# Quality assurance in elemental analysis of airborne particles

S.M. Almeida [a,*], M.A. Reis [a], M.C. Freitas [a], C.A. Pio [b]

[a] *Instituto Tecnológico e Nuclear, Apartado 21, Estrada Nacional 10, 2686-953 Sacavém, Portugal*
[b] *Departamento de Ambiente e Ordenamento, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

## Abstract

Instrumental neutron activation analysis (INAA) and particle induced X-ray emission (PIXE) are commonly used to yield multielemental data in atmospheric studies. In this work the quality assurance of the analytical data is discussed based on two studies. The first is a precision study, involving sampling and analysis of air particulate matter in the size ranges of the aerodynamic diameter (AD) <2.5 μm and 2.5 μm < AD < 10 μm, using two Gent collectors, operating side-by-side, on a daily basis. Mass concentrations obtained by gravimetry, for the two collectors, were compared showing a very good reproducibility. Elemental analysis was carried out in different parts of the same filter, testing both the homogeneity of the aerosol sample and the precision of the techniques. A relation between the elemental concentration and the differences obtained for different parts of the same filter was observed. Results suggest that, for the elements studied, data are reproducible to within 5–15%. In the second INAA and PIXE analysis of different sections of the same filter are discussed. Results indicate a good agreement for the determination of K, Fe and Zn by the two techniques.
© 2003 Elsevier Science B.V. All rights reserved.

*Keywords:* Airborne particles; INAA; PIXE; Accuracy; Precision; Homogeneity

## 1. Introduction

The techniques instrumental neutron activation analysis (INAA) [1,2] and particle induced X-ray emission (PIXE) [3] have already demonstrated their potential to yield both accurate and precise measurements of air particulate matter (APM) [4–6]. However, it is important to make sure that the results are free of bias and within statistical control [7]. In APM studies there are three main points that influence the experimental outcome:

(i) *The sampling methodology.* Hopke et al. [8], Toro and Cortés [4] and Almeida et al. [9] collected multiple samples with Gent collectors, at the same sampling site during the same sampling period. The agreement of the particulate matter results was very good indicating that collectors are operating in a reproducible way. The calibration of the Gent collector was done by intercomparisons with commercially available PM10 dichotomous sampler and quite reasonable agreement was obtained [5]. Hopke et al. [8] compared the Gent collector with a commercial PM10 beta gauge and with an IMPROVE-design 2.5 μm cut-point cyclone. Artaxo et al. [10] also made a parallel

---
* Corresponding author. Tel.: +351-21-994-6156; fax: +351-21-994-1039.
*E-mail address:* smarta@itn.mces.pt (S.M. Almeida).

sampling that validates the Gent collector against beta gauge instrument.

(ii) *The laboratory conditions.* The gravimetric analytical procedure should be evaluated. Contaminations, aerosol loss from a filter, electrostatic charging of filters or differences in humidity easily cause deviations from the real value.

(iii) *The verification of analytical results.* The analysis of two fractions of an aerosol filter could serve to verify the *homogeneity* of the aerosol sample, but it is also very important to check how *reproducible* the analytical method is [7]. Furthermore, Zeisler et al. [11], Salma et al. [12] and Maenhaut and Cafmeyer [13] cut filters in parts and the portions were submitted to parallel INAA and PIXE determinations in order to assess the *accuracy* of the techniques.

Inter-laboratory comparisons are very cumbersome but also extremely useful for quality assurance and quality control purposes. Bombelka et al. [14] prepared a large scale intercomparison of aerosol trace elements analysed by the analytical methods INAA, PIXE, XRF, AAS, OES-ICP and PhAA. Results show a general agreement of all techniques based on the analysis of filter pieces taken from 250 aerosol samples.

Reference materials play a fundamental role in the quality assurance of chemical measurements. A good reference material is chosen to closely match the major and important minor element concentrations of the material analysed. The presently available NIST SRM 2783 was set to market in the beginning of 2002, which makes that at the time of this study no certified reference materials was available for real air filter samples.

In this work an analytical quality control exercise was carried out with the analysis of samples collected simultaneously with two Gent collectors and with analysis of different parts of the same filter with different techniques.

## 2. Experimental

APM was collected using Gent collectors provided with a NILU stacked filter unit (SFU). The SFU contains two 47 mm diameter Nuclepore®

polycarbonate filters with pore sizes of 8 and 0.4 μm, placed in series. Upstream of the coarse filter is a pre-impactor stage. At a flow rate of 15–16 l/min, a pre-impaction stage intercepts particles larger than about 10 μm aerodynamic diameter (AD) and the filter with 8 μm pore size (coarse filter) has a 50% collection efficiency at about 2.5 μm AD. Consequently, the aerosol particles are separated into a coarse (10 μm < AD < 2.5 μm) and a fine (AD < 2.5 μm) size fraction. A detailed description of the sampling equipment is given by Hopke et al. [8] and Maenhaut [15].

