

## Quality assessment on airborne particulate matter of $k_0$ -INAA

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The analysis of airborne particulate matter (APM) by  $k_0$ -NAA was assessed using: (1) BCR reference material (RM) simulated air-filters, (2) synthetic air-filters prepared by spiking blank filters with standard solutions, and (3) real APM filters.  $k_0$ -INAA is a suitable technique for the analysis of APM, delivering accurate and precise results. However, the quality assessment of APM analysis appears to be a difficult task.

### Introduction

Since 1987 APM measurements are made at the Technological and Nuclear Institute using two analytical techniques:  $k_0$ -standardized instrumental neutron activation analysis ( $k_0$ -INAA)<sup>1</sup> and particle induced X-ray emission (PIXE).<sup>2</sup> Both techniques are suitable for non-destructive multi-elemental analysis of APM. Other competing methods require a time-consuming dissolution of APM filters and are generally applicable to a small group of elements.<sup>3</sup>

The objective of APM measurements is to monitor air pollution sources affecting the quality of air. Factor analysis was used for the identification of these sources. It is a data reduction method based on correlations between accurately determined data sets, thus allowing the identification of data variability other than the analytical variance.

Three types of samples were analysed to investigate the accuracy and precision of  $k_0$ -NAA:

BCR-128 filters, prepared by depositing fly ash powder on methyl cellulose films, thus simulating dust loaded filters.<sup>4</sup> These filters have certified mass fractions for As, Cu, Fe, Mn, Zn and indicative values for Cr, Ni, S, V. We monitored As, Cr, Cu, Fe and Zn.

Simulated air-filters prepared by spiking known amounts of standard solutions (containing Ba, Ca, Cd, Co, Fe, K, Na or Zn) onto Nuclepore<sup>®</sup> polycarbonate filters. The nominal concentrations simulated real APM filters.

Real APM filters divided into two parts.

### Experimental

#### Preparation of BCR-128

All filters were rolled, put into a thin aluminum foil and irradiated in the Portuguese Research Reactor for one hour at a thermal neutron flux of  $1.99 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ . After irradiation, the samples were

removed from the aluminum foil and transferred to polyethylene containers. Gamma-spectra were recorded with high purity germanium detectors (FWHM~1.8 keV at 1332 keV), 2–3 days after irradiation to monitor As, Cu, Zn, and 4 weeks later to determine Cr, Fe, Zn. 1 mm diameter wires of 0.1% Au–Al alloy were co-irradiated as neutron flux monitors.

#### Preparation of simulated air filters

Riedel-de Hën 1 g/l standard solutions were diluted to obtain element amounts similar to those found in real APM filters. The solutions containing Ba, Ca, Cd, Co, Fe, K, Na or Zn were spotted on glass-supported polycarbonate filters, which were subsequently dried under an infrared lamp. The preparation for irradiation was the same as for BCR filters. Samples were irradiated for 11 hours at a thermal neutron flux of  $9.8 \cdot 10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ . Gamma-spectra were recorded 2–3 days after irradiation to monitor Ca, Cd, K, Na, Zn and 4 weeks later to monitor Ba, Co, Fe and Zn.

#### Preparation of real APM filters

Two “Gent” stacked filter unit (SFU) samplers<sup>5</sup> were used (denoted as BOX and BOY). The SFU unit from NILU (Norwegian Institute for Air Research) contained two Nuclepore<sup>®</sup> polycarbonate filters with pore diameters of 8  $\mu\text{m}$  and 0.4  $\mu\text{m}$ . A flow rate of 15–16 l/min was used. The coarse fraction corresponds to APM collected with an equivalent aerodynamic diameter (EAD) between 10 and 2.5  $\mu\text{m}$ , while the fine fraction corresponds to APM collected with EAD lower than 2.5  $\mu\text{m}$ .

The samplers worked at close distance (3 meters) for 24-hour periods during 45 days. The filter loadings were determined gravimetrically in a controlled clean room (class 10,000) using a Mettler Toledo balance with a sensitivity of 0.1  $\mu\text{g}$ . Each filter was divided into two equal parts and elemental analysis of each half-filters

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was carried by  $k_0$ -INAA. The composition of the half-filters, obtained from one sampler, and those from the two samplers, were compared.

Samples were irradiated for 7 hours at  $1.99 \cdot 10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ . As, Br, K, La, Na and Sm were determined 2–3 days after irradiation; while Cr, Fe, Hg, Sb, Se, Sc and Zn were determined four weeks later.

## Results and discussion

### BCR-128

Table 1 lists the results obtained in this work with the corresponding 95% confidence interval together with the certified/indicative values provided in the BCR-128 certificate. Except for Cu (close to the detection limit), a good agreement between the experimental results and the certificate values is observed. Higher uncertainties are obtained for As and Zn, for which the deconvolution of multiplets was required.

