Uncertainty Evaluation in Quantities Obtained From PIXE Elemental Analysis of Atmospheric Aerosols

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Abstract. In most of the published studies that deal with the elemental analysis of atmospheric aerosols, carried out, for example, with Particle Induced X-ray Emission (PIXE) or X-ray Fluorescence (XRF), concentrations of the elements are combined to obtain further results about other quantities. Examples of this are the calculation of variables related to Soil, Sulfate, Non-Soil Potassium, or Organic Matter. Frequently the experimental uncertainty is overlooked in these new calculations, or there are even confusions regarding nomenclature. Furthermore, the elemental concentrations used to compute the derived magnitudes are often correlated, as is the case of Al, Si, Ca, Ti, and Fe in the *Soil* variable. In this work, an evaluation of the experimental uncertainty of some of these quantities is presented, especially when there are correlated quantities, based on the *ISO Guide for the Evaluation of Uncertainty*. Here, elemental concentrations in samples of PM_{10} collected in downtown Mexico City are used to illustrate the method, so it can be followed to evaluate straightforwardly the experimental uncertainty in this kind of studies.

Keywords: Aerosols, PIXE, uncertainty, soil.

INTRODUCTION

The analysis of atmospheric aerosols is one of the main applications of Particle Induced X-ray Emission (PIXE) [1]. Although the data obtained with PIXE is not complete with regard to all the components of the aerosols, very useful information can be obtained from the measured elemental concentrations. Examples of this are the application of multivariate statistical methods to identify sources and their apportionment, receptor modeling using chemical balance techniques, or the determination of contributions from sources with assumed composition. Following the last idea, several authors have defined quantities that make use of the elemental concentrations found in the analyzed samples, to predict the role of those quantities or trying to reconstruct the total mass of the aerosols [2-4]. However, some of the works using these quantities overlook the evaluation of the experimental uncertainty, which is influenced by many factors, and that may have an effect on the conclusions reached in each study. As stated in the *ISO Guide for the Evaluation of Uncertainty* [5], "a measurement result is complete only when accompanied by a quantitative statement of its uncertainty. The uncertainty is required in order to decide if the result is adequate for its intended purpose and to ascertain if it is consistent with other similar results." Therefore, in this work an example of the procedure suggested in this *Guide* is shown, applied to quantities derived from elemental concentrations obtained after PIXE analysis of atmospheric aerosols in Mexico City.

QUANTITIES DERIVED FROM ELEMENTAL CONCENTRATIONS

As the results obtained with PIXE analysis of aerosol samples is most of the times presented as concentration of an element in air (mass per unit volume of air), it is possible to determine the concentration of other quantities defined as follows [2]:

$$Soil = 2.20Al + 2.49Si + 1.63Ca + 1.94Ti + 2.38Fe,$$

$$(1)$$

$$Sulfate = 4.125S, \qquad (2)$$

$$NSK = K - 0.52Fe. \qquad (3)$$

In these equations, *Soil* represents the concentration of soil derived particles, *Sulfate* is the ammonium sulfate concentration, and *NSK* is the concentration of K with an origin other than soil (such as smoke), and *Al, Si, Ca, Ti, Fe, S,* and *K* represent the concentrations of the corresponding elements. Eqs. (1) and (3) are obtained through the oxide forms and crustal ratios of the elements. The measurement of the concentrations of each element must include the evaluation of the corresponding uncertainty. In particular, the concentration C_Z of element Z is given by the equation

$$C_Z = \frac{N_{X,Z} \pi \left(\dfrac{D}{2}\right)^2}{k(Z) N_P Q_R t}. \qquad (4)$$

