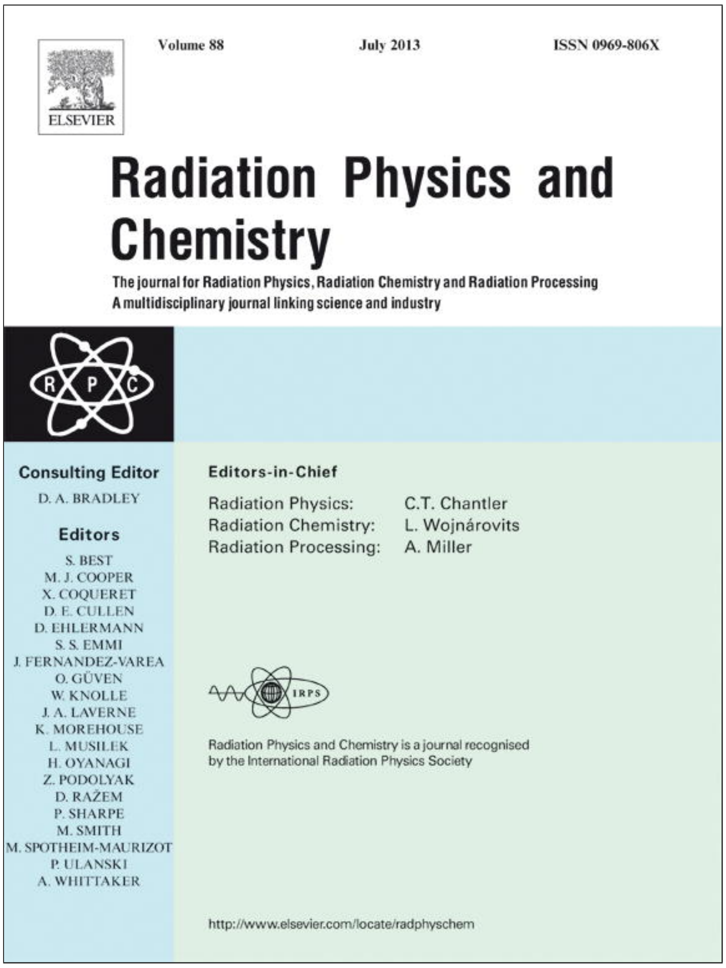

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Quantification by SEM–EDS in uncoated non-conducting samples

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HIGHLIGHTS

- SEM–EDS quantification of insulating samples without conductive coating is proposed.
- Charging effects are considered by inputing the Duane–Hunt limit as incident energy.
- Changes in X-ray spectra due to charging were studied by Monte Carlo simulations.
- The methodology has shown to be suitable for the analysis of archaeological pigments.
- It may be applied in forensic or archaeological samples, ancient artwork, etc.

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ABSTRACT

An approach to perform elemental quantitative analysis in a conventional scanning electron microscope with an energy dispersive spectrometer has been developed for non-conductive samples in which the conductive coating should be avoided. Charge accumulation effects, which basically decrease the energy of the primary beam, were taken into account by means of the Duane–Hunt limit. This value represents the maximum energy of the continuum X-ray spectrum, and is related to the effective energy of the incident electron beam. To validate the results obtained by this procedure, a non-conductive sample of known composition was quantified without conductive coating. Complementarily, changes in the X-ray spectrum due to charge accumulation effects were studied by Monte Carlo simulations, comparing relative characteristic intensities as a function of the incident energy. This methodology is exemplified here to obtain the chemical composition of white and reddish archaeological pigments belonging to the Ambato style of “Aguada” culture (Catamarca, Argentina 500–1100 AD). The results obtained in this work show that the quantification procedure taking into account the Duane–Hunt limit is suitable for this kind of samples. This approach may be recommended for the quantification of samples for which coating is not desirable, such as ancient artwork, forensic or archaeological samples, or when the coating element is also present in the sample.

