.83
11	0.82	0.03	0.87
12	0.69	0.03	0.89
13	0.59	0.02	0.92
14	0.58	0.02	0.94
15	0.37	0.01	0.95

Table 2. 15 first eigenvalues obtained from the PCA applied to data from *in situ* oxidation sample and proportion of total variance explained (normalized to unity). Accumulated proportion is shown.

Variable	a ₁	a ₂	Variable	a ₁	a ₂	Variable	a ₁	a ₂
4770	0.161	-0.02	4966	0.036	0.159	5173	-0.169	0.106
4781	0.187	0.068	4977	0.108	0.233	5184	-0.109	0.128
4792	0.136	0.011	4988	0.062	0.094	5195	-0.151	0.219
4803	0.139	0.053	4999	0.097	-0.06	5206	-0.189	-0.078
4814	0.174	0.008	5010	0.059	0.191	5217	-0.151	-0.004
4824	0.128	0.225	5021	0.038	0.012	5228	-0.176	-0.053
4835	0.131	0.257	5032	0.031	0.15	5239	-0.177	-0.009
4846	0.15	0.035	5042	0.091	0.222	5250	-0.157	0.189
4857	0.19	0.09	5053	-0.112	0.249	5260	-0.179	0.088
4868	0.113	0.055	5064	-0.071	-0.003	5271	-0.185	0.03
4879	0.17	0.067	5075	-0.08	-0.017	5282	-0.17	0.091
4890	0.158	0.096	5086	-0.105	0.032	5293	-0.168	0.062
4901	0.158	0.182	5108	-0.136	0.119	5304	-0.17	-0.007
4912	0.174	0.005	5119	-0.123	0.119	5315	-0.151	0.195
4922	0.168	-0.103	5130	-0.455	0.071	5326	-0.158	0.104
4933	0.124	0.225	5140	-0.065	0.252	5337	-0.128	-0.054
4944	0.106	-0.025	5151	-0.093	0.132	5348	-0.157	0.03
4955	0.091	0.198	5162	-0.122	0.219	5358	-0.07	0.12

Table 3. Eigenvectors obtained from PCA applied to Cr multilayer sample.

λ	Value	Proportion	Accumulated Proportion
1	λ	Value	Proportion
2	1	23.524	0.428
3	2	7.022	0.128
4	3	5.480	0.100
5	4	4.802	0.087
6	5	4.116	0.075
7	6	3.193	0.058
8	7	2.901	0.053
9	8	2.408	0.044

Table 4. Non-zero Eigenvalues obtained from PCA applied to Cr multilayer sample.

FIGURE CAPTIONS

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6 **Figure 1.** Sample of a simple spectrum measured from Cu Multilayer sample, without normalization.
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9 **Figure 2.** Normalized RRS-peak tails of the 30 spectra measured of the pure Cu sample oxidized “*in*
10 *situ*”.
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14 **Figure 3.** Grouping of 30 spectra measured in the “*in situ*” Cu oxidation experiment, using Euclidean
15 distance between different energies in RRS tail. Clustering of oxidized state spectra is
16 represented in continued lines. In dashed line the pure Cu spectra cluster.
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21 **Figure 4.** Visualization of the variability of spectra in the space generated by the first two principal
22 components of the PCA performed on the energies selected. In black circles (●) the pure Cu
23 spectra and in white triangles (Δ) the oxidized state spectra.
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28 **Figure 5.** Clustering of spectra obtained in the Cr “*in situ*” oxidation experiment in energy space using
29 Euclidean distance.
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34 **Figure 6.** Normalized RRS tail energy region of Cr multilayer sample spectra. 10 spectra superposed,
35 each one corresponding to a different depth penetration.
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39 **Figure 7.** Visualization of the variability of 10 spectra in the plane of the first two principal components
40 obtained from the PCA applied to energies of RRS peak. Two groups are identified. Numbers
41 in graph order sequentially according to increasing incident angle. Black circles (●) represent
42 upper layer spectra and white triangles (Δ) lower layer spectra according to the theoretical
43 calculation of penetration deepness.
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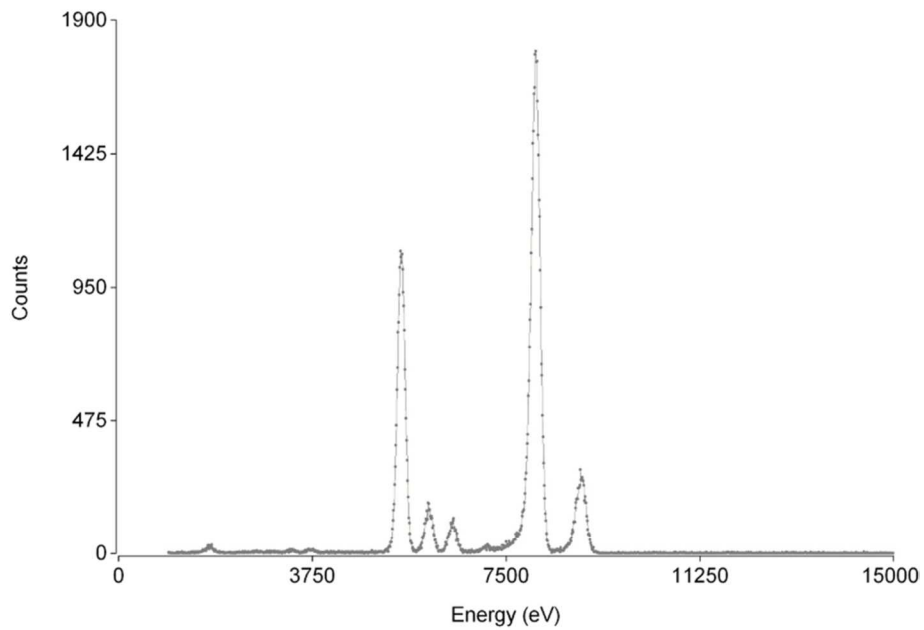


