

A procedure for overlapping deconvolution and the determination of its confidence interval for arsenic and lead signals in TXRF spectral analysis

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We studied the applicability and validity range of a mathematical procedure on the basis of the principia of maximum likelihood for the identification and quantification of arsenic and lead. This procedure has showed to be appropriate for analyzing two or more signals that interfere with each other or for the quantification of a small signal in a very noisy environment, but a complete study of determination of its confidence interval in samples in which one element in the overlap is present in a concentration lower than the other elements was not studied previously. The identification implemented provides very exact values of relative concentrations for cases that are difficult to process using other adjustment methods. The proposed procedure is applied to experimental cases, analyzing liquid solutions through total reflection X-ray fluorescence to determine a range of concentrations for the detection of traces of arsenic signals in the presence of large lead interfering signals and vice versa. Copyright © 2013 John Wiley & Sons, Ltd.

Introduction

The total reflection X-ray fluorescence (TXRF) technique analysis has produced an important advance in the quantification of very TXRF small amounts of analytes. This is because TXRF has very low detection limits, unlike the traditional energy dispersive X-ray fluorescence technique. These low detection limits are due to drastically reduced backgrounds produced by the sample, given that the sample carrier produces a total reflection of the incident radiation by the special geometry designed. With TXRF, elements can be found from *silicon* to *uranium*.

The TXRF is proposed as an excellent tool for analyzing traces of elements from different types of samples. At present, the ability to determine metal concentrations to elucidate their composition is of great importance for applications such as the prospection of energetic materials,^[1,2] geology and mining,^[3] studies of catalytic processes,^[4,5] biochemistry or cellular toxicity studies,^[6,7] material physics,^[8,9] and archeology.^[10]

The portability and efficiency of TXRF as technique in the spectral analysis of highly toxic elements are a very important task; one of the dangerous kinds of pollution in aquatic systems is the addition of materials containing heavy metals in aqueous samples, in specific: arsenic and lead are typically present at trace level,^[11] but high concentrations of those elements in water used in industry may be highly damaging. The environmental problems are related to their high tendency to accumulate in vital organs of humans and animals.

A typical problem in the detection and quantification of those elements in TXRF is the overlap in the fluorescence signals (arsenic K and lead L lines) that affect negatively the quality of the results. This problem has enhanced the optimization of analysis and handling of data, to improve the results and resolve this overlapping.^[12,13]

The procedure presented here for identifying and quantifying spectral signals is based on the methods of maximum likelihood, developed on previous works for the deconvolution of trace

mercury and other heavy metals,^[14] but a complete study of determination of its confidence interval in samples in which one element in the overlap is present in a concentration lower than the other elements was not studied previously. If one element is in a small proportion compared with others, its correct identification and quantification are complex.

The proposed procedure was applied to a wide number of experimental cases to determine traces of arsenic signals in the presence of large lead interfering signals and vice versa. We study how this mathematical procedure produces improvements in the detection of small signals with low sensitivity in TXRF analysis. This criterion established also can be applied in other spectroscopic techniques,^[11,15] in which their spectra grow linearly with time.

Theory

Spectral analysis

The number of counts in a particular peak in any TXRF spectrum is directly proportional to the acquisition time; hence, the relative intensities are dependent only on the relative proportions of the elements in the sample and on their relative detection sensitivities. The intensity, I_i , of the signal produced by the element i detected by a TXRF setup is^[16]

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$$I_i = \int_{E_{\text{abs}}}^{E_{\text{max}}} I_0(E) G \frac{w}{\sin \varphi} \sigma_j^i(E) C_i f(E_j^i) \varepsilon(E_j^i) dE \quad (1)$$

where E_{abs}^i is the energy of the absorption edge of element i , E_{max} being the maximum energy of the excitation spectrum, E_j^i is the energy of the j line of element i , $I_0(E)$ is the spectral distribution of the exciting radiation, G is the geometry factor, σ_j^i is the fluorescence cross-section for the j shell of element i , $f(E_j^i)$ is the absorption factor for the fluorescence radiation between the sample and the detector, and ε is the relative detector efficiency for the energy E_j .

When the sample depositions can be approximated to the thin film geometry, a simplified expression for Eqn (1) is obtained, and it was implemented in the models of the intensity of the signal produced.^[17] In this work, we verified experimentally that all samples satisfied conditions required in Eqn (1) to obtain a linear relationship between the amount of mass irradiated and the intensity of the line measured.