1. Introduction

Electron probe microanalysis (EPMA) is a powerful analytical tool, which allows chemical quantification of the elements present in samples of different characteristics, along a wide range of specimen compositions (Goldstein et al., 1992; Reed, 1993). In some specific cases, the accuracy attained may be determinant, since small variations of elemental concentrations may strongly influence the conclusions drawn regarding the characteristics of a specific sample. An alternative analytical tool is scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDS) attached, which provide means for rapid, non-destructive, sensitive multi-elemental and relatively low cost analysis.

It is usual to realize a conductive coating on insulating materials, thus avoiding the effect of charge accumulation, which modifies the effective energy of the incident electrons, and also can produce heating of the sample. However, depending on the material used and the coating thickness, this film may give rise to different inconveniences, such as sample alteration and absorption of soft X-rays emitted by the sample, generation of undesired characteristic photons within the conducting material and attenuation and deviation of primary electrons. For quantitative purposes, carbon is generally chosen to this aim, since it weakly absorbs high energy X-rays, whereas in the case of low energy lines (S−Kα, O−Kα, F−Kα, etc.) it may give rise to important uncertainties. The avoidance of this conductive coating is an important challenge when involving low energy X-rays or when characterizing specimens which must remain unaltered, as forensic or archaeological samples (Schwoeble and Exline, 2000; Aloupi et al., 2000; Krüsemann, 2001; Hortolà, 2005; Schleicher et al., 2008).

In most quantification software programs commercially available, the influence of the conductive coating on the sample composition is

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not taken into account. Some recent programs involve certain corrections for X-ray absorption in the conductive layer; however, in most cases, results are not reliable, since the conductive film mass thickness is not accurately known and the programs are unable to deal with samples of non-homogeneous composition. The undesired effects mentioned above could compensate when comparing sample with standards, but it is not always possible to perform the coating in exactly the same way—standards are usually coated in advance. On the other hand, the deposition of conductive material on the samples is invasive to some extent, since it may alter the samples under study. For these reasons the conductive coating should be avoided when possible.

The present work aims to give an important step forward in the chemical quantitative characterization of samples by a procedure neither destructive nor invasive, which avoids the use of conductive coatings for SEM–EDS analysis. The proposed methodology is exemplified through the quantification of archaeological pigments corresponding to the Ambato style of Aguada culture (Catamarca province, Argentina), which according to different studies flourished during the IV and XII centuries AD (Baldini et al., 2002; Laguens and Bonnin, 2005; Pantorrilla and Núñez Regueiro, 2006).

The X-ray spectra involved in the quantification procedure were acquired for pigment samples without coating. The charge accumulation on the sample surface produces a repulsive potential to the incident electron beam, decreasing its energy. The effective electron incident energy was taken into account by means of the Duane–Hunt limit, which represents the maximum energy of the continuum X-ray spectrum produced by the incident beam impacting the sample (Newbury, 2002). In addition, the changes on the intensity of the characteristic peaks from the X-ray spectra due to this effect were also studied by Monte Carlo simulations. In order to validate the results, a known sample with chemical composition similar to those of the specimens studied here was analyzed with the methodology proposed in this work.

2. Electron probe quantitation

When a finely collimated electron beam impinges on a flat material, the characteristic intensity emitted by each element of an unknown sample can be used not only to identify the elements present in the sample. They may be recorded and then compared with the corresponding intensities emitted from standards of known concentrations. This comparison originates in the raw assumption that the emitted characteristic intensities proportionally relate to the mass concentrations of the corresponding elements, which allows to eliminate geometrical and physical factors very difficult to determine (Reed, 1993). With adequate procedures for data reduction, the different matrix effects are taken into account, usually referred to as “*ZAF* corrections” (Goldstein et al., 1992). These matrix corrections were originally separated as differences in the generation of X-rays and scattering of the incident beam (*Z*, for atomic number correction), absorption effects (*A*), and secondary fluorescence enhancement (*F*). These matrix correction factors strongly depend on the experimental conditions, mainly on the incident beam energy, X-ray take-off angle and differences in composition of the standards used as compared to the unknown samples.