The reproducibility of the sampling and analysis procedure was studied with the help of two collectors, working simultaneously side-by-side in 24 h-periods during 45 days. The filter loads were measured by gravimetry using a Mettler Toledo balance with 0.1 μg readability placed in a controlled clean room (class 10,000). Filter weight before and after sampling is obtained as the average of three measurements in agreeing by less than 5 μg. Elemental analysis was carried out in quarter filters by PIXE and in half filters by INAA. PIXE analysis was carried out at a Van de Graaff accelerator, in vacuum and two X-ray spectrum were taken for each of the samples; one with a 1.2 MeV proton beam and no absorber in front of the Si(Li) detector for low energy X-ray elements and another with a 2.4 MeV proton beam and a 250 μm Mylar® filter to detect elements with atomic number higher than 20. The beam area at the target was 20 mm². For INAA analysis, filter halves were rolled up and put into a thin foil of aluminium and irradiated for 7-h at a thermal neutron flux of $1.2 \times 10^{13}$ cm$^{-2}$ s$^{-1}$ in the Portuguese Research Reactor. After irradiation the sample was removed from the aluminium foil and transferred to a polyethylene container. For each irradiated sample, two gamma spectrum were measured with hyperpure germanium detectors, one spectrum 2–3 days after the irradiation and the other one after 4 weeks. The $k_0$ method [16] was used and 1mm diameter wires of 0.1% Au–Al were co-irradiated as comparators.

In order to assess the accuracy of the methods by a comparison of INAA and PIXE, one Gent collector worked in 24 h-periods during 104 days. Filter loads were measured according to the

procedure described before. Filters were divided in three parts: one half was analysed by INAA and one quarter was analysed by PIXE.

## 3. Results and discussion

### 3.1. Reproducibility

APM mass concentrations were obtained by dividing filter loads by the volume of air filtered. The PM10 mass concentration was calculated by the sum of fine and coarse particles mass. Particle mass concentration uncertainty was calculated by taking the standard deviation of the three mass replicates and assuming 3% uncertainty for the volumetric flow measurement. Fig. 1 presents the comparison of the total, coarse and fine mass concentration for side-by-side Gent collectors.

It should be emphasised that the actual concentrations in the samples are not known, thus the following interpretation is based on a relative assessment. However, these results not only serve to study the reproducibility of the collectors but also

as quality assurance for the gravimetric analytical procedure.

Results in Fig. 1 show that the collectors were working in a comparable way with respect to the collected mass and the sampled volume. Pearson correlation coefficients can be directly obtained from the regression coefficients and are 0.97, 0.99 and 0.95 for total, coarse and fine fractions. This shows that apart from a very small bias towards excess of mass in *collector 1* both collectors are sampling the same amount of APM.

Fig. 2 presents the differences between the APM mass concentration obtained by the *collector 1* and *collector 2* normalised by the average ($D_{\mathrm{m}}$) and the histogram of the correspondent frequencies.

The correlation of $D_{\mathrm{m}}$ with the APM concentration data is insignificant, therefore the variability in the differences is not concentration dependent.

According to Fig. 2 the dispersion of the values in PM10 are visibly lower than in fine and coarse fractions. Some of the worse results could be explained by differences observed in the fluxes of the two collectors, which could cause a disparity in
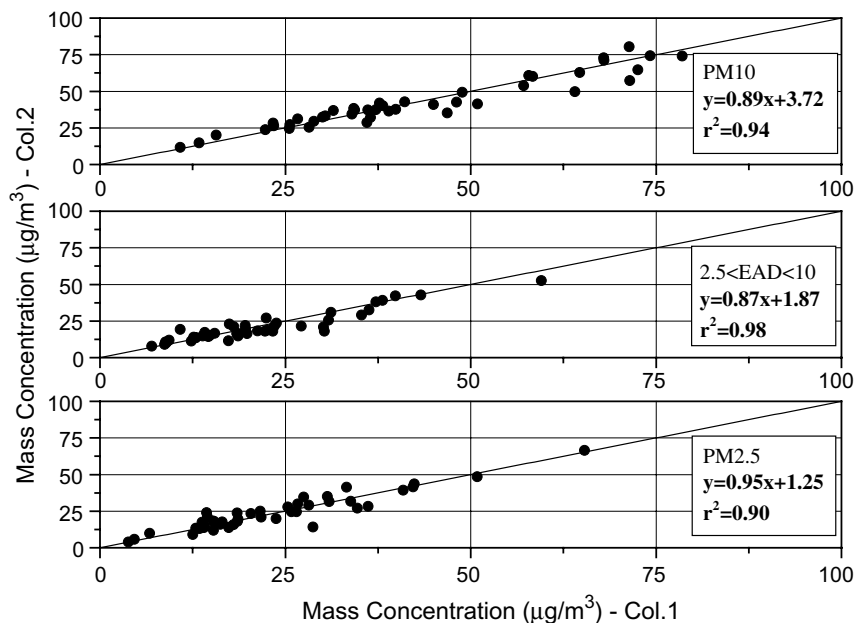


Fig. 1. Comparison of APM mass concentrations obtained from *collector 1* and *collector 2* for total, coarse and fine fractions.
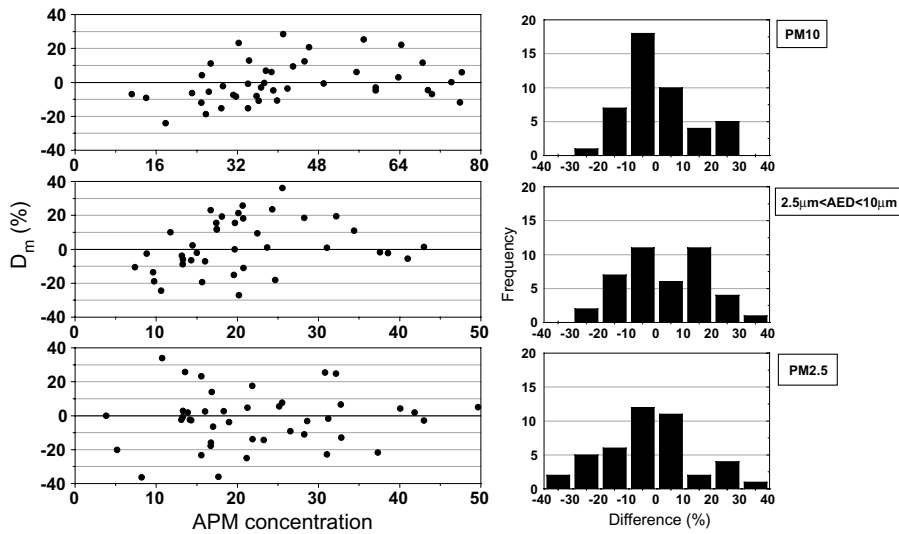
Fig. 2. Differences between APM mass concentrations obtained by *collector 1* and *collector 2* normalised by the average ($D_m$) and histogram of the correspondent frequencies for PM10, 10 μm < AED < 2.5 μm and PM2.5.

their cut-points. That is why there are fewer differences in total fraction where only 10 μm cut-point is considered.