Figure 1. Sample of a simple spectrum measured from Cu Multilayer sample, without normalization

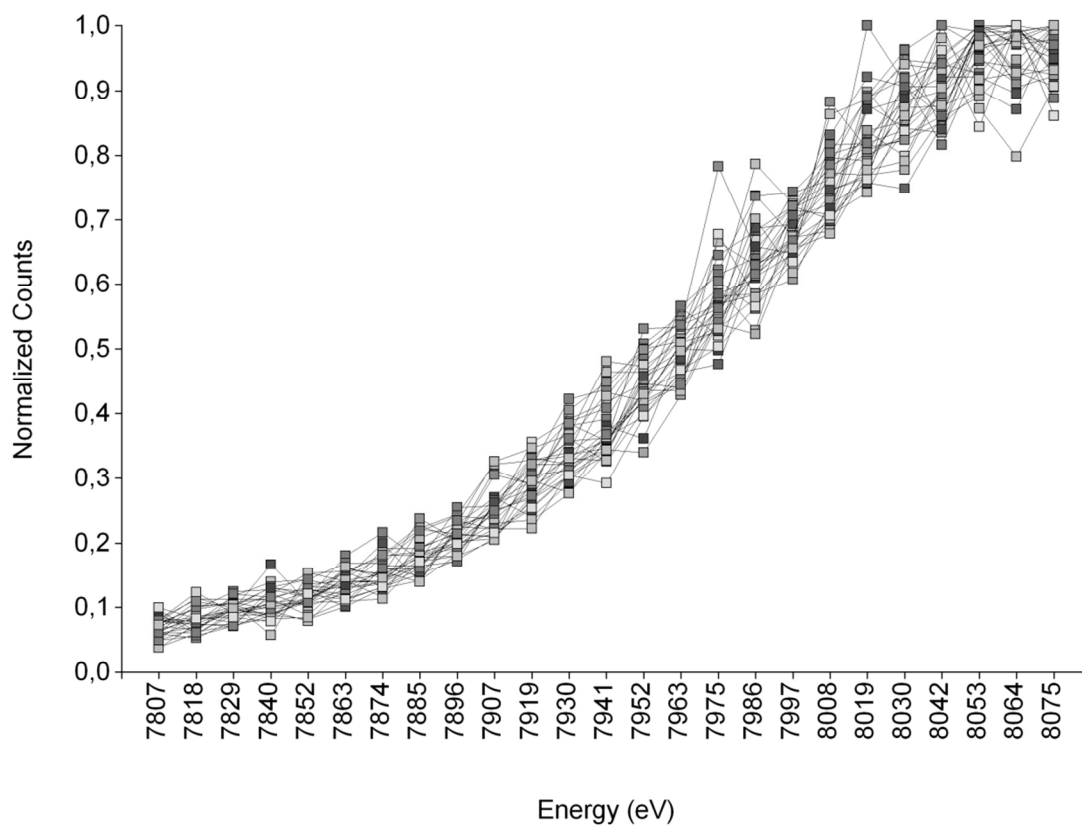


Figure 2. Normalized RRS-peak tails of the 30 spectra measured of the pure Cu sample oxidized “*in situ*”.