All elements in the sample are involved when computing matrix effects, with a complex functional dependence on the concentrations. The iterative process underlying in the assessment of composition is usually implemented in black-box programs included in the instruments used. In this work the free code MULTI (Trincavelli and Castellano, 1999) was used instead. The quantification of unknown samples with up to 18 elements can be carried out with this algorithm, several standards being used if desired, in any combination, which can range from only one standard containing all the elements of the unknown sample to one separate standard for each analyte. This software also allows to perform analysis of undetected light elements when stoichiometric relationships can be provided. To carry out the analysis, several *ZAF* correction models may be selected, from which the Gaussian model for the *ZA* correction (Packwood and Brown, 1981) modified by Riveros and coworkers (Riveros et al., 1992) along with Reed's fluorescence correction factor *F* (Reed, 1965) were chosen for the present analysis.

As mentioned above, when dealing with insulating specimens, a conductive coating is required. If this coating is inadequate or even not present, the pointed spectral modifications will lead to wrong quantifications unless this effect is properly taken into account. In this work, the charging effects were considered by assessing the Duane–Hunt limit (Newbury, 2002) mentioned above. To this aim, the background was fitted in an energy region below the point where the continuum spectrum counts vanish (Trincavelli et al., 1998); the Duane–Hunt limit obtained by this procedure is considered here as the effective incident beam energy, and therefore is used as input in the quantification routine.

3. Monte Carlo simulations

In order to analyze the variations in the X-ray spectra as a consequence of surface charge accumulation and the effect of carbon coating in the samples and mineral standards used, a set of Monte Carlo simulations was performed. To this aim, the example main program PENCYL distributed with the 2003 version of the PENELOPE routine package (Salvat et al., 2003) was used. This code allows the simulation of the different interactions undergone by an electron beam in a material medium, including characteristic and continuum X-ray generation.

An important feature of this main program is that it is optimized for cylindrical geometries constituted by different layers. The output provided for X-ray emission is discriminated for each photon energy, and integrated for all possible take-off directions. For this reason, the PENCYL program was modified in order to only account for photons emitted according to the experimental setup used; this is an important issue in order to adequately compare results, since the absorption correction may drastically change for different take-off angles (Reed, 1993). With the purpose of reducing statistical uncertainties, all azimuth angles were integrated for the corresponding take-off angle selected, in view of the symmetry characterizing the normal-incidence EPMA experiment for the flat homogeneous samples used (Salvat et al., 2006).

Several simulations were realized in order to study the changes in the X-ray spectrum with different parameters. First, a set of simulations for normal incident electron beams with energies 13, 13.5, 14, 14.5 and 15 keV was performed for an archaeological sherd sample PM41 of typical Aguada chemical composition, which was previously characterized in Activation Laboratories Ltd. (Ontario, Canada).

Bearing in mind that all the samples analyzed here are fine particle agglomerates which must be compacted under mechanical pressure (see Experimental), their density may differ from one compaction to another, which might influence the determination of characteristic intensities (Sorbier et al., 2004). In order to survey this behavior, a second set of simulations was performed for mass densities ranging from 2 g/cm^3 to 6 g/cm^3, which includes all the possible cases involved in the samples studied here.

All simulations were run in a cluster facility at the *Facultad de Matemática, Astronomía y Física* of the *Universidad Nacional de Córdoba*, which involves 3.0 GHz Pentium IV hyperthreading processors.

In the simulations carried out, the incident electron trajectories are surveyed down to a threshold energy, since no further ionization is possible under this value. This criterion permits to obtain results with appropriate statistical uncertainties in reasonable CPU times, avoiding the computation of events out of interest. With this restriction, relative errors around or below 1% for all characteristic intensities were obtained for 5×10^9 primary electrons.