If the characteristic signals corresponding to each of the elements are known, a spectrum, M , made up of n elements, can be expressed through Eqn (1) as the product of two vectors:

$$M = I_0 N (F_{z=1} F_{z=2}, \dots, F_{z=n}) \begin{pmatrix} (wS)_{z=1} \\ (wS)_{z=2} \\ \vdots \\ (wS)_{z=n} \end{pmatrix} \quad (2)$$

The first vector contains information on the characteristic functions, F_i , for each element with atomic number i ($Z=i$). The characteristic functions, F_i , are obtained empirically from the characteristic spectrum of the element by irradiating a pure sample of the respective element. This function does not change if none of the experimental parameters on the instrument are modified; that is, given an identical geometry of excitation, we obtain identical detectors for all the samples, gains for the amplifiers, electronics of data collection, and so on. These spectra are divided by the integral of the region of interest (ROI), the set of channels or energies in which the element and the signal are defined). Finally, the functions obtained are normalized by dividing each count for each channel in the region by the integral of the ROI (net area). If the influence of the background and the fluctuations of the statistical count are small, all the characteristic spectra, F_i , of a given element should be identical in shape for any time of acquisition and concentration (if the statistical fluctuations are neglected).

The second vector contains information of the composition of the sample, such as the amount of sample w and the sensitivity of the signal detection S (which includes the physical properties of each element, the efficiency of detection for a given energy, and the geometric configuration). In the specific case of overlapping spectra of two elements under study, any obtained spectrum, M , can be expressed according to Eqn (2)

$$M = I_0 N_0 [w_B B_N S_B + w_C C_N S_C] \quad (3)$$

where the signal of the resulting overlap, M , is obtained as a linear combination of the functions $F_1 = B_N$ and $F_2 = C_N$, the characteristic functions for elements B and C , respectively. The subscript N indicates that both functions are normalized.

Strictly speaking, M , B_N , and C_N are a set of numbers $M(j)$, $B_N(j)$, and $C_N(j)$, where j is the number of the channel that goes from the beginning to the end of the ROI of the spectrum. The joint signal of the overlap is found in the ROI.

In this work, we implemented a method of adjustment with a formulation of normalized functions. Therefore, we must write the adjusted function in its normalized form. For this, we must calculate its integral in the ROI between the limiting energies, E_i and E_f .

$$\int_{E_i}^{E_f} M dE = I_0 N_0 [w_B S_B + w_C S_C] \quad (4)$$

For this region, the characteristic normalized functions of elements B and C have a unitary area and, therefore, are simplified.

Defining the ratio of concentrations in which the two elements are found as $\phi = w_B/w_C = C_B/C_C$, we obtain

$$M_N = \frac{\phi S_{C/B} B_N + C_N}{1 + \phi S_{C/B}} \quad (5)$$

The normalized spectrum of the adjusted overlap becomes a function made up of the two mono-elemental functions of the elements involved, multiplied by factors of concentration and detection sensitivities.

Treatment of data from the spectrographic signal

The magnitude of the data measured, m , is often expressed as the number of events or counts. When the problem is the recovery of a small signal in a strong background, a procedure for obtaining the best result has been developed with a formulation based on the maximum likelihood approach.

This problem is dealt with using a given set of measured data, m , and a function, F , both as function of a variable x . The function F represents the response presence of an element or a given physical phenomenon that can be found within the measured data, affected by an intensity, α .

The function, $F(x)$, which must be known to be quantified, is expressed as a discrete value, $F(x_i)$. In a sequence of data, $m(x_i)$, we must determine the most likely value of α which affects $F(x_i)$ (See Figure 1). The treatment developed herein establishes an interval of confidence, $\Delta\alpha$, for the parameter of the intensity, α .

The random function (stochastic) $G(x_i)$ is defined. The associated probability distribution function (pdf) is a normalized Gaussian function centered on the value $\alpha F(x_i)$, and the variance of this function is given by σ_j^2 (the uncertainty or standard deviation of the count of channel j) (See Figure 2).