Here, $N_{X,Z}$ is the number of X-ray photons emitted by element Z, D is the diameter of the particle deposit on the filter, $k(Z)$ is the response function of the X-ray detection system, N_P is the ion beam integrated charge used to obtain the spectrum for this sample, Q_R is the actual air flow (corrected for calibration, as well as local temperature and pressure), in the sampling device, and t is the time required to collect the sample. To facilitate the explanation, no stopping of ions or X-ray absorption corrections are used in this work. The application of Eq. (10) from ref. [5] to Eq. (4) results in an equation for the evaluation of the combined uncertainty $u_C(C_Z)$ for this elemental concentration:

$$u_C^2(C_Z) = C_Z \left[\frac{u^2(N_{X,Z})}{N_{X,Z}^2} + \frac{4u^2(D)}{D^2} + \frac{u^2(k(Z))}{(k(Z))^2} + \right.$$
$$\left. + \frac{u^2(N_P)}{N_P^2} + \frac{u^2(Q_R)}{Q_R^2} + \frac{u^2(t)}{t^2} \right], \qquad (5)$$

where $u(X)$ represents the combined uncertainty for quantity X. As explained in ref. [2], this procedure is valid when the quantities involved in the determination of C_Z are not correlated, which is actually the case. However, when the evaluation of the quantities *Soil* or *NSK* is required, it happens that the elemental concentrations for the elements Al, Si, K, Ca, Ti, and Fe are correlated, sometimes with high correlation coefficients. Therefore, it is necessary to use Eq. (13) from ref. [5], which states that the combined uncertainty $u_C(f)$ for a quantity f derived from other N correlated quantities x_i with uncertainties $u(x_i)$ is given by:

$$u_c^2(f) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) +$$
$$+ 2\sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i) u(x_j) r(x_i, x_j). \qquad (6)$$

In this equation $r(x_i, x_j)$ is the correlation coefficient between quantities x_i and x_j. Therefore, the application of this equation to a quantity like *Soil* from Eq. (1) results in a sum of 15 terms.

EXAMPLE: UNCERTAINTY IN *SOIL* FROM PM$_{10}$ SAMPLES

As an example of the use of the procedure explained above, the uncertainty in the *Soil* variable is computed for a set of PM$_{10}$ samples collected in Downtown Mexico City (building of the *PUEC-UNAM*) during the year 2005. The sampling device is a *Minivol Portable Sampler* (Airmetrics, Eugene, OR, USA). Airborne particles were deposited onto 47 mm *Nuclepore* polycarbonate filters with 0.4 µm pore size, from April 6 to September 18, 2005, every three days, along 24 h, starting at 8:00 h in the morning of each day. The filters were then analyzed with PIXE to measure the elemental concentrations. A 2.5 MeV H+ beam, produced by the 9SDH-2 Pelletron accelerator at Instituto de Física, UNAM (IFUNAM), was employed to induce the X-rays. Two detectors (an Amptek Si PIN diode and a Canberra LEGe) registered the X-rays emitted by the sample. The Si PIN detector (located at a 30° direction from the beam) had a 35 µm thick Kapton pierced filter, to collect the X-rays from light elements, while the LEGe detector (45° from the beam direction) used a 35 µm Al filter to eliminate X-rays from those elements. Thus, the first detector gave information for elements Si to Ti, while the second one was used for elements heavier than Ti. Alternatively, a further PIXE analysis of the samples with a 0.7 MeV proton beam (produced by the 0.7 MV Van de Graaff accelerator at IFUNAM), and using a Canberra Si(Li) detector with an ultra-thin Be window, provided information on lighter elements (Mg and Al), taking advantage of the low background in the X-ray spectra. In all cases, the detector response functions $k(Z)$ were determined with a set of MicroMatter thin film standards. The QXAS computer code was employed to obtain the X-ray peak areas in each spectrum.

To obtain the uncertainties in each elemental concentration, all the factors in Eq. (5) were considered, also as recommended by Maenhaut [6]. The deposit diameter was measured with a digital caliper, the uncertainty in $k(Z)$ came mainly from the thin film standard thickness uncertainty, while repeated observations of the integrated charge in the Faraday cup were done to determine uncertainty. The actual flow Q_R was obtained from the calibration curve (provided by the manufacturer of the sampler), and measurements of local pressure and temperature. Finally, the uncertainty in collection time is found in the sampler manual. Once the elemental concentrations are computed, the correlation matrix is calculated for the required elements (Al. Si, Ca, Ti, and Fe), for the whole sample set. This matrix is shown in Table 1.