4. Materials

In order to validate the procedure proposed for the quantification of non-coated samples, a milled sherd specimen, for which chemical analysis was previously performed in Activation Laboratories Ltd. (Ontario, Canada), was studied without conductive coating. This sample, labeled as PM41, was specially selected since it bears a composition similar to that of the analyzed pigments, and also because the previous quantification evidenced that losses on ignition were below $<1\%$; this ensures no systematic errors are introduced, particularly in the determination of light elements.

In addition, some archaeological pigments were analyzed. Only a few tens of milligrams were available for these samples, which consisted of aggregates of small particles. The six pigments studied have been labeled as S1, S2, S3, S4 (white), S5 and S6 (red).

5. Experimental

X-ray spectra were acquired in a scanning electron microscope LEO 1450 VP with an energy dispersive spectrometer attached. The Sapphire Ultra-Thin Window X-ray detector allows the detection of elements with atomic number greater than 5, with a resolution of 129.2 eV for the Mn–Kα line. In all cases, the acquisition live time was 200 s, nominal incident beam energy E_o=15 keV, 500 pA probe current and 33.42° take-off angle. This choice for the irradiation parameters used for the acquisition of spectra ensures a detection limit of 500–1000 ppm. In order to guarantee the stability for the acquisition of each spectrum, the probe current was checked at the beginning and at the end of each measurement with a Faraday cup; this allowed to verify that probe current variations always remained within 1%. In all cases, spectra were acquired at low magnification, scanning all the selected area for analysis.

Sample surfaces must be flat for conventional quantitative analysis by SEM–EDS and the electron beam must impact perpendicular to the specimen surface. In order to attain this condition, samples were ground and then compacted in a sample holder specially developed to this aim (Galván Josa et al., 2009a). This compaction was completed by subjecting samples to a pressure of 8 ton/cm^2 for 20 min; this allowed to achieve a small amount of compacted sample (10 mg), which covered an area of 0.5 cm^2. The standards used for quantitative analysis were the SPI® commercial mineral standards, which are carbon coated.

In order to obtain characteristic intensities, spectra were processed with the program AXIL (Van Espen et al., 1987). An important issue which must be taken into account in order to achieve reliable quantitative results is the correct deconvolution of the spectra in the low energy region. For example, in the case of Pb, the energy dispersive detector cannot separate the Pb-M lines from S–Kα line, as exemplified in Fig. 1, where the spectral region involving Pb-M and S-K lines are shown for the case of sample S2. Pb-M lines are quite more intense than L-lines since the incident energies used inefficiently ionize the Pb-L edge; this should encourage their use and therefore their correct determination. For this reason, despite the difficulties associated with their deconvolution, the quantification of lead was performed here taking into account the Pb–Mα line. To this aim, the intensity of the Pb–Mα line was determined with the program AXIL by taking into account the relative transition probabilities of the decays to the M subshells given by Perkins et al. (1991).

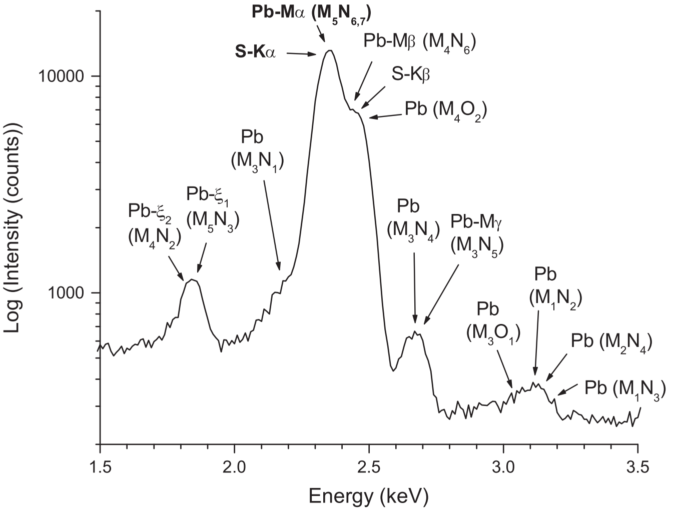

Fig. 1. X-ray lines corresponding to the S2 sample.