Hopke et al. [8] made a similar study with four sampling periods and obtained a good agreement for three of them ($D_m < 5\%$). However, he obtained a discrepancy for one sample period ($D_m = 21\%$ for fine fraction concentration, $D_m = 17\%$ for coarse fraction concentration and $D_m = 23\%$ for total concentration).

For elemental analysis six sampling periods were chosen (three sampling periods for PIXE analysis and three sampling periods for INAA analysis). The correspondent mass concentrations show a very good agreement between the two

collectors to reduce to a minimum the sources of error not originating in the analytical methods. In this way, the reproducibility of the analytical methods could be tested. In Table 1, APM total mass concentration obtained from collector 1 and 2 for these 6 days is shown.

For PIXE analysis, filters were cut in four fractions and elemental mass concentration was determined for each fraction. For INAA analysis, filters were cut in two fractions and elemental analysis was carried out in each half of the filter.

PIXE results for the interesting elements to check the reproducibility are shown in Table 2. The standard deviation is presented for the 4 quarters of the same filter ($SD_{4p}$) and for the 8 filter

Table 1
Fine, coarse and total particulate mass concentration obtained from collector1 (C1) and collector 2 (C2) for the filters analysed by PIXE and INAA

|  | Fine mass C1 (μg/m³) | Fine mass C2 (μg/m³) | Coarse mass C1 (μg/m³) | Coarse mass C2 (μg/m³) | Total mass C1 (μg/m³) | Total mass C2 (μg/m³) |
|---|---|---|---|---|---|---|
| PIXE | 30.92 ± 0.80 | 31.5 ± 2.3 | 43.3 ± 1.7 | 42.7 ± 2.9 | 74.2 ± 2.1 | 74.2 ± 3.9 |
| PIXE | 14.0 ± 2.5 | 14.3 ± 1.8 | 14.84 ± 0.93 | 15.17 ± 0.84 | 28.8 ± 2.8 | 29.5 ± 2.1 |
| PIXE | 28.2 ± 1.6 | 29.1 ± 1.6 | 39.8 ± 1.2 | 42.1 ± 2.1 | 68.0 ± 2.2 | 71.2 ± 2.8 |
| INAA | 13.20 ± 0.38 | 13.33 ± 0.38 | 12.34 ± 0.26 | 11.17 ± 0.24 | 25.55 ± 0.58 | 24.50 ± 0.57 |
| INAA | 3.83 ± 0.24 | 3.83 ± 0.16 | 6.99 ± 0.16 | 7.78 ± 0.21 | 10.82 ± 0.32 | 11.61 ± 0.31 |
| INAA | 16.48 ± 0.35 | 17.59 ± 0.37 | 19.66 ± 0.43 | 19.67 ± 0.44 | 36.13 ± 0.75 | 37.26 ± 0.78 |

Table 2
Elemental concentration measured by PIXE (values in ng/m$^3$)