Table 1. Element contents in BCR-128 and results obtained in this work

Element	Certified value, mg/kg	This work** ( $n = 6$ ), mg/kg
Cu	$176 \pm 9$	$190 \pm 134$
As	$48 \pm 2.3$	$47 \pm 7.1$
Fe	$33800 \pm 700$	$31900 \pm 53$
Zn	$581 \pm 29$	$553 \pm 53$
Cr*	(180)	$193 \pm 4.5$

\* Informative value.

\*\*  $\pm 95\%$  confidence level.

Table 2. Element contents in simulated air filters prepared by deposition of standard solutions and results obtained in this work

Element	Prepared filters,* $\mu\text{g}$	This work** ( $n = 8$ ), $\mu\text{g}$
Na	$5.00 \pm 0.25$	$5.12 \pm 0.44$
K	$5.00 \pm 0.25$	$5.20 \pm 0.31$
Fe	$5.00 \pm 0.25$	$5.39 \pm 0.49$
Ba	$0.500 \pm 0.036$	$0.396 \pm 0.041$
Cd	$0.100 \pm 0.007$	$0.100 \pm 0.011$
Co	$0.00500 \pm 0.00036$	$0.00487 \pm 0.00047$
Ca	$50.0 \pm 4.3$	$50.4 \pm 4.5$
Zn	$0.500 \pm 0.036$	$0.528 \pm 0.053$

\* Uncertainties refer to errors on volume measurements.

\*\*  $\pm 95\%$  confidence level.

Table 3. Kendall rank order correlation coefficient and corresponding significance (into brackets) for concentration data of fine, coarse and PM10 fractions obtained by BOX and BOY samplers

Fine fraction	Coarse fraction	PM10 fraction
0.795 (0.000)	0.791 (0.000)	0.874 (0.000)

### Simulated air filters prepared by deposition of standard solutions

Table 2 shows the element contents in the prepared filters and the values obtained in this work with the associated uncertainties. Good agreement between the element contents in the prepared filters and our measurements was obtained. Furthermore, good reproducibility is achieved. The discrepancies with expected values may reveal some inhomogeneity due to spiking, or concentrations close to the detection limits (Ba, Ca and Cd).

### Real APM filters

APM was determined by gravimetry for fine and coarse fractions. The mass obtained was divided by the volumetric flow to determine the mass concentration. The PM10 mass is calculated summing fine and coarse particles mass. Figure 1 presents the comparison of PM10, coarse and fine mass concentration for filters from BOX and BOY samplers. As the actual concentrations in the samples are not known, our interpretation is based on relative assessment.

Figure 1 shows that samplers were equivalent with respect to collected mass and sampled volume. Correlation coefficients of 0.94, 0.98 and 0.90 were found for PM10, coarse and fine fractions, respectively. The slopes of the lines for BOY/BOX are 0.89, 0.87 and 0.95. The Kendall rank-order correlation coefficients and the corresponding significance (Table 3) were computed to the 6th-decimal, then rounded.

For PM10 a maximum difference between the samplers of 20% was found. 88% of the sampling periods have differences lower than 15%. 46% of the cases have differences lower than 5%.

For coarse fractions, the maximum difference was of 40%. 78% of the sampling periods have differences lower than 15%. 29% have differences lower than 5%.

For fine fraction, the maximum difference was of 48%. 71% of the sampling periods have differences lower than 15%. 47% of the cases have differences lower than 5%.

HOPKE et al.<sup>6</sup> made a similar study with four sampling periods and obtained a good agreement for three of them (<5%). Discrepancies found for one sampling period was of 21, 17 and 23%, for fine, coarse and PM10 fractions, respectively. According to HOPKE,<sup>6</sup> significant differences between mass fractions occur for lower mass values. Additionally, bad results arose from different sampled volumes, inaccurate positioning of the filters or inappropriate sealing of the sampling unit.<sup>6</sup>

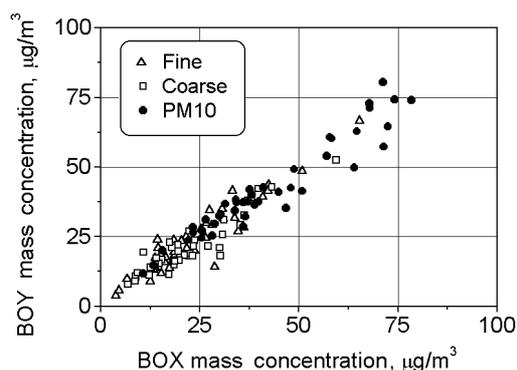


Fig. 1. Comparison of filter mass concentrations obtained in sampler BOX and sampler BOY for PM10, coarse and fine fractions

We only used filters produced during three sampling periods where both samplers collected similar mass concentrations. The objective of this experiment was to test the reproducibility of the analytical methods while monitoring similar filters. To quantify the homogeneity of the particles in the filter and the precision of the technique, filters were cut in two fractions and elemental analysis was carried out in each half of the filter. For each pair of half-filters, two parameters were determined: (1) the average elemental concentration and (2) the corresponding relative standard deviation (RSD, %). Figure 2a presents the relation between these two parameters for each of the elements investigated. When comparing the two different parts of the same filter, 32% of the pairs have an RSD lower than 5% while 81% of the pairs have an RSD lower than 15%. Significant differences (RSD = ca. 20%) are found for Cr, Hg, Sc and Zn. Br, Fe, K, Na and Sm present good agreement (RSD < 10%) between the two parts of the filters.