Table 1
Mass concentrations obtained for sample PM41 using the nominal incident energy (15 keV) and those determined through the Duane–Hunt limit (13.2 keV).

PM41 SAMPLE (wt%)			
Element	ActLabs	$E_o^{DHL}=13.2$ keV	E_o=15 keV
O[a]	47.57	46.17	35.1
Na	3.19	2.35	2.02
Mg	0.62	0.80	0.64
Al	10.98	10.28	7.85
Si	29.07	28.92	21.77
K	2.20	3.04	2.80
Ca	0.60	0.76	0.49
Ti	0.49	0.40	0.25
Mn	0.06	0.16	0.09
Fe	4.93	5.20	2.84
Total	99.71	98.08	73.85

[a] Assessed by stoichiometry.

The concentrations for light elements were assessed by stoichiometric relations: in most cases, oxide relations were used, whereas the carbon concentration was associated with a calcite phase—as previously identified through XRD (Galván Josa et al., 2009a, 2009b).

6. Results and discussion

The input value for the incident beam energy in the quantification procedure performed with the program MULTI was taken as the Duane–Hunt limit value E_o^{DHL} obtained from a fit of the experimental spectrum, as mentioned above. The influence of the value taken for E_o on the concentrations obtained for this sample is exemplified Table 1. Clearly the dependence of the *ZAF* matrix corrections on the incident energy is not equal for all elements, since relative concentrations may be strongly altered even for similar E_o values.

With the aim of testing this choice for the effective incident energy, the sample PM41, previously analysed in Activation Laboratories Ltd. (Ontario, Canada), was quantified with program MULTI using the nominal value for E_o and the fitted E_o^{DHL} value. The results, displayed in Table 1, show that the procedure proposed here is suitable for this kind of samples. It can be seen that the most remarkable discrepancies appear in the minor elements; however, since no normalization is performed by the program MULTI, the sum of concentrations close to 100% is an important indicator for the reliability of the results.

Table 2 shows the compositional results obtained for each sample using the fitted E_o^{DHL} values. In those cases for which the effective incident energy is noticeably different from the nominal one, the set of concentrations is shown for both E_o and E_o^{DHL}. The low values for the total sum of concentrations for samples S4, S5 and S6 are an unequivocal evidence that reasonable results can only be obtained if an effective incident energy lesser than the nominal E_o value is used in the quantification routine. As discussed below, the concentrations for elements with higher atomic number (Fe, Ca, K) are the most affected by these differences in the incident energy considered.

The set of reddish and white pigments were previously characterized by X-ray diffraction through a Rietveld refinement procedure (Galván Josa et al., 2009a), where the effects induced by the preferred orientation inherent to the sample preparation method were considered. Although in some cases the major phase peaks were overlapped with the principal lines of minor phases, the numerical criteria of fit obtained in Galván Josa et al. (2009a) were quite reasonable for the rather small amount of material available. The chemical characterization obtained through the methodology proposed in this work is in good agreement with the elemental composition inferred from the mineralogical quantification reported in Galván Josa et al. (2009a).

As mentioned above, due to the carbon coating in the standards used, this element cannot be directly quantified. On the other hand, variations in the thickness of this coating may remarkably influence the oxygen characteristic intensity detected, since carbon is an efficient absorber for such photon energies (Limandri et al., 2010). For this reason, oxygen was not straightforwardly determined from characteristic intensities either, but through stoichiometric relations. Oxygen was associated to other elements as oxides, whereas carbon was associated to calcium, assuming all calcium is present as calcite, as corroborated by X-ray diffraction (Galván Josa et al., 2009a).

For the samples analyzed, in this incident energy range the dependence of the *ZAF* matrix corrections on E_o is not equal for all elements, being more important for elements with higher Z values. This dependence is directly related to the overvoltage value E_o/E_j, E_j being the ionization energy involved in the characteristic emission for element j. In the case of Fe (the lowest overvoltage involved here), the ionization cross section strongly varies around 15 keV (Goldstein et al., 1992). However, this is not a simple problem, since absorption effects also depend on the incident energy, even for light elements (Reed, 1993).