| | Fine | | | | | | | | | | | Coarse | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1-SFU-a | 1-SFU-b | 1-SFU-c | 1-SFU-d | SD$_{4p}$ | 2-SFU-a | 2-SFU-b | 2-SFU-c | 2-SFU-d | SD$_{4p}$ | SD$_{8c}$ | 1-SFU-a | 1-SFU-b | 1-SFU-c | 1-SFU-d | SD$_{4p}$ | 2-SFU-a | 2-SFU-b | 2-SFU-c | 2-SFU-d | SD$_{4p}$ | SD$_{8c}$ |
| Al | 820 | 780 | 780 | 780 | 2 | 870 | 900 | 870 | 920 | 3 | 7 | 1000 | 1100 | 1300 | 880 | 15 | 1300 | 1300 | 1100 | 940 | 14 | 14 |
| Si | 2100 | 2000 | 2000 | 2000 | 2 | 2300 | 2300 | 2300 | 2300 | 2 | 7 | 2700 | 2800 | 3200 | 2200 | 15 | 3100 | 3200 | 2700 | 2300 | 14 | 14 |
| K | 610 | 630 | 600 | 590 | 3 | 650 | 660 | 660 | 680 | 2 | 5 | 730 | 750 | 750 | 710 | 3 | 800 | 770 | 680 | 600 | 13 | 9 |
| Ti | 130 | 130 | 130 | 120 | 4 | 140 | 140 | 140 | 140 | 2 | 6 | 160 | 150 | 150 | 150 | 1 | 140 | 160 | 140 | 130 | 8 | 7 |
| Mn | 16 | 16 | 15 | 14 | 4 | 16 | 16 | 16 | 18 | 6 | 6 | 29 | 29 | 26 | 26 | 6 | 26 | 28 | 27 | 22 | 9 | 8 |
| Fe | 820 | 830 | 820 | 780 | 3 | 890 | 880 | 890 | 910 | 2 | 6 | 1400 | 1400 | 1300 | 1300 | 5 | 1200 | 1300 | 1200 | 1100 | 6 | 7 |
| Ni | 4.0 | 4.8 | 4.4 | 4.9 | 8 | 4.8 | 4.7 | 3.9 | 5.4 | 13 | 10 | 3.9 | 3.6 | 4.0 | 3.3 | 9 | 2.8 | 3.7 | 3.9 | 3.2 | 15 | 12 |
| Cu | 10 | 12 | 11 | 12 | 9 | 13 | 11 | 12 | 12 | 6 | 8 | 11 | 12 | 10 | 11 | 5 | 10 | 11 | 8.0 | 8.3 | 17 | 14 |
| Zn | 41 | 45 | 42 | 40 | 5 | 44 | 43 | 45 | 43 | 3 | 5 | 90 | 98 | 91 | 92 | 4 | 89 | 103 | 89 | 91 | 7 | 5 |
| Pb | 26 | 28 | 28 | 28 | 5 | 27 | 24 | 28 | 33 | 14 | 10 | 59 | 61 | 62 | 61 | 2 | 70 | 64 | 59 | 67 | 7 | 6 |
| | | | | | | | | | | | | | | | | | | | | | | |
| Al | 68 | 40 | 59 | 52 | 21 | 54 | 56 | 58 | 46 | 9 | 15 | 46 | 57 | 60 | 44 | 15 | 48 | 47 | 70 | 77 | 25 | 22 |
| Si | 140 | 120 | 130 | 120 | 6 | 130 | 130 | 120 | 110 | 6 | 6 | 130 | 130 | 130 | 130 | 3 | 110 | 110 | 180 | 180 | 29 | 21 |
| K | 18 | 61 | 68 | 66 | 45 | 57 | 61 | 56 | 62 | 5 | 28 | 66 | 70 | 84 | 66 | 12 | 77 | 79 | 76 | 79 | 2 | 9 |
| Ti | 300 | 310 | 310 | 310 | 2 | 310 | 310 | 300 | 320 | 2 | 2 | 170 | 170 | 170 | 180 | 1 | 170 | 170 | 180 | 190 | 4 | 4 |
| Mn | 3.7 | 3.9 | 3.6 | 2.9 | 13 | 3.3 | 3.3 | 3.2 | 3.8 | 8 | 10 | 2.5 | 2.6 | 2.4 | 2.4 | 4 | 2.9 | 1.3 | 3.3 | 3.6 | 36 | 25 |
| Fe | 54 | 53 | 60 | 60 | 6 | 54 | 51 | 50 | 53 | 4 | 7 | 130 | 120 | 120 | 120 | 3 | 110 | 110 | 110 | 130 | 10 | 7 |
| Ni | 1.5 | 2.7 | 3.6 | 3.1 | 34 | 3.0 | 2.8 | 2.4 | 2.0 | 17 | 25 | 1.6 | 1.9 | 2.2 | 1.4 | 19 | 2.6 | 1.3 | 1.6 | 1.4 | 35 | 26 |
| Cu | 2.5 | 3.6 | 3.2 | 3.3 | 15 | 3.2 | 3.4 | 2.9 | 2.8 | 8 | 11 | 3.3 | 2.0 | 4.3 | 2.3 | 35 | 1.9 | 1.9 | 2.0 | 2.5 | 15 | 34 |
| Zn | 7.8 | 19 | 21 | 19 | 36 | 17 | 19 | 17 | 19 | 7 | 24 | 9.1 | 9.1 | 7.7 | 15 | 33 | 6.3 | 8.5 | 6.0 | 8.5 | 19 | 33 |
| Pb | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| | | | | | | | | | | | | | | | | | | | | | | |
| Al | 680 | 620 | 670 | 660 | 4 | 690 | 670 | 520 | 560 | 14 | 10 | 780 | 890 | 770 | 820 | 6 | 770 | 780 | 790 | 780 | 1 | 5 |
| Si | 1700 | 1600 | 1600 | 1600 | 3 | 1700 | 1700 | 1300 | 1400 | 12 | 9 | 2100 | 2300 | 2000 | 2100 | 6 | 1900 | 2000 | 2000 | 2000 | 3 | 6 |
| K | 550 | 540 | 540 | 530 | 1 | 550 | 550 | 480 | 520 | 6 | 4 | 540 | 590 | 510 | 580 | 7 | 490 | 520 | 540 | 500 | 4 | 7 |
| Ti | 78 | 73 | 80 | 75 | 4 | 84 | 72 | 73 | 77 | 7 | 5 | 130 | 147 | 126 | 140 | 7 | 114 | 126 | 131 | 127 | 6 | 8 |
| Mn | 14 | 13 | 13 | 12 | 4 | 14 | 14 | 12 | 12 | 10 | 7 | 20 | 20 | 19 | 20 | 2 | 20 | 19 | 20 | 19 | 3 | 2 |
| Fe | 770 | 740 | 750 | 720 | 2 | 760 | 730 | 690 | 720 | 4 | 3 | 1100 | 1200 | 1100 | 1200 | 5 | 1000 | 1100 | 1100 | 1100 | 3 | 7 |
| Ni | 3.5 | 4.7 | 3.8 | 4.7 | 14 | 4.4 | 4.8 | 3.4 | 4.1 | 14 | 13 | 4.1 | 5.0 | 5.1 | 6.4 | 19 | 4.0 | 3.7 | 4.8 | 5.1 | 14 | 18 |
| Cu | 18 | 16 | 17 | 15 | 8 | 18 | 16 | 13 | 16 | 12 | 10 | 18 | 23 | 18 | 18 | 14 | 17 | 17 | 17 | 20 | 8 | 11 |
| Zn | 64 | 60 | 64 | 64 | 3 | 63 | 67 | 61 | 61 | 5 | 4 | 75 | 83 | 79 | 76 | 5 | 68 | 68 | 77 | 78 | 8 | 7 |
| Pb | 11 | – | 14 | – | 16 | – | 9 | 9 | – | 2 | 20 | 15 | 12 | 12 | 14 | 11 | – | – | 14 | 14 | 3 | 9 |

SD4p – relative standard deviation of the concentration obtained for the 4 parts of the same filter.
SD8c – relative standard deviation of the concentration obtained for the 8 parts of filter (4 providing from collector 1 and 4 providing from the collector 2).

quarters (4 provided by collector 1 and 4 provided by collector 2) ($SD_{8c}$).