Each of the $G(x_i)$ is described by the Gauss function as

$$G_{(\alpha F(x_i), \sigma_j^2, m_i)} = \frac{1}{\sqrt{2\pi\sigma_j}} e^{-\frac{(m_i - \alpha F(x_i))^2}{2\sigma_j^2}} \quad (6)$$

Once the measurement has been carried out, we have a set of points $\{(x_i, m_i)\}$ ($i=1, \dots, n$), the probability of obtaining the set of results $\{m_i\}$, supposing that the pdf of the random variables, $G(x_i)$, is the product of the probabilities of each variable $G(x_i)$ adopting the value m_i .

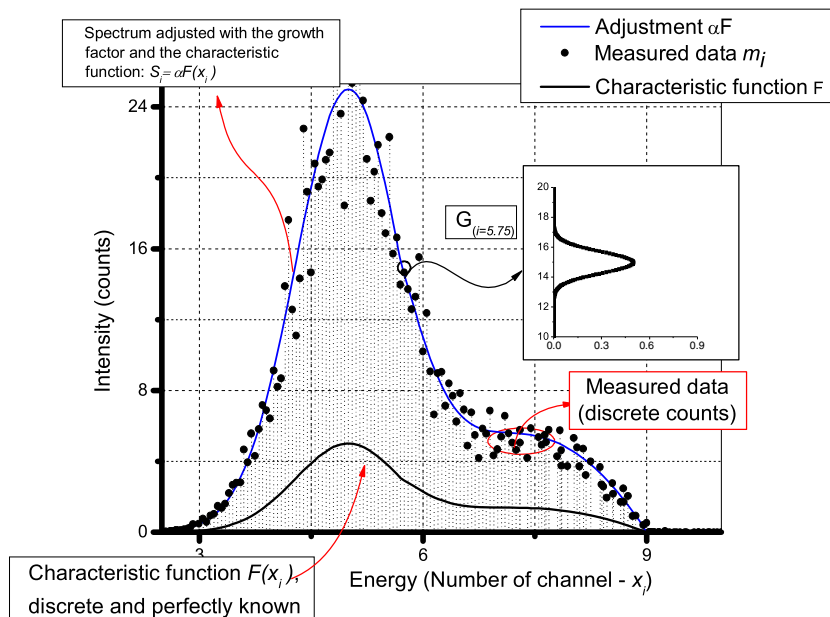


Figure 1. A discrete experimental data set, depending either on energy or channel number, is shown made of points (x_i, m_i) or (E_i, m_i) . In this set of data m , a function $F(x_i)$ must be found, affected by a parameter α . Each point m_i is described by a random Gaussian function with centroid in the value $\alpha F(x_i)$. A particular Gaussian function, $G(i=5.75)$, is represented inside of the main graphic.

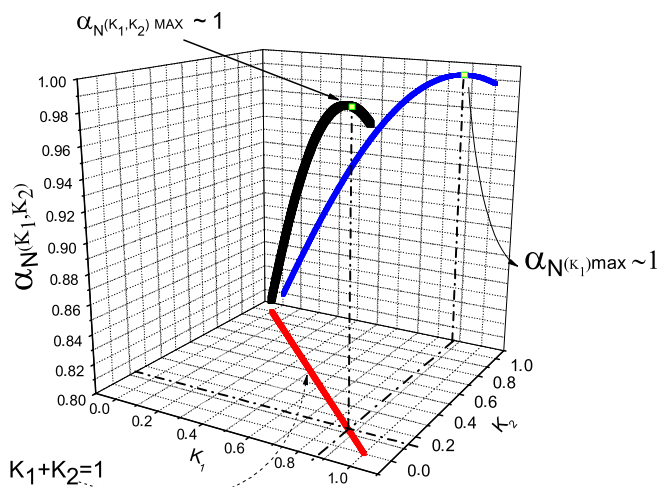


Figure 2. Maximization of the parameter α_N as a function of the factors K_1 and K_2 , with the condition $K_1 + K_2 = 1$.