In order to survey the influence of the value for E_o in the characteristic intensities, simulated X-ray spectra for the sample PM41 were obtained for incident energies of 13.0, 13.5, 14.0, 14.5 and 15.0 keV. Both bremsstrahlung and characteristic X-ray production were considered in the simulated spectra. For each E_o value a characteristic intensity $I(E_o)$ was therefore obtained, which can be compared to the corresponding measured line I_{15} for 15 keV. The relative intensity differences $[I(E_o)-I_{15}]/I_{15}$ obtained by this means are displayed in Fig. 2, which corroborates the fact that the higher the atomic number (i.e. the lower the overvoltage), the more important these relative differences become. This also implies that a straight renormalization of the concentrations obtained by the quantification routine is, in most cases, unsuitable.

Since during sample preparation the compaction procedure might produce different effects on the agglomerates, an additional set of Monte Carlo simulations was run for densities 2, 3, 4, 5 and 6 g/cm^3 corresponding to sample PM41, which largely includes the range of possible values for the resulting densities. Fig. 3 shows the ratios for all characteristic intensities normalized to those corresponding to density 4 g/cm^3. It can be seen that all values remain close to 1, exceptionally reaching a difference up to 2%, a deviation lesser than the statistical uncertainties for this set of simulations. Therefore, the possible variation in the sample compaction procedure can be neglected for quantification purposes. In addition, the Duane–Hunt limit will not be modified by any possible density variation; its value mainly depends on the specimen conductivity.

7. Conclusions

In this work, a routine has been implemented for the quantification of non-conducting samples which cannot be coated for SEM–EDS examination. Surface charge accumulation effects were taken into account by determining the Duane–Hunt limit, in order to assess the effective incident energy. As a validation of the methodology proposed here, the chemical concentrations obtained for a known sample have shown to be reliable when compared to those

Table 2
Elemental concentrations (wt%) of white pigments obtained with SEM–EDS analysis.

Sample	S1	S2	S3	S4		S5		S6	
E_o (keV)	14.6	15	14.8	13.1	15	12.3	15	13.7	15
Element									
C[a]	11.4	1.2		9.9	4.4	2.9	3.0	0.7	0.5
O[a]	47.6	20.2	60.9	44.1	27.1	50.4	44.7	44.3	35.7
Na		0.7		0.3	0.3	1.1	1.0	0.6	0.5
Mg	0.2			1.7	1.3	1.7	1.4	0.8	0.7
Al	0.3	0.9		1.8	1.3	9.0	6.6	6.6	5.6
Si	1.0	4.8		8.5	5.7	23.8	16.7	21.0	17.4
P				0.1	0.1				
S		5.7	17.7					2.7	2.2
K	0.3	0.6		3.8	2.2	7.0	3.9	5.0	3.9
Ca	38.2	1.6	21.3	26.6	14.7	0.5	0.3	2.0	1.5
Mn		1.0							
Fe	0.2	2.3		1.8	0.8	4.6	2.2	17.4	12.0
Pb[b]		62.1		0.3	0.2				
Total	99.2	101.1	99.9	98.9	58.1	101.0	79.8	101.1	80.0

[a] Assessed by stoichiometry.

[b] Calculated through Mα−line intensities.