There are significant differences for Ni and Cu. Ti, Mn and Fe show a good agreement between collectors and between different parts of the same filter. The statistical uncertainty of PIXE measurements was in the order of 10% for Ni and Cu and lower than 3% for Ti, Mn and Fe. For Al and Si the agreement is better for fine fractions than for the coarse ones. This may reflect either better Al and Si homogeneity in PM2.5 filters or enhance problems in the quantification of Al and Si in the coarse particles due to matrix effects. For almost all elements the agreement decreases in the second

sampling period. Table 1 indicates lower APM total mass concentration and Table 2 shows lower elemental concentrations for this sampling period.

The results for INAA analysis are shown in Table 3. The standard deviation is presented for the 2 parts of the same filter ($SD_{2p}$) and for the 4 parts of 2 filters (2 provided by collector 1 and 2 provided by collector 2) ($SD_{4c}$).

There are significant differences for Sc, Cr and As. INAA counting statistical errors for Sc and As was in the order of 30% and 20%, respectively. For Na, Fe, Br, La and Sb there is a very good agreement between different parts of the same filter and between collectors.

Table 3
Elemental concentration measured by INAA (values in ng/m$^3$)

| | Fine | | | | | | | Coarse | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1-SFU-a | 1-SFU-b | $SD_{2p}$ | 2-SFU-a | 2-SFU-b | $SD_{2p}$ | $SD_{4c}$ | 1-SFU-a | 1-SFU-b | $SD_{2p}$ | 2-SFU-a | 2-SFU-b | $SD_{2p}$ | $SD_{4c}$ |
| Na | 330 | 360 | 6 | 300 | 330 | 6 | 7 | 1190 | 1900 | 1 | 1900 | 1700 | 8 | 5 |
| K | 39 | 36 | 5 | 32 | 38 | 11 | 8 | 110 | 134 | 14 | 119 | 100 | 12 | 12 |
| Sc | 0.034 | 0.029 | 10 | 0.085 | 0.033 | 62 | 58 | 0.013 | 0.014 | 6 | 0.014 | 0.012 | 9 | 7 |
| Cr | 3.7 | 4.4 | 12 | 4.0 | 1.7 | 56 | 34 | – | – | – | – | – | – | – |
| Fe | 23 | 27 | 12 | 27 | 29 | 5 | 10 | 87 | 83 | 3 | 82 | 78 | 3 | 5 |
| As | 0.090 | 0.069 | 19 | 0.087 | 0.076 | 9 | 12 | 0.047 | 0.054 | 9 | 0.076 | 0.078 | 2 | 25 |
| Br | 4.7 | 5.1 | 5 | 2.6 | 3.0 | 10 | 32 | 2.1 | 2.1 | 1 | 3.6 | 3.2 | 7 | 29 |
| La | 0.028 | 0.033 | 11 | 0.026 | 0.026 | 1 | 11 | 0.085 | 0.10 | 13 | 0.089 | 0.088 | 1 | 8 |
| Sb | 0.19 | 0.20 | 4 | 0.15 | 0.19 | 13 | 10 | 0.24 | 0.25 | 3 | 0.26 | 0.24 | 5 | 3 |
| Sm | 0.015 | 0.013 | 8 | 0.0011 | 0.00094 | 11 | 100 | 0.0090 | 0.0089 | 0 | 0.0069 | 0.0078 | 8 | 12 |
| Na | 320 | 340 | 4 | 370 | 380 | 2 | 8 | 1300 | 1300 | 4 | 1100 | 1100 | 5 | 11 |
| K | 59 | 45 | 19 | 50 | 54 | 5 | 12 | 82 | 66 | 15 | 85 | 78 | 6 | 11 |
| Sc | – | – | – | – | – | – | – | 0.038 | 0.035 | 6 | 0.028 | 0.045 | 34 | 20 |
| Cr | 6.4 | 6.0 | 5 | 6.7 | 6.1 | 7 | 6 | – | – | – | – | – | – | – |
| Fe | 43 | 46 | 6 | 39 | 41 | 3 | 7 | 89 | 83 | 5 | 62 | 88 | 24 | 16 |
| As | 0.13 | 0.15 | 12 | 0.16 | 0.18 | 7 | 13 | – | 0.12 | – | 0.026 | – | – | 92 |
| Br | 0.80 | 1.2 | 30 | 1.1 | 0.99 | 6 | 18 | 1.8 | 2.6 | 26 | 1.8 | 1.6 | 8 | 22 |
| La | 0.033 | 0.036 | 5 | 0.040 | 0.039 | 0 | 8 | 0.10 | 0.089 | 10 | 0.067 | 0.083 | 16 | 18 |
| Sb | 0.30 | 0.33 | 7 | 0.32 | 0.34 | 4 | 6 | 0.25 | 0.24 | 3 | 0.23 | 0.20 | 9 | 9 |
| Sm | 0.0037 | 0.0034 | 7 | 0.0056 | 0.0038 | 26 | 24 | 0.013 | 0.0096 | 22 | 0.0084 | 0.0085 | 1 | 22 |
| Na | 200 | 250 | 13 | 250 | 260 | 2 | 10 | 1100 | 1100 | 1 | 1000 | 1000 | 1 | 7 |
| K | 17 | 18 | 3 | 25 | 23 | 6 | 19 | 66 | 64 | 2 | 80 | 58 | 24 | 15 |
| Sc | 0.066 | 0.13 | 45 | 0.13 | 0.14 | 5 | 28 | 0.044 | 0.043 | 2 | 0.057 | 0.12 | 49 | 55 |
| Cr | 6.2 | 7.2 | 10 | 10.4 | 6.1 | 37 | 27 | 0.82 | 2.9 | 79 | 2.2 | 1.8 | 12 | 44 |
| Fe | 35 | 30 | 10 | 26 | 28 | 6 | 13 | – | 30 | – | – | 48 | – | 31 |
| As | 0.022 | 0.026 | 11 | 0.035 | 0.032 | 6 | 20 | – | – | – | – | – | – | – |
| Br | 1.7 | 2.1 | 15 | 2.1 | 2.1 | 2 | 10 | 11 | 12 | 5 | 13 | 11 | 9 | 7 |
| La | 0.015 | 0.016 | 3 | 0.018 | 0.018 | 1 | 11 | 0.044 | 0.042 | 4 | 0.037 | 0.036 | 2 | 10 |
| Sb | 0.26 | 0.27 | 2 | 0.38 | 0.29 | 18 | 18 | 0.10 | 0.34 | 78 | 0.19 | 0.13 | 27 | 58 |
| Sm | 0.0025 | 0.0027 | 6 | 0.0011 | 0.0012 | 10 | 46 | 0.0046 | 0.0054 | 11 | 0.0026 | 0.0021 | 15 | 42 |