That is, it is the product of the $G(x_i)$, which we can call L :

$$L(m_1, m_2, \dots, m_n, \alpha) = G(\alpha F(x_1), \sigma_1^2, m_1) \times G(\alpha F(x_2), \sigma_2^2, m_2) \cdots \times G(\alpha F(x_n), \sigma_n^2, m_n) \quad (7)$$

Given that the function $\ln(x)$ increases monotonously in x , maximizing L is equivalent to maximizing $\ln(L)$:

$$\ln(L) = -\sum_{i=1}^n \frac{[m_i - \alpha F(x_i)]^2}{\sigma_i^2} + \sum_{i=1}^n \ln\left(\frac{1}{\sqrt{2\pi\sigma_i^2}}\right) \quad (8)$$

Finding the derivative with respect to α of this expression and equalling it to zero, we obtain the most likely value of for the set

of data $\{m_i\}$.^[14,18,19] A normalized version of α can be considered as a criteria of comparison of similarity of the measured spectrum, m_N , with the characteristic normalized function sought, F_N . In this case, the two data series should take a value for the α_N close to 1.

$$\alpha_N = \frac{\sum_{i=1}^n \frac{(m_N)_i * (F_N)_i}{(\sigma_N)_i^2}}{\sum_{i=1}^n \frac{(F_N)_i^2}{(\sigma_N)_i^2}} \quad (9)$$

Application of the spectral analysis procedure for the quantification of relative concentrations of lead-arsenic signals

To apply the procedure described earlier, we need to construct a characteristic function $F(E_i)$ that represents the overlap of the monoenergetic spectra of lead and arsenic multiplied by the factors that give the information of their detection sensitivities and relative concentrations. For this, we use Eqn (5), obtaining a theoretical discrete and normalized function, $F_N(E_i)$ representing the overlap of the lines K and L of lead and arsenic:

$$F_N(E_i) = \frac{\phi S_{As/Pb} (As_N)_i + (Pb_N)_i}{1 + \phi S_{As/Pb}} \quad (10)$$

By evaluating the parameter α_N on the measured spectrum, the value obtained for these two data series is close to 1 only if the data measured correspond to a spectrum with the adjusted signals of Pb and As in their respective concentrations.

The statistical scatter of the measured and normalized data corresponding to each channel i , $(\sigma_N)_{ii}$, is calculated using the standard uncertainty equation.^[20]

$$\begin{aligned}
 (\sigma_N)_i &= \sqrt{\sum_k \left(\frac{\partial(m_N)_i}{\partial x_k} \right)^2 \Delta x_k^2} \\
 &= \sqrt{\frac{m_i}{\left(\sum_{i=1}^n m_i\right)^2} + \frac{m_i^2}{\left(\sum_{i=1}^n m_i\right)^3}} \quad (11)
 \end{aligned}$$

Now, it is necessary to find a normalized function that maximizes the parameter of comparison, α , equalling it to 1. For this, we take Eqn (10) and write it in function of two unknown coefficients that carry the information of the sensitivity and relative concentration of the elements:

$$F_N(E_i) = \frac{\phi S_{As/Pb} (As_N)_i + (Pb_N)_i}{1 + \phi S_{As/Pb}} = K_1 (As_N)_i + K_2 (Pb_N)_i \quad (12)$$

These K_1 and K_2 values are constrained by a normalizing condition given that F_N , As_N , and Pb_N are normalized functions:

$$K_1 + K_2 = 1 \quad (13)$$

Thus, we can find the equation for α_N in function of a single parameter, K_1 :

$$\alpha_N(K_1) = \frac{\sum_{i=1}^n \frac{[K_1(m_N)_i * (As_N)_i + (1 - K_1)(m_N)_i * (Pb_N)_i]}{(\sigma_N)_i^2}}{\sum_{i=1}^n \frac{[K_1(As_N)_i + (1 - K_1)(Pb_N)_i]^2}{(\sigma_N)_i^2}} \quad (14)$$

As can be seen in the aforementioned equation, we obtain a function of variable K_1 whose maximum should tend towards a value of 1 (see Figure 2). This provides the value of the coordinates (K_1 , K_2) that maximize the α_N . This pair of values is used to find the relative concentration of the elements.

The information on the relative concentrations of these coefficients is obtained by replacing the coefficients in the characteristic function, Eqn (12). From this, we obtain the proportion

$$\frac{K_1}{K_2} = \phi S_{As/Pb} \quad (15)$$

Thus, if the relative sensitivity of the detection of the elements is known for the ROI in which the spectrum is being analyzed, the relative concentration in which the elements are found, ϕ , can easily be determined with Eqn (15).