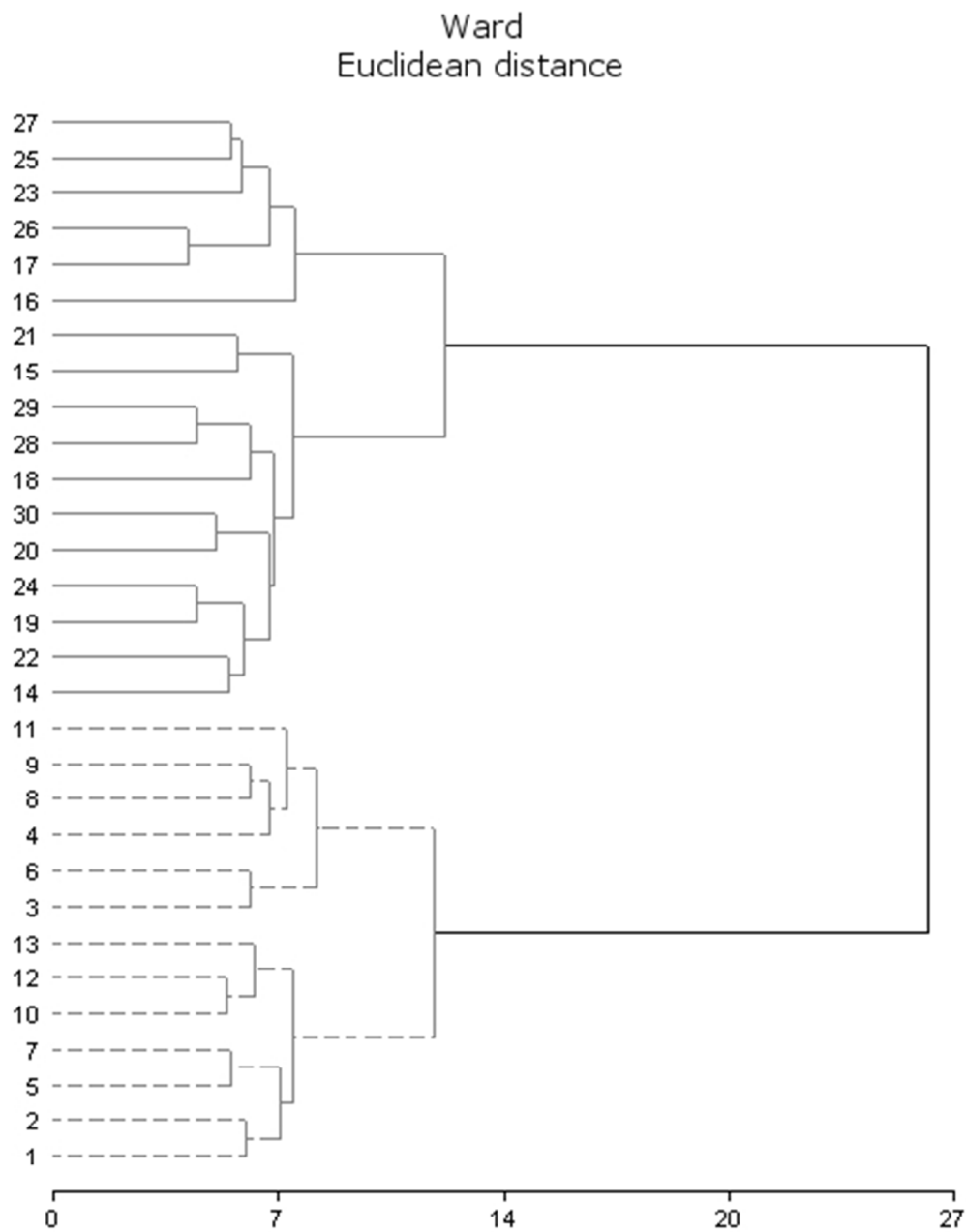
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Figure 3. Grouping of the 30 spectra of the “*in situ*” Cu oxidation experiment, using Euclidean distance between different energies in RRS tail. In continued line the clustering of the oxidized state spectra. In dashed line the pure Cu spectra cluster.