SD2p – relative standard deviation of the concentration obtained for the 2 parts of the same filter.
SD4c – relative standard deviation of the concentration obtained for the 4 parts of filter (2 providing from collector 1 and 2 providing from the collector 2).

To better quantify the differences observed between parts of the same filter, histograms of the $SD_{4p}$ and $SD_{2p}$ frequencies are shown in Fig. 3.

Fig. 3(a) (PIXE and INAA data) shows that 36% of the cases have a $SD_{4p}$ and $SD_{2p}$ lower than 5% and 83% of the cases have a $SD_{4p}$ and $SD_{2p}$ lower than 15%. Fig. 3(b) (PIXE data) indicates that 40% of the cases have a $SD_{4p}$ lower than 5%, while graph 3c (INAA data) shows only 32% of the pairs with $SD_{2p}$ lower than 5%. The frequency of cases with $SD_{4p}$ and $SD_{2p}$ lower than 15% is 84% in PIXE and 81% in INAA.

In order to investigate if the differences obtained are dependent on the concentration, Fig. 3(d–f) present a comparison between $SD_{4p}$ and $SD_{2p}$ and the average of the element on the filter. In graph 3d $SD_{4p}$ and $SD_{2p}$ data for coarse and fine fraction are displayed for elements determined by INAA and PIXE. In Fig. 3(e) (PIXE data) and 3(f) (INAA data) the different elements in both fractions are analysed. In Figs. 4 and 5 some of the more relevant elements determined by PIXE and INAA are analysed separately.

Fig. 3(d) indicates that coarse and fine particles show similar $SD_{4p}$ and $SD_{2p}$ patterns.

Fig. 3(e) (PIXE data) indicates an inverse relation between elemental concentration and $SD_{4p}$. The elements Ni, Cu and Zn, which are in lower concentrations, have higher $SD_{4p}$. For the comparison between different parts of the same filter, the average of the $SD_{4p}$ for these elements is 17%, 10% and 10%, respectively. Al, Ti and Fe, which are in higher elemental concentrations, have lower $SD_{4p}$. The average of the $SD_{4p}$ for these elements is 8.8%, 3.4% and 3.5%, respectively.

When elements are studied separately (see Fig. 4) and there is a significant difference in the elemental concentration, higher $SD_{4p}$ are also associated with lower concentrations, which is the case of Ni, Cu and Zn. Ni has 26% of average $SD_{4p}$ for concentrations lower than 3 ng/m$^3$. For higher concentrations the average of the $SD_{4p}$ is 12%. The average of the $SD_{4p}$ for Cu is 12% for concentrations lower than 5ng/m$^3$, while for higher concentrations the average of the $SD_{4p}$ is 8.8%. Zn has an average $SD_{4p}$ of 22% for concentrations lower