Identifying the presence of monoelemental signals in spectra with overlapping emission lines

The monoelemental spectra of lead and arsenic are largely similar, their respective emission lines $L\alpha_{1,2}$ and $K\alpha_{1,2}$ overlap, in the region near 10.5 keV (see Figure 3).

The challenge for the proposed methodology is to recognize the presence of one signal over another given extreme relative concentrations, that is, when there is a large concentration of arsenic over lead and vice versa. For this, we need information from three different comparisons, along with their respective errors, to discriminate the presence of a signal in the measured spectrum.

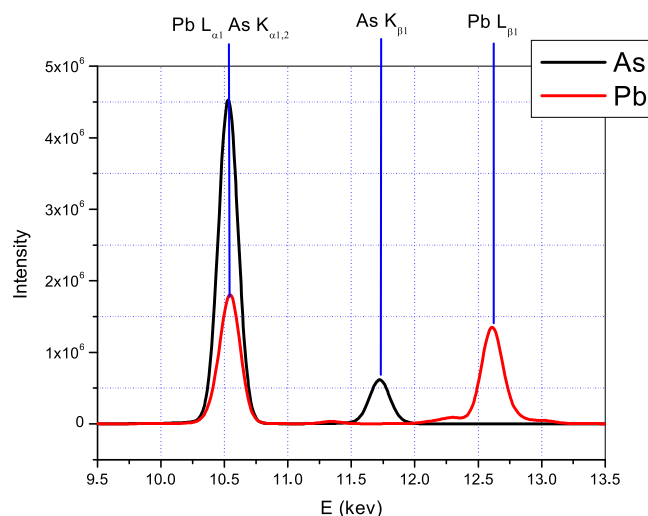


Figure 3. Theoretical spectrum of the superposition of the signals of arsenic and lead.

We calculate the normalized alpha parameter, α_N , for the measured spectrum, adjusting first for only one monoelemental function and later for two monoelemental functions.

It should be remembered that the normalized alpha parameter tends to be 1 when the adjusted function corresponds to the elements of the measured spectrum. If the said function, F_N , does not correspond, the alpha value should drop between (0, 1).

That is,

$$\alpha_N = \frac{\sum_{i=1}^n \frac{(m_N)_i * [K_1(As_N)_i + K_2(Pb_N)_i]}{(\sigma_N)_i^2}}{\sum_{i=1}^n \frac{[K_1(As_N)_i + K_2(Pb_N)_i]^2}{(\sigma_N)_i^2}} \sim 1 \quad (16)$$

$$\alpha_N^{Pb} = \frac{\sum_{i=1}^n \frac{(m_N)_i * (Pb_N)_i}{(\sigma_N)_i^2}}{\sum_{i=1}^n \frac{(Pb_N)_i^2}{(\sigma_N)_i^2}} < 1 \quad (17)$$

$$\alpha_N^{As} = \frac{\sum_{i=1}^n \frac{(m_N)_i * (As_N)_i}{(\sigma_N)_i^2}}{\sum_{i=1}^n \frac{(As_N)_i^2}{(\sigma_N)_i^2}} < 1 \quad (18)$$

Experimental

We used a spectrometer S2 PICOFOX (Bruker) for all the TXRF analysis made for the proposed procedure. The system is enclosed in a biological X-ray shield adequately designed.

The system includes

1. An air-cooled metal-ceramic X-ray tube with a molybdenum target that operates at a maximum of 50 W of power, at 50 kV, and 1.5 mA.
2. A multilayer monochromator.
3. A high-resolution, Peltier-cooled XFlash silicon drift detector (SDD) that does not need a liquid nitrogen cooling system,

with a 10-mm² active area and energy resolution of <160 eV to 100 Kcps (Mn K line, 5.9 keV).

The spectrometer S2 PICOFOX TXRF is a versatile instrument, able to analyze traces of elements in different types of samples. It is completely independent of any means of cooling and, therefore, suitable for *in situ* analysis. Other advantages of the S2 PICOFOX are its simple calibration routine and capacity for multielemental analysis.

Preparation of artificial samples

The samples were prepared using a solvent that can be dried by evaporation (herein, double distilled and deionized water) as a matrix. A micropipette was used to deposit 5 µl of solution from each sample on a quartz reflector (30 mm diameter); this was dried with an infrared lamp.