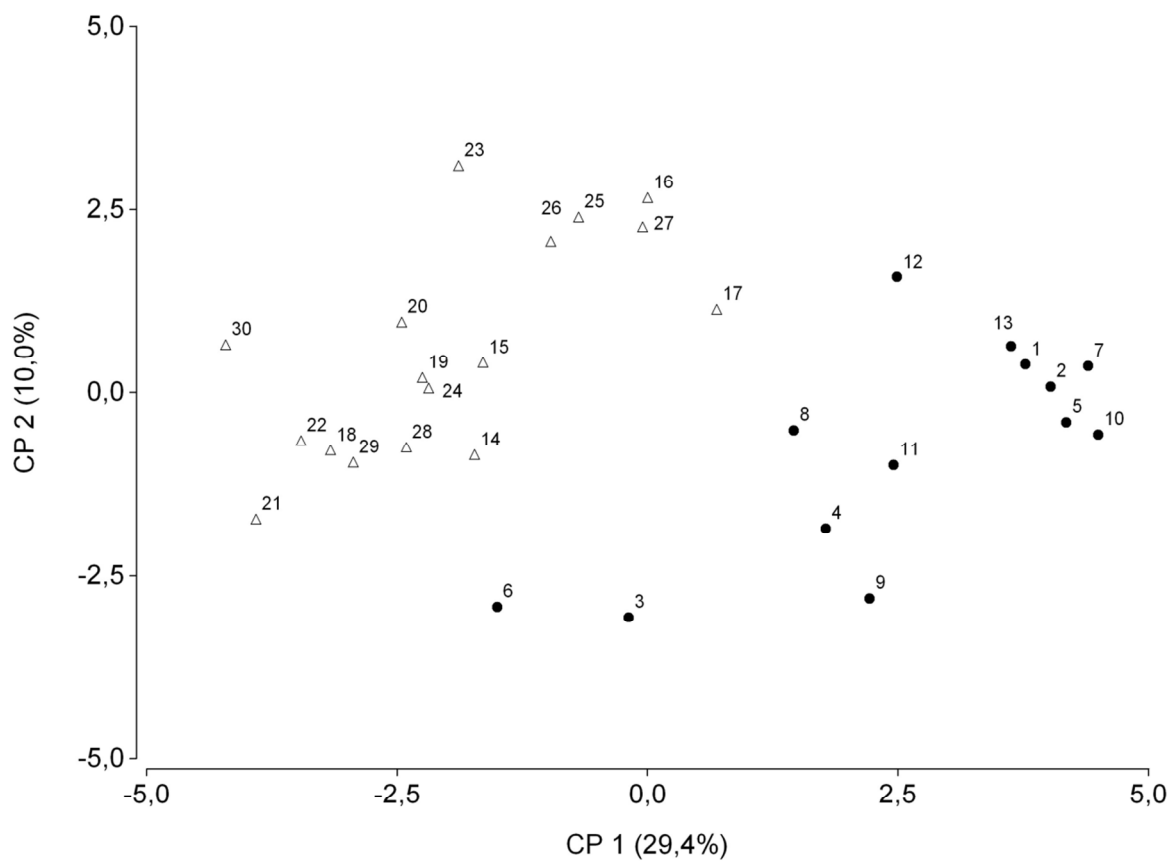


Figure 4. Visualization of the variability of spectra in the space generated by the first two principal components of the PCA performed on the energies selected. In black circles (●) the pure Cu spectra and in white triangles (Δ) the oxidized state spectra.

