Characterization of Atmospheric Particles by Electron Probe X-Ray Microanalysis

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Summary: Microchemical glass standards were used to validate a quantitation method based on peak-to-background (P/B) ratios from electron probe x-ray microanalysis spectra. This standardless method was applied to the determination of concentrations of individual particles from Mα or Lα lines, as well as from Kα lines. The algorithm was tested on particulate glass samples for diameters ranging from 1 to 20 μm. The determined concentrations did not depend on particle size. The certified values for elements were well matched, except for Na, which may migrate under electron bombardment. Finally, classification of qualitative results obtained for aerosol particles was completed by the P/B quantitative method.

Key words: environmental aerosols, electron microprobe, spectral deconvolution, standardless analysis

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Introduction

In many applications of environmental particulate analysis, the exact knowledge of the composition of the particles can be of great value. Particulate pollutants in the atmosphere consist of a mixture of suspended solid or liquid particles originating from different natural and anthropogenic sources. In many applications such as source profiling, the qualitative information on the type of individual particles is sufficient to classify typical sources.

However, many sources emit particles with a similar major element composition, and the quantitative information may result in a better identification of the sources. When industrial particles are characterized, the corrosion or erosion process can be better traced back if quantitative information is available.

For chemical characterization of atmospheric particles, electron probe x-ray microanalysis (EPMA) is a widely applied technique that can provide excellent possibilities for automated analysis. For source profiling of aerosol samples, semiquantitative approaches using the net peak intensities combined with chemometric methods such as cluster and factor analyses are generally used (De Bock *et al*. 1998, Treiger *et al*. 1995). However, quantitative results are required in some applications where the origin of the particles has to be identified without question.

For the quantitation of single particles, basically two approaches are possible. The peak-to-background (P/B) method (Small *et al*. 1979, Statham and Pawley 1978) has the advantage that most instrumental factors are cancelled out. On the other hand, the background intensity under the peak has to be statistically significant. The other approach is to use physical models to account for the effects of particle size and shape, such as employing Monte Carlo simulations, which requires precise input parameters for the experimental conditions and is demanding in terms of computation time (Armstrong and Buseck 1975, Ro *et al*. 1999).

The approach taken in this paper is to use a P/B procedure (Trincavelli and Van Grieken 1994), in which P/B ratios appear only once, and therefore the large uncertainties related to spectral deconvolution and background subtraction are not so important (see "P/B Method" section below). On the other hand, fluorescence yield coefficients and intensity ratios are required, which in certain cases may be important sources of errors. The quantitation routine is performed by an iterative process carried out by the code MULTI (Trincavelli and Castellano 1999), a program originally developed with the purpose of allowing the analyst to choose among different matrix-correction models and several expressions for the parameters involved.

Heavy metals such as lead are frequent components of aerosols originating from several industrial sources and

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traffic. Due to their strong toxic effects on the higher organized life, it can be of importance to give quantitative values for them. Overlapping of K and L lines might be a typical problem in environmental analysis of highly polluted samples. For instance, the K-alpha line of arsenic overlaps with the L-alpha line of lead, while sulfur K lines overlap with M lines of lead. For general applications, the program was adapted to quantify in a flexible mode either from L or M lines, if necessary.

Experimental

This work was based on electron probe microanalysis on NBS standard samples. Two different standards were measured: SiO_2–PbO–K_2O–Na_2O–BaO glass (NBS 89) and SiO_2–CaO–Na_2O–K_2O–Al_2O_3 glass (NBS 91). In both cases, the glass standards were reduced to small (1–20 µm) diameter sizes. The standard particles were suspended in a solution of 1% rubber cement in normal hexane. They were then filtered on a Nuclepore filter (Whatman International Ltd., Kent, U.K.) with 0.4 µm pore size, whose low mean atomic number is convenient to minimize the influence of bremsstrahlung from the substrate.

Part of the filter was glued by adhesive tape to an Al sample-holder and coated by a thin carbon layer to prevent charging and heating during scanning electron microsope examination. X-ray spectra of individual particles were collected using a PHILIPS 505 SEM (FEI Philips, Peabody, Mass., USA) equipped with a Link Si(Li) detector (Oxford Instruments, Cambridge, U.K.). One to three analyses at accelerating voltages of 20, 17, or 14 keV were performed on each of the standard glass particles chosen. To reduce absorption effects, the analysis points were selected in a region of the particle that faced the x-ray detector. The measurement time was 200 or 250 s, resulting in typical total spectrum integrals ranging from 25,000 to 270,000 counts. The particle diameters were estimated by visual observation of the microscope images.

Spectra Processing

The x-ray spectra obtained for the particles were processed by a least squares fitting method using the AXIL code of Van Espen et al. (1985). Since the accuracy of the P/B method is very sensitive to the background determination, special attention was devoted to unbiased estimation of the background. The processed peaks and background intensities under the peaks were used as input for the code MULTI.