A set of different samples (see Table 1) was prepared. None of the compounds presented special risks for handling. Commercial reagents (*monoelemental certificate Merck*) were used; these reagents were certified volumetric standards, containing a certified concentration of 1000 mg/l (1000 ppm). Solutions were prepared with mixtures of concentrations from 1 to 40 ppm. The solutions containing the monoelemental samples of lead and arsenic were prepared with concentrations of 40 ppm. Irradiation and data collection times were preset at 1000 s for each sample, and one measurement was carried out for each sample.

Data analysis

All the data were acquired in the spectrometer PICOFOX. For all the quantitative data, the instrument was operated using its normal energy levels with data acquisition times of 1000 s. The TXRF instrument used in this study was calibrated in the routine manner.

We consider that the uncertainty of the concentrations of the artificial samples was produced because of the instrumental error of preparation. The interpretation of the spectra and the

elemental evaluation were first carried out using the X-ray analysis software, SPECTRA 5.3 (Bruker), provided with the equipment (S2 PICOFOX 6.0).

The SPECTRA software has a database with spectra showing the characteristic and relative sensitivities of all the elements. Thus, the relative concentrations at which the elements are found can be quantified. The software allows users to obtain a reference value that does not necessarily have to coincide with the theoretical preparation value given in Table 1.

If the background obtained with this technique (using portable samples of silicon and a water matrix) is very small, the methodology consists of adjusting a measured spectrum that can be considered to be a greater background. This is then removed directly from the measured data, and only the spectrum containing information on the elements (and not on any other source) is used. To model and then remove the background require first adjusting it; references with methods regarding the modeling of the background can be found in references and in software packages such as AXIL and WINQXAS.^[21,22]

Once the background is eliminated from the counts of the measured spectrum, an ROI is chosen that consists of the channels of energy in which information on the two elements under analysis is found. For the cases of lead and arsenic, the channels made up between the energies 8.4824 and 16.0215 keV were taken to be the ROI.

The spectra are normalized, and then, we calculated the value of the coefficients, K_1 and K_2 , that maximize the parameter, α_N .

Results

The problem consists of determining the limits of ϕ , in which the new method is capable of identifying the presence or absence of the signal of an element. For this, we need to compare the three adjustments of Eqns (16)–(18).

Figure 4 shows the value of α_N for all the samples, ordered according to their relative concentrations, ϕ , obtained with Eqn

Table 1. Values of α_N parameter for the set of samples classified by the relative concentration of lead on arsenic

$\phi = C_{Pb}/C_{As}$	$\alpha_N \pm \Delta\alpha_N$		$\alpha_N^{As} \pm \Delta\alpha_N^{As}$		$\alpha_N^{Pb} \pm \Delta\alpha_N^{Pb}$	
45.590	0.9927	0.0015	0.16652	0.00062	0.9906	0.0015
16.850	0.98957	0.00043	0.27695	0.00023	0.98166	0.00043
10.001	0.9938	0.0012	0.33788	0.00069	0.9769	0.0012
5.259	0.9933	0.0013	0.44604	0.00084	0.9557	0.0012
3.615	0.9922	0.0014	0.50150	0.00096	0.9303	0.0013
3.277	0.9850	0.0017	0.5106	0.0012	0.9147	0.0017
2.297	0.9904	0.0016	0.5749	0.0013	0.8831	0.0016
1.962	0.9890	0.0019	0.5985	0.0014	0.8599	0.0017
1.375	0.9924	0.0013	0.6574	0.0010	0.8013	0.0011
1.276	0.9768	0.0031	0.6611	0.0025	0.7755	0.0027
0.861	0.9918	0.0012	0.72934	0.00099	0.69425	0.00096
0.831	0.9893	0.0015	0.7324	0.0013	0.6832	0.0013
0.804	0.99406	0.00071	0.74102	0.00061	0.67815	0.00059
0.668	0.9741	0.0016	0.7528	0.0014	0.6165	0.0013
0.368	0.9840	0.0016	0.8347	0.0014	0.4569	0.0011
0.307	0.9898	0.0018	0.8595	0.0017	0.4124	0.0011
0.300	0.9669	0.0037	0.8425	0.0034	0.3979	0.0024
0.034	0.9753	0.0014	0.9564	0.0014	0.06952	0.00038