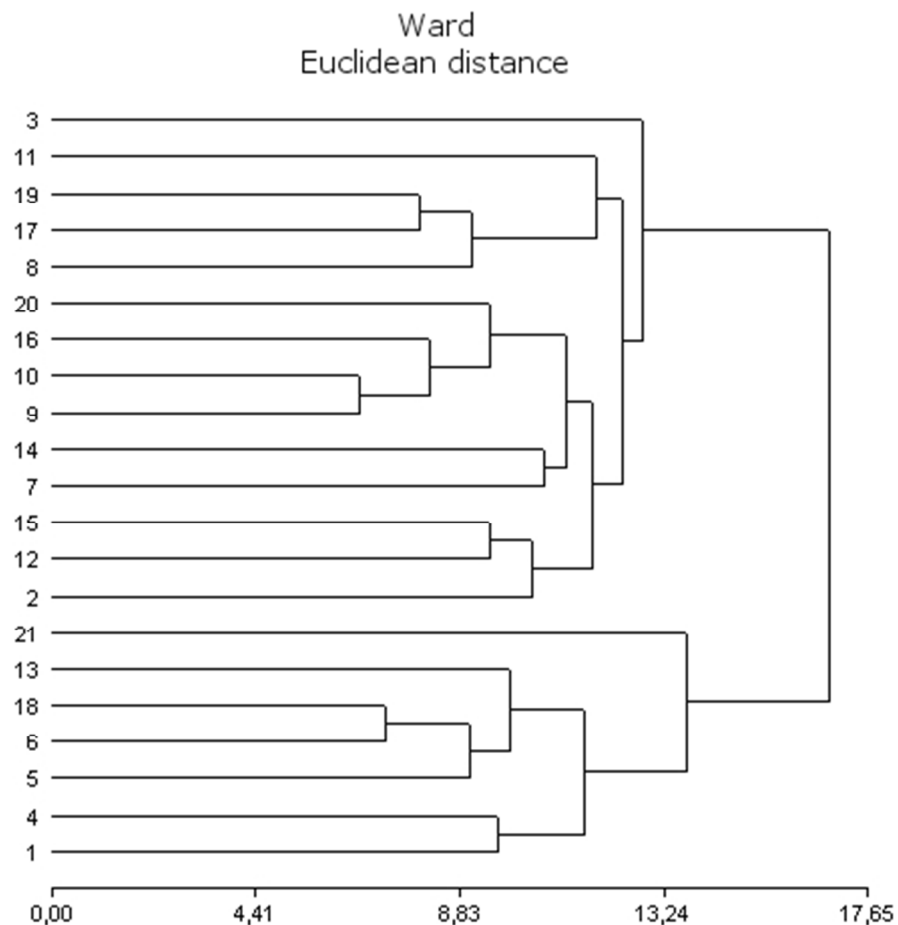
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Figure 5. Clustering of spectra obtained in the Cr *in situ* oxidation experiment in energy space using Euclidean distance.