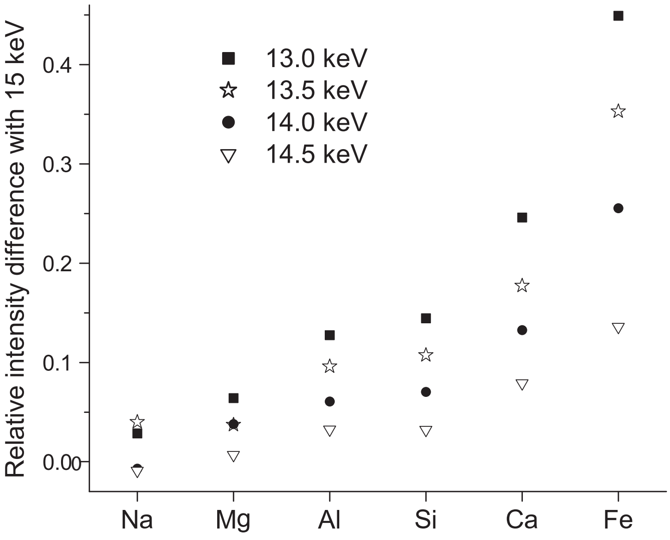

Fig. 2. Simulated relative differences $[I(E_o)–I_{15}]/I_{15}$ between characteristic intensities from sample PM41 for different incident energies $I(E_o)$ and the corresponding I_{15} for 15 keV.

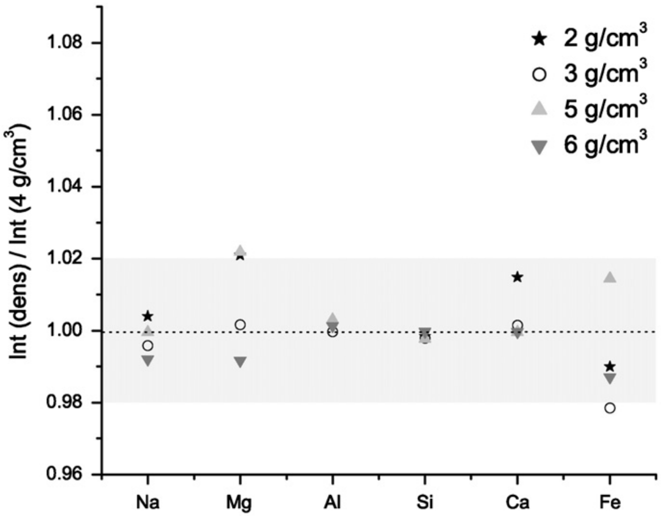

Fig. 3. Monte Carlo X-ray characteristic intensities obtained for sample PM41 assuming different values for mass densities, normalized to those corresponding to density 4 g/cm^3. The interval with differences below 2% has been highlighted.

resulting from a well-established conventional analysis. Then, the quantification of Aguada archaeological pigments was carried out, for which reasonable chemical compositions were obtained.

The sum of the concentrations assessed was used as an important indicator for the reliability of the results. In the samples studied, the sums of the concentrations obtained by considering the Duane–Hunt limit as the effective incident energy were much closer to 100% than those produced when using the nominal incident energy, which in some cases may descend below 60%. This issue is extremely important, particularly because available commercial software programs never take into account charging effects. In addition, a normalization process, in most cases, could lead to incorrect results.

A clear way for appreciating the variations in the concentrations associated to the changes in the incident energy is to check the corresponding relative differences between the concentrations obtained with the nominal energy and those derived from the Duane–Hunt limit. These relative differences can be important, even over 50% for those cases in which the effective incident energies strongly differ from the nominal ones. Relative differences are negative in most cases, i.e., concentrations are underestimated when using the nominal value for E_o. This fact is consistent with the low sum of the assessed concentrations, which is always smaller when E_o is used instead of the Duane–Hunt limit estimate E_o^{DHL}.

Monte Carlo simulations allowed to corroborate that the strongest differences in characteristic intensities occur for the highest atomic numbers (Fe in the present case), when changing from the nominal incident energies to the effective values. This is closely related to the more important variation in the ionization cross sections for the energy values involved.

The present approach for the analysis of uncoated non-conducting samples may be useful for the characterization of different kind of samples which cannot be altered for performing chemical analysis; such is the case of forensic specimens, paleontological pieces, artwork studies, archaeological paints scraped from surfaces, etc. It may also be useful when small amounts of material are available or when the most convenient conducting coating involves one of the elements which must be quantified.

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