In order to investigate the reproducibility of the whole process, i.e., including samplers, gravimetric procedure, homogeneity of the deposit and analytical techniques, four halves obtained for each sampling period from the BOX and BOY samplers were compared. The computed average concentrations and RSD are presented in Fig. 2b. As expected, when filters provided by different samplers are compared the standard deviation increases. Only 59% of the pairs have an RSD lower than 15%. Cr, Hg, Sc, Sm and Zn present higher differences (RSD > 20%) between filters. For K, La, Na and Sb the agreement is better (RSD = ca. 10%).

These differences could be due to a non-homogeneous distribution on the surface of the filter. Small amounts of an element present on the filter may cluster in a small number of particles. However, the scatter of results decreases with increasing mean element concentration (Na in Fig. 2b). As and Sm have concentrations close to the detection limits. Analyses of the blanks indicate that the Br and Cr contents are high ( $[Cr]_{\text{fine}} = 13 \mu\text{g/g}$ ;  $[Br]_{\text{fine}} = 9.9 \mu\text{g/g}$ ;  $[Cr]_{\text{coarse}} = 18 \mu\text{g/g}$ ;  $[Br]_{\text{coarse}} = 18 \mu\text{g/g}$ ). For some samples, the amount of Cr and Br is very low in the coarse and fine fraction, respectively. Finally, the precision of Cr and Zn in real APM filters was worse than that obtained in BCR-128 and in simulated air filters. In real APM filters the spectrum background is higher, the Cr peak is positioned on a higher Compton edge, and the  $^{65}\text{Zn}$  peak appears in a multiplet together with the  $^{46}\text{Sc}$  and  $^{152}\text{Eu}$  peaks.

TORO et al.<sup>7</sup> analyzed by INAA, samples collected simultaneously with three “Gent” samplers and in the same sampling stations. The maximum standard deviations observed for Al, As, Br, Ca, Cl, Cu, Fe, Na, V and Zn (between 10% and 28%) support our results.

## Conclusions

This study confirms that  $k_0$ -INAA technique is a useful tool for the determination of elemental concentrations in APM. Our work is one of the first thorough investigations on the precision and accuracy of  $k_0$ -INAA technique in the field of APM filter analysis. Very few reference materials are available and the existing ones are not adequate for APM measurements (inappropriate matrix and element concentration to simulate atmosphere conditions).

Accurate results were obtained by  $k_0$ -NAA for BCR-128. Unfortunately, only few elements were certified and concentrations were several order of magnitude higher than those expected in real APM filters. Furthermore, the filter substrates used in the BCR material was different from the one used for APM (methyl cellulose and polycarbonate, respectively) and may behave differently towards irradiation. Accurate and precise ( $\pm 10\%$ ) results were obtained by  $k_0$ -NAA when analyzing simulated synthetic filters, but even these filters do not simulate enough the complexity of real APM filters. A large range of elements and concentrations can be collected on real filters, inducing additional spectral interferences.