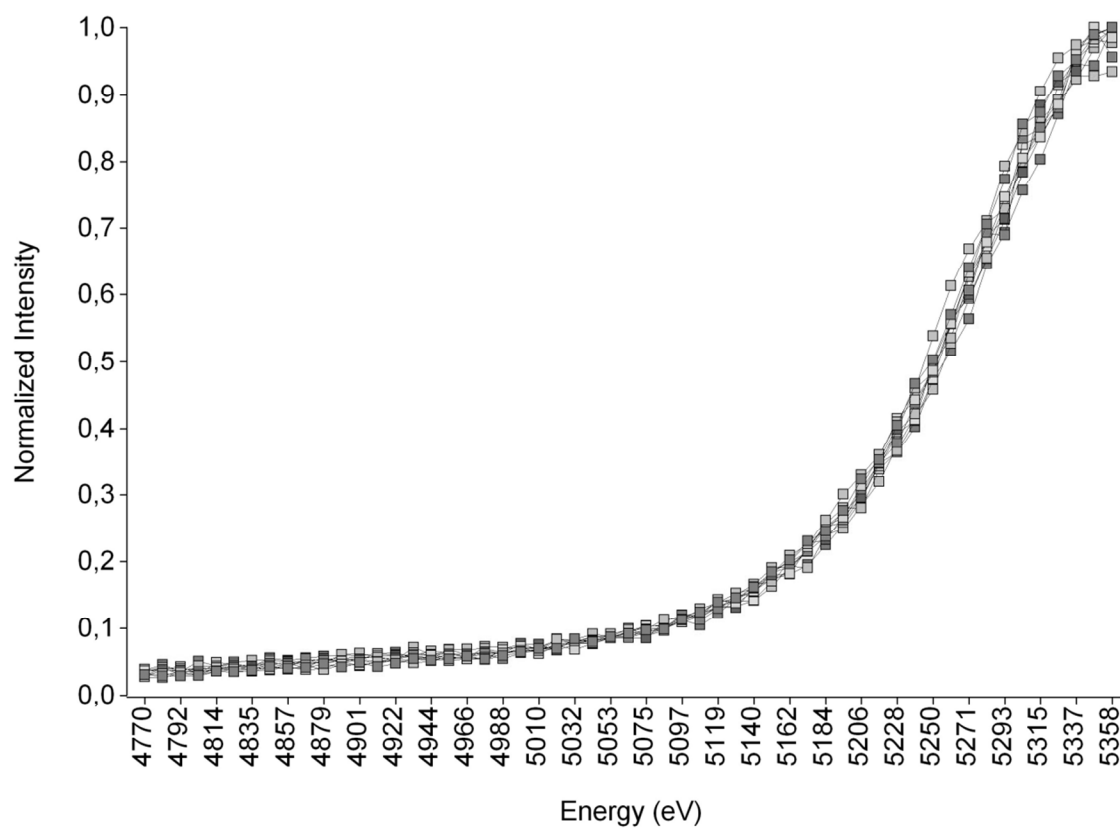


Figure 6. Normalized energy region of RRS tail from Cr multilayer sample. 10 spectra superposed, each one corresponding to a different depth penetration.

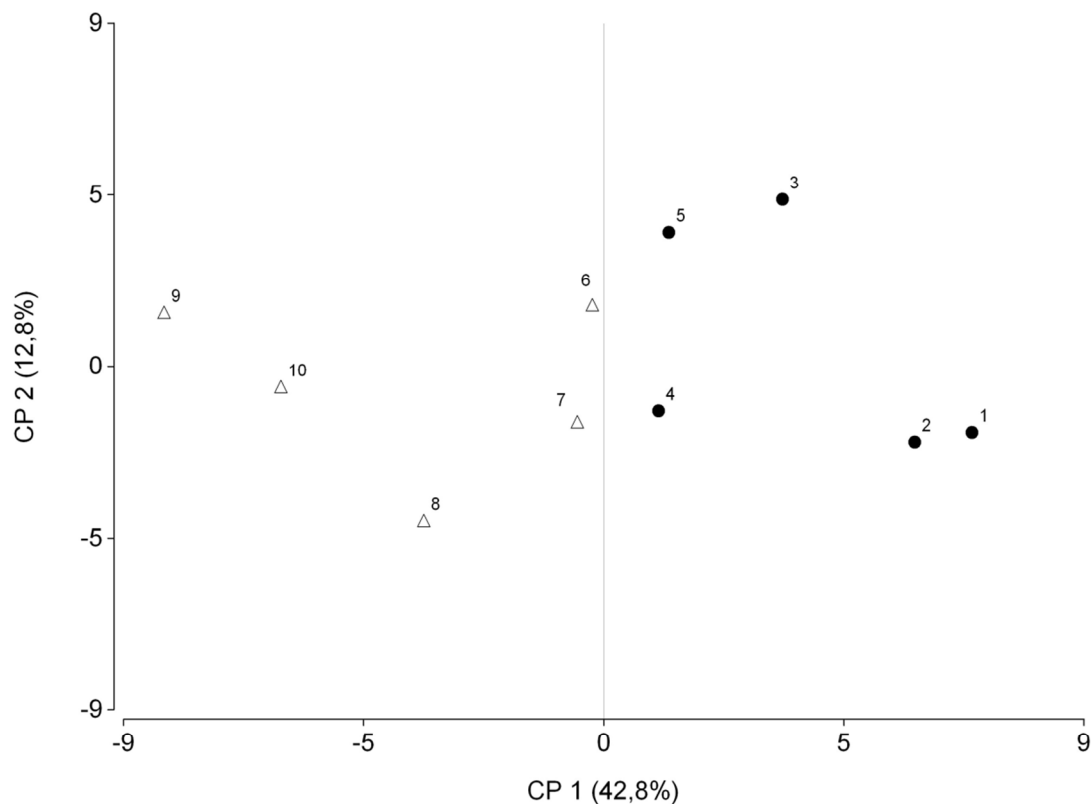


Figure 7. Visualization of the variability of 10 spectra in the plane of the first two principal components obtained from the PCA applied to energies of RRS peak. Two groups are identified. Numbers in graph order sequentially according to increasing incident angle. Black circles (●) represent upper layer spectra and white triangles (Δ) lower layer spectra according to the theoretical calculation of penetration deepness.