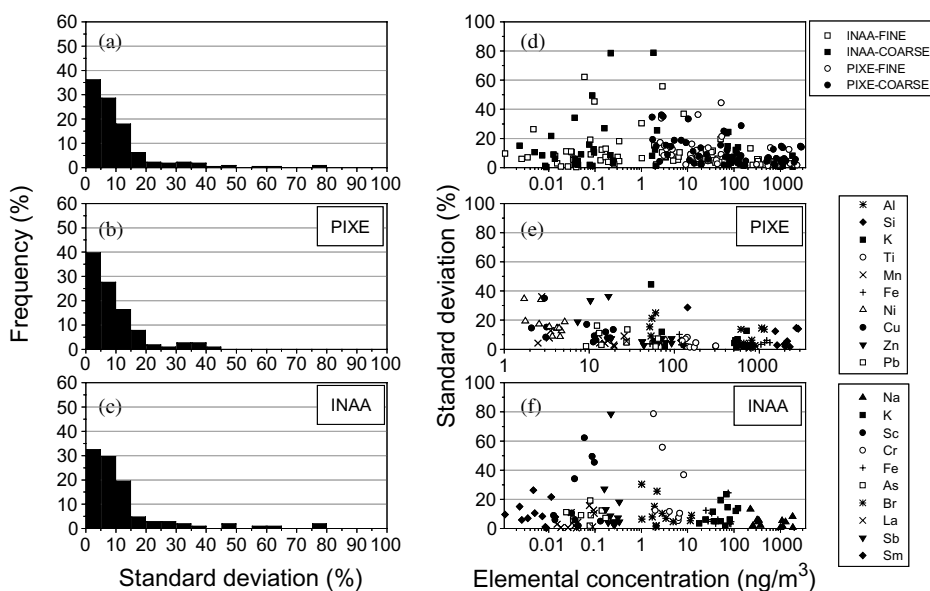

Fig. 3. Frequency (%) of SD4p (PIXE) and/or SD2p (INAA) obtained for the comparison between different fractions of the same filter for PIXE and INAA (a), PIXE (b) and INAA (c) for both fine and coarse filters. Relation between SD4p (PIXE) and/or SD2p (INAA) and the elemental concentration obtained for the comparison between parts of the same filter, for PIXE and INAA (d), PIXE (e) and INAA (f) for both fine and coarse filters.
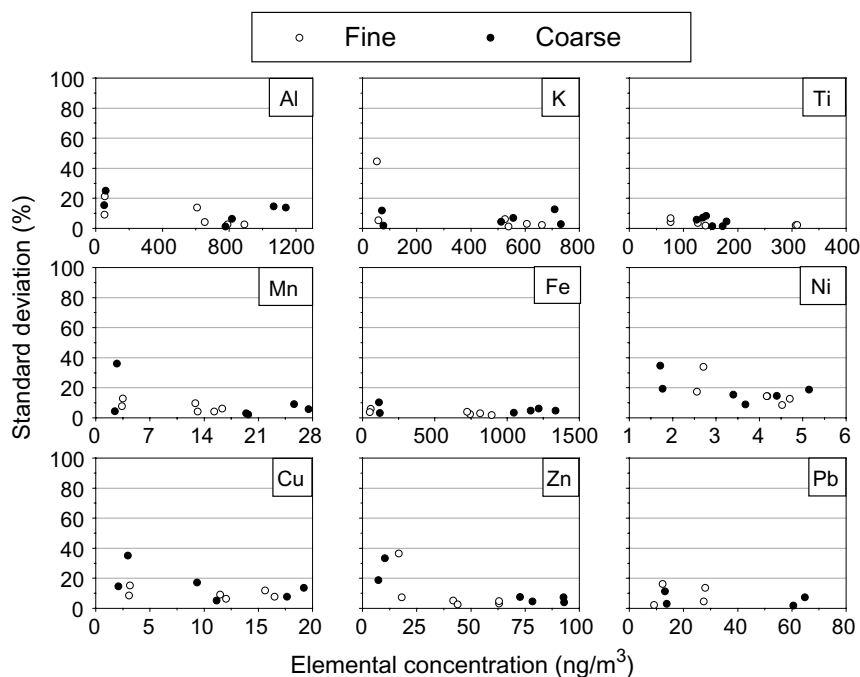
Fig. 4. Relation between the SD4p and the elemental concentration obtained for the comparison between parts of the same filter for the elements determined by PIXE.

than 20 ng/m$^3$. For higher concentrations the SD$_{4p}$ is 3.9%.

These results may be explained by a less homogeneous distribution of the element mass over the whole surface of the filter. This effect is more relevant for the composition of minor elements in APM such as Ni and Cu, although nearly irrelevant elements with higher concentrations such as Al, Si, K and Ti. The small amounts of an element present in the filter are in some cases concentrated in a very small number of particles. Therefore, the element involved cannot be properly distributed over the filter.

The proximity of the detection limit could also explain these results. The detection limit of the technique should be at least three times lower than the amount of analyte measured in actual samples. In INAA and PIXE, the detection limits highly depend on the presence of other elements in the sample (because of their impact on the Compton γ-ray background in INAA, or on spectral interference in PIXE) [12]. As a consequence, the detection limits vary from sample to sample and

are lowest for the lightest-loaded samples. Therefore, blank filters were used to find out the minimum detection limit. The detection limits in ng/m$^3$ were derived assuming a volume of 24 m$^3$. Table 4 indicates that Mn and Ni concentrations measured for some samples are lower than three times the detection limit. Cu and Pb concentrations are also very near the detection limit. This fact explains high differences between quarters of filters for these elements.

For elements that were detected in the blank filters the net amount (after blank correction) in a real sample should present concentration values higher than $3s_{var}$ [12]. The standard deviation of the blank value $(s_{var})$ is derived from the spread in the various individual blank filter values and, thus, it is a measure of the blank variability. For PIXE the elements measured in the blanks are in a very low amount compared with the contents in the real filter samples.