The Lα line, and in the case of lead the Mα line, were used to determine the barium concentration. In the other cases, Kα lines were considered. The lead Mα transition rate was obtained by parameter optimization from a spectral region, using the code POEMA (Bonetto et al. 2001). The method consists of performing minimization of quadratic differences between experimental and predicted values (in fact, a χ^2 minimization) for different regions of the spectrum by means of an iterative process. These quadratic differences depend on several parameters that may be optimized through the expressions chosen for the predicted spectrum—in the present case, the lead Mα transition rate. An exhaustive description of the complete procedure is detailed in the original work.

Peak-to-Background Method

The standardless P/B method assumes that the bremsstrahlung and fluorescent photons originate from the same sample region and that the bremsstrahlung emission is isotropic. Under these assumptions, shape and size effects are eliminated, as detailed by Trincavelli and Van Grieken (1994). The characteristic intensity P_i for a given line of the element i can be expressed as

$$P_i \propto C_i \, (\text{ZAF})_i \, \omega_i \, f_i \, \varepsilon_i \, I \, t \, \Delta\Omega/(4\pi) \qquad (1)$$

where C_i is the mass concentration of the element i, Z, A, and F are the atomic number, absorption, and fluorescence correction factors, respectively, ω_i is the fluorescence yield coefficient, f_i is the line intensity ratio, ε_i is the detection efficiency for E_i, I is the beam current, t is the acquisition live time and $\Delta\Omega$, the solid angle subtended by the detector. On the other hand, the bremsstrahlung corresponding to the peak considered can be written as

$$B_i \propto \text{f}(Z,E_i,E_o) \, A \, \varepsilon_i \, I \, t \, \Delta\Omega \qquad (2)$$

where f is a function of the mean atomic number Z, the energy E_I, and the beam energy E_o.

From the last two equations,

$$C_i \propto P_i/B_i \, \text{f}(Z,E_i,E_o)/(ZF\omega_i f_i) \qquad (3)$$

Since the interaction volume for secondary fluorescence in bulk specimens is much larger than the total volume of small particles, the influence of the correction factor F can be neglected. The atomic correction factor was taken from Riveros et al. (1992), while the model f(Z,E_i,E_o) for the bremsstrahlung is the one given by Trincavelli et al. (1998).

Results and Discussion

To test the applicability of the method, the dependence of the obtained concentrations on the particle size was tested. The calculated concentrations for the certified NBS standards were ordered according to the particle diameter. The results are displayed on Figure 1a, b, where the bars on each point represent the largest standard deviation for this particle. As can be seen, no systematic deviation depending on the diameter is observed. The continuum emitted from the substrate might be expected to influence the spectrum of interest, except when the particle size ap-

proaches the bulk situation. However, the calculated concentrations are insensitive to the substrate radiation in all the cases, since their values remain the same for smaller particle sizes. The reason that concentrations do not depend on substrate background, even when the spectra may be altered, is that a first approach proportionality between sample and substrate bremsstrahlung may be assumed, the proportionality constant being the ratio between the corresponding mean atomic numbers (Kramers 1923). The resulting factor when the P/B ratio is performed is cancelled out during the normalization step.

To check the method for different excitation conditions (which, in fact, produce different correction factors), spectra were recorded at 20, 17, and 14 kV for the NBS 89 standard. The results, shown in Figure 2, do not indicate correlation between the concentrations and beam energy, except for the sodium concentration, an element which must be disregarded as explained below.
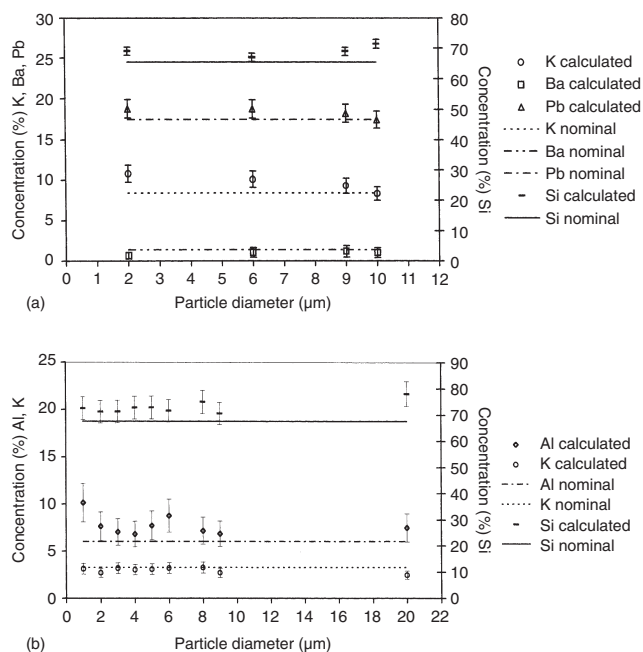

FIG. 1   (a) Determined concentration versus particle diameter for NBS 89 glass standard. (b) Determined concentration versus particle diameter for NBS 91 glass standard.
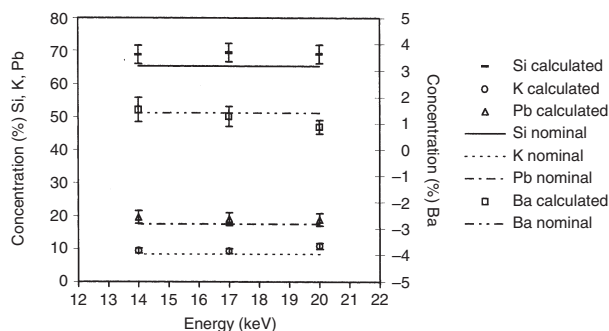

FIG. 2   Determined concentration versus incident beam energy for NBS 89 glass standard.