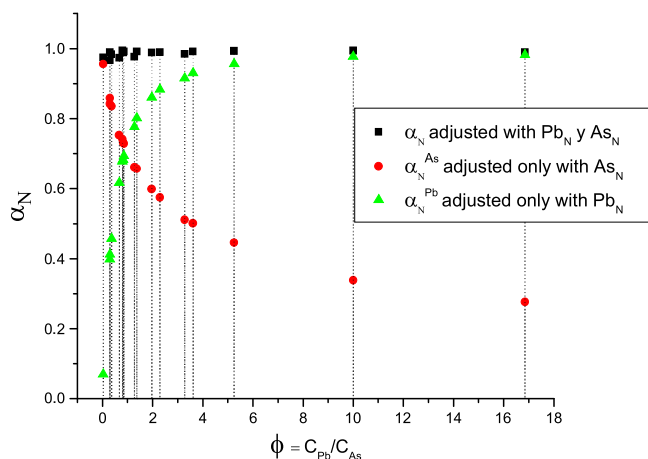


Figure 4. Values of parameter α_N with complete and incomplete adjustments (only one element), plotted for a range of different relative concentrations, ϕ . The data are shown in Table 1.

(15). Moreover, it shows the calculation of the alpha parameter with incomplete adjustments, considering only lead, α_N^{Pb} , and only arsenic, α_N^{As} .

The adjustment with only arsenic approaches the value of α_N when the lead in the sample decreases, and the adjustment with only lead approaches the value of α_N when the concentration of lead is much greater than that of arsenic. The values obtained are shown in Table 1.

With the values in Table 2, we used the criterion of Eqns (16)–(18), and we compared the values of the complete and incomplete adjustments when these were close, taking the difference considering the uncertainties obtained.

The aforementioned table shows the limits of the relative concentrations that the new method can identify for the signals of lead and arsenic in a sample. It was not possible to determine the presence of arsenic over lead at a ratio $C_{Pb}=45.5 * C_{As}$. Thus,

Table 2. Differences between the value of parameter α_N with full adjustment and with an adjustment of a single element

$\varphi = C_{Pb}/C_{As}$	$(\alpha_N - \Delta\alpha_N) - (\alpha_N^{As} + \Delta\alpha_N^{As})$	$(\alpha_N - \Delta\alpha_N) - (\alpha_N^{Pb} + \Delta\alpha_N^{Pb})$
45.590	0.82399	-0.0009
16.850	0.71196	0.0071
10.001	0.65402	0.0145
5.259	0.54519	0.0352
3.615	0.48836	0.0592
3.277	0.47147	0.0669
2.297	0.41265	0.1041
1.962	0.38721	0.1256
1.375	0.33271	0.1887
1.276	0.31009	0.1955
0.861	0.26034	0.2955
0.831	0.25398	0.3032
0.804	0.25172	0.3146
0.668	0.21839	0.3548
0.368	0.14635	0.5245
0.307	0.12693	0.5745
0.300	0.11736	0.5630
0.034	0.01598	0.9040

the adjustment with the two elements could not be differentiated from an adjustment with only the lead function. On the other hand, the procedure identified the presence of a lead signal in a sample in which the ratio of concentration was $C_{Pb} = 0.03 * C_{As}$ and could even be lower.

Conclusions

We studied the applicability and validity range of a mathematical procedure for the identification and quantification of arsenic and lead. This procedure has showed to be appropriate for analyzing two or more signals that interfere with each other or for the quantification of a very small signal in a very noisy environment, but a complete study of determination of its confidence interval in samples in which one element in the overlap is present in a concentration much lower than the other elements was not studied previously.

The procedure proposed an identification criterion that was successful for most of the samples, being able to identify the presence of one signal over the other for very small ratios, with very critical concentrations.

Because of the similarity of the monoenergetic spectra of lead and arsenic and the total overlap of their emission lines, $L\alpha_{1,2}$ and $K\alpha_1$, in the region near 10.5 keV, the selection of this test for the method was very appropriate. The procedure was successfully applied for the deconvolution and subsequently quantification of the two elements.

The method proposed can also be applied easily to other overlaps, even with any technique of dispersive energy spectroscopy because it only requires information on the characteristic monoenergetic functions or the background that is present in the ROI. If quantification is desired, it is necessary to know the relative sensitivity of the equipment for the two elements in question, and if the concentrations are very low, the method is optimized with a high counting statistics, so it takes a longer time of measurement.

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