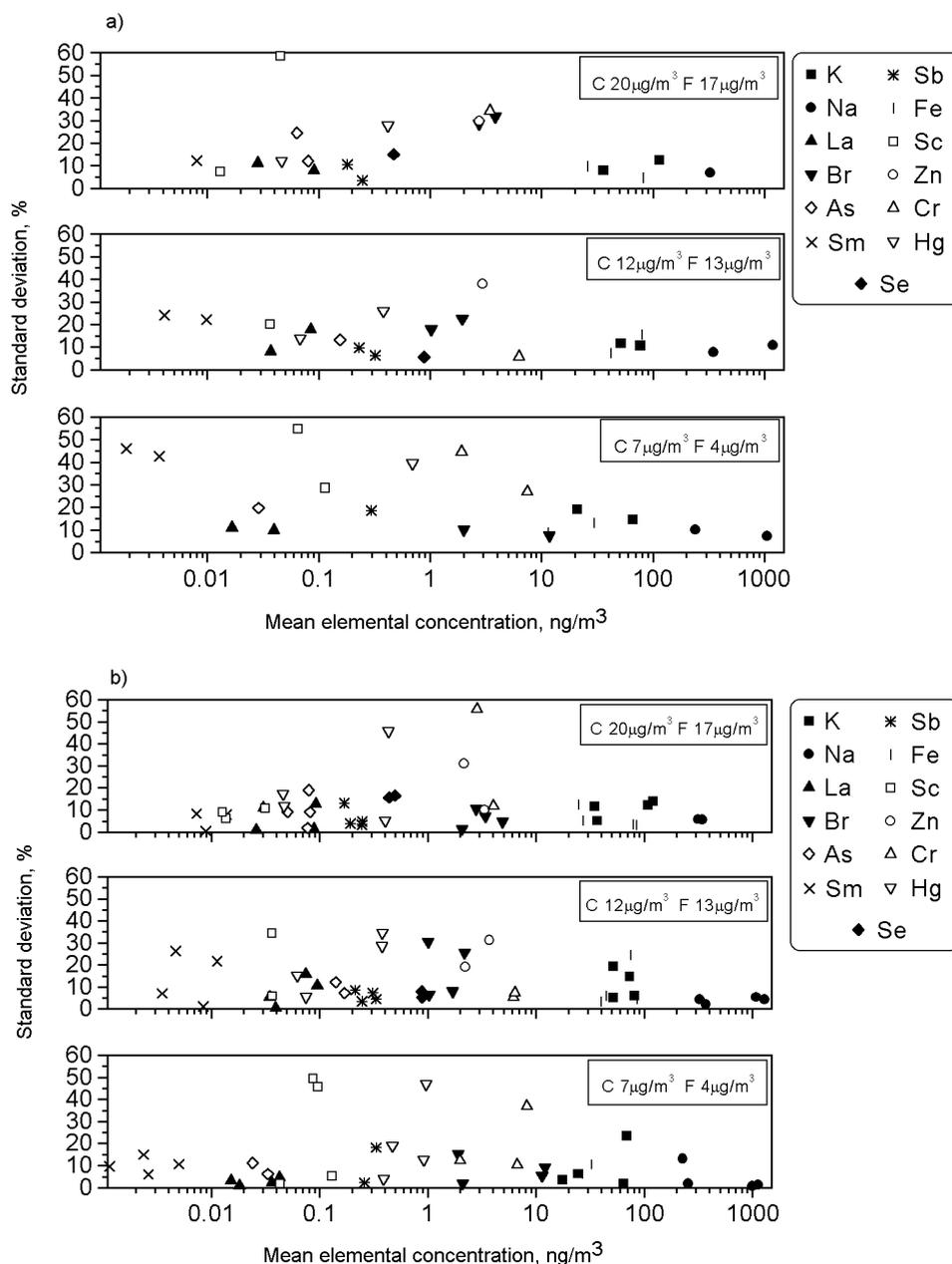


Fig. 2. Standard deviation of elemental concentrations for 2 halves of the same filters for 3 samples (a) for 4 halves of filters provided by two different samplers for 3 samples (b) (C – coarse mass concentration; F – fine mass concentration)

Finally, the reproducibility of the sampler, the sampled volume and the size of the particles collected influence directly the reproducibility and the homogeneity of the filters produced. The quality control of  $k_0$ -NAA for APM filters seems to be a difficult task, but our results suggest that it is reasonable to expect a reproducibility of the order of 5–15% for the elements investigated.

## References

1. F. DE CORTE, The  $k_0$ -Standardization Method – A Move to the Optimization of Neutron Activation Analysis, Agrégé Thesis, Belgium, 1987.
2. S. A. E. JOHANSSON, J. L. CAMPBELL, PIXE – A Novel Technique for Elemental Analysis, Wiley, 1988.
3. R. M. PARR, S. F. STONE, R. ZEISLER, Environmental Protection: Nuclear Analytical Techniques in Air Pollution Monitoring and Research, IAEA Bulletin, Austria, 2/1996.

4. Community Bureau of Reference, The Certification of the Surface Density ( $\text{kg}/\text{m}^2$ ) of BCR CRM 038 ("Fly Ash From Pulverised Coal") Comprised in Methyl Cellulose Films Simulating Dust Charged Filters – BCR 128, Belgium, 1988.
5. W. MAENHAUT, The "Gent" Stacked Filter Unit (SFU) Sampler for the Collection of Atmospheric Aerosols in Two Size Fractions: Description and Instructions for Installation and Use, CRP E4.10.08, IAEA, Belgium, 1992.
6. P. K. HOPKE, Y. XIEN, T. RAUNEMAA, S. BIEGALSKI, S. LANDSBERGER, W. MAENHAUT, P. ARTAXO, D. COHEN, *Aer. Sci. Technol.*, 27 (1997) 726.
7. P. TORO, E. CORTÉS, *J. Radioanal. Nucl. Chem.*, 221 (1997) 127.