The applicability of the method can be seen from the results presented in Tables I and II, which list the mean and standard deviation of the calculated concentrations. There is a good agreement (< 8% difference) between the measured and nominal concentrations of silicon, potassium, and lead in NBS 89 standard and for silicon, potassium, and calcium in NBS 91. There is poor agreement for sodium, probably because this element can migrate under electron beam bombardment. Similar problems were observed by Lineweaver (1963). He suggested that Na$^+$ ions are attracted away from the surface by incident electrons that come to rest at a finite depth; other authors found that this effect is particularly strong when analyzing glasses (Ribbe and Smith 1966). Lesser discrepancies arise for barium and aluminum.

The standardless P/B method was used to analyze unknown particulate samples as well. For this purpose, 300 individual aerosol particles collected from a Hungarian cave were analyzed. The net peak intensities were used as variables for hierarchical clustering (Massart and Kaufman 1983). Figure 3a shows the qualitative results from the classification. In a subsequent step, a representative particle of each class was quantified by the P/B algorithm. The quantitative concentrations obtained, shown in Figure 3b, can be used for deposition modeling or other environmental impact assessment.

Conclusions

The standardless P/B method has shown good analytical performance for microchemical glass standards containing elements in a wide atomic number range from Al to Pb, and particle diameters ranging from 1 to 20 μm. Except for sodium, the measured and nominal concentrations

TABLE I   Calculated and certified concentrations for NBS glass standard 89

	Calculated concentrations (%)	Nominal concentrations (%)
Na	2.63 ± 0.54	5.7
Si	69.25 ± 0.83	65.35
K	8.70 ± 0.69	8.4
Ba	1.03 ± 0.19	1.4
Pb	18.39 ± 0.36	17.5

TABLE II   Calculated and certified concentrations for NBS glass standard 91

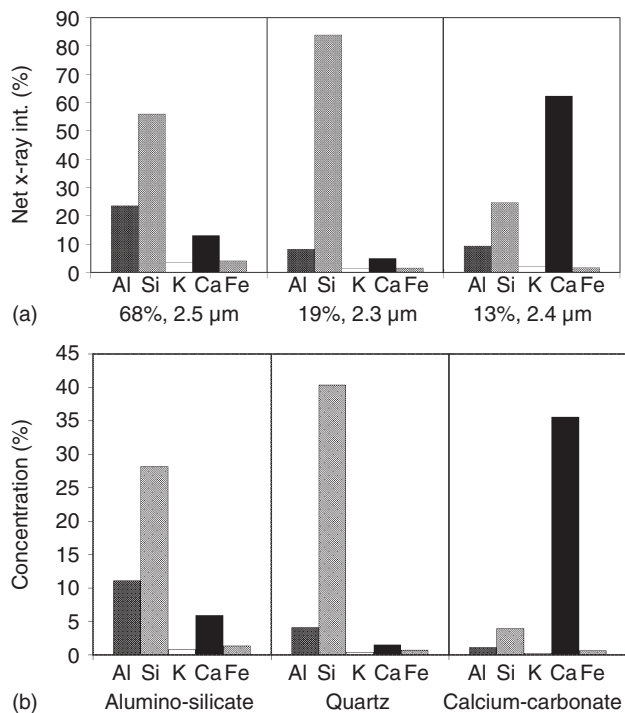|	Calculated concentrations (%)	Nominal concentrations (%)
Na	6.50 ± 0.51	8.48
Al	7.90 ± 0.72	6.01
Si	72.67 ± 1.24	67.53
K	3.04 ± 0.14	3.25
Ca	9.89 ± 1.47	10.48

FIG. 3 (a) Characteristic particle classes of aerosol sample originating from a cave. Classification was carried out based on the net x-ray intensities of the marked elements. The abundance of each class is displayed as well as its average particle diameter. (b) Elemental concentrations of one particle corresponding to each class calculated by MULTI.

agreed within 30% (mostly whithin 8%). No bias was found in the concentration determinations for either particle diameter or incident electron energy. The discrepancy in the measured Na concentrations is thought to be due to elemental migration inside the particle when electron energy is deposited in glass samples. Single particle EPMA results presented here for a dust sample from a Hungarian cave show the applicability of P/B in atmospheric aerosol studies.

This paper shows that standardless P/B can be used with good precision level for the determination of particle concentrations from Mα lines and Lα lines, as well as Kα lines. This capability allows analysis of certain problem ele-

ments found in environmental aerosol samples, such as Pb, As, and S.

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