TABLE 1. Correlation matrix for elemental concentrations.

	Al	Si	Ca	Ti	Fe
Al	1	0.957	0.519	0.512	0.659
Si		1	0.550	0.398	0.638
Ca			1	0.476	0.853
Ti				1	0.471
Fe					1

Thus, it is possible now to apply eq. (6) to compute the combined uncertainty of the *Soil* variable for each sample. Fig. 1 shows the results for this quantity as a function of the sampling date, with the corresponding uncertainty.
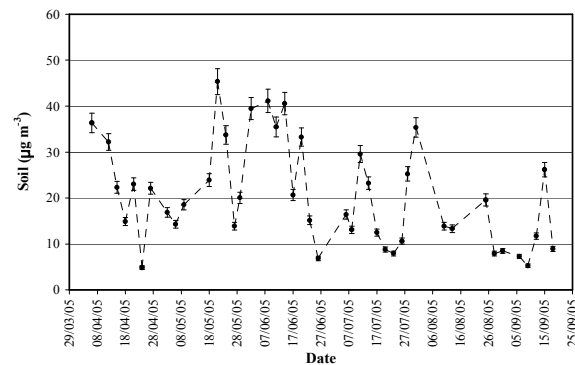

FIGURE 1. *Soil* variable concentrations for samples along the study period, considering the elemental variables are correlated for uncertainty evaluation.

The effect of considering the correlation among elemental concentrations is displayed in Fig. 2, where an error between both uncertainties (without and with correlation) is plotted as a function of the sample collection date. This error ε_U is defined as:

$$\varepsilon_U = \frac{u_{C,U}(Soil) - u_{C,C}(Soil)}{u_{C,C}(Soil)} \times 100. \quad (7)$$

In this equation, $u_{C,U}(Soil)$ refers to the combined uncertainty evaluated without correlation and $u_{C,C}(Soil)$ represents the uncertainty evaluated with correlation. This error is defined solely for the purpose of this work. It is apparent that the uncertainty may be underestimated by as much as 30% when the correlation is not taken into account.
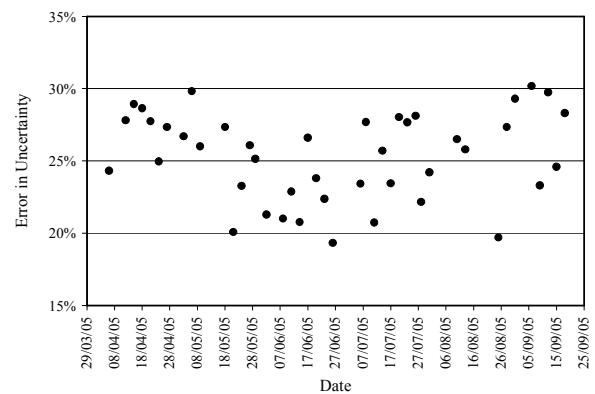

FIGURE 2. Error in the combined uncertainty of the *Soil* variable concentrations for samples along the study period.

Although in this particular example the conclusions reached after evaluating the concentrations of the *Soil* variable are not altered, in other instances it may be the case. An example is the non-soil K variable (*NSK*) in eq. (3), where the result may be very close to zero, thus concluding that the variable was not detected for a particular sample [7].

CONCLUSIONS

The above example showed the procedure for the proper evaluation of the total combined uncertainty in derived quantities obtained in the analysis of aerosol samples. Although rather cumbersome, this process is necessary to obtain correct uncertainties, in agreement with current official standards. The "new" uncertainties may alter the conclusions reached in a particular study.

It must be noted that this method was applied to a particular case (aerosol elemental analysis), but it must be considered and extended to other samples, like thick or intermediate-thickness targets.

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