In elements measured by INAA there are significant differences for Sm, Sc, Cr and Br. The average SD$_{2p}$ for these elements is 10%, 14%, 9.3%
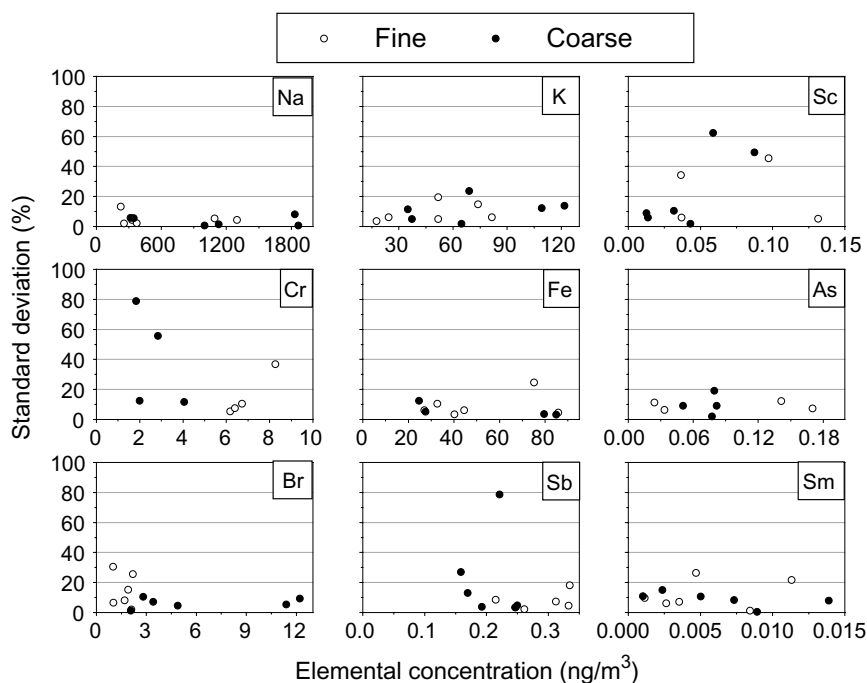
Fig. 5. Relation between the SD2p and the elemental concentration obtained for the comparison between parts of the same filter for the elements determined by INAA.

Table 4
Detection limits in ng/m³ for elements measured by INAA and PIXE

|     | PIXE |     | INAA |
| --- | --- | --- | --- |
| Al | 5.3 | Na | 0.018 |
| Si | 4.1 | K | 1.5 |
| K | 1.3 | Sc | 0.00064 |
| Ti | 0.80 | Cr | 0.12 |
| Mn | 0.56 | Fe | 6.9 |
| Fe | 0.31 | As | 0.0066 |
| Ni | 0.42 | Br | 0.0079 |
| Cu | 0.48 | La | 0.0015 |
| Zn | 0.68 | Sb | 0.0093 |
| Pb | 3.2 | Sm | 0.00045 |
|     |     | Zn | 0.31 |

and 10%, respectively. However, Na, K and Fe element concentrations present a good agreement between parts of filters. The average of the $SD_{2p}$ for these elements is 4.4%, 10% and 7.9%.

Fig. 3 indicates that in INAA results the association between elemental concentration and $SD_{2p}$ is not evident. The homogeneity of the filter does not interfere so much in INAA analysis. In fact,

INAA is a bulk analysis of the entire sample, whereas PIXE analyses only 20 mm² of the filter sample, which corresponds to the beam area and homogeneity is a very important property especially when a minimum sample is analysed. Moreover, INAA detection limit depends more on the element than in PIXE. An element with higher concentration could be closer to the detection limit comparing with an element with minor concentration. According to Table 4 As and Sm are near the detection limits. The study in blanks filters, by INAA, indicates that the contents of Cr and Br are very high. For some samples and for Cr in coarse fraction and Br in the fine fraction, the amount of these elements in the filter is lower than $3s_{var}$. This explains the higher disagreement between pairs of filter for Cr (in coarse fraction) and Br (in fine fraction).

When INAA elements are analysed separately (see Fig. 5), the relation between elemental concentration and the standard deviation, previously observed in PIXE, is not find. However, in INAA elements the range of concentrations determined is

very small and therefore is not significant to observe any relation.

To test the reproducibility of the whole process, including the reproducibility of the collectors, the gravimetric analytical procedure, the homogeneity of the deposition and the analytical techniques, the frequency of the $SD_{8c}$ and $SD_{4c}$ is shown in Fig. 6(a–c). Moreover, the correlation between the mean elemental concentration of the parts of filters provided by the two collectors and the associated $SD_{8c}$ and $SD_{4c}$ is presented in Fig. 6(d–f).

As expected, when parts provided by different collectors are compared the $SD_{8c}$ and $SD_{4c}$ increases. Fig. 6(a) (PIXE and INAA data) indicates that 8.8% of the cases have a $SD_{8c}$ and $SD_{4c}$ lower than 5% and 69% of the cases have a $SD_{8c}$ and $SD_{4c}$ lower than 15%.

Fig. 6(b) (PIXE data) shows that 80% of the cases have a $SD_{8c}$ lower than 15%. 12% of the cases have a $SD_{8c}$ lower than 5%. Fig. 6(c) (INAA data) indicates a higher dispersion of values; 56% of the cases have a $SD_{4c}$ lower than 15%.

The association between the standard deviation and the elemental concentration is also visible

when filters provided from collector 1 and 2 are compared.

Toro and Cortés [4] analysed by INAA samples collected simultaneously with three Gent collectors at the same sampling station. The maximum standard deviation obtained for Al, As, Br, Ca, Cl, Cu, Fe, Na, V and Zn was 15%, 10%, 9.5%, 27%, 22%, 28%, 19%, 7.9%, 13% and 24%, respectively.

### 3.2. Accuracy

The multi-technique analytical approach not only provides results for a larger number of elements but, for several elements, also provides results from two independent techniques. INAA and PIXE can be considered reliable for these elements. Therefore, the degree of agreement can be used to estimate the uncertainty due to method bias.

APM was sampled with a Gent collector in 24 h-periods during 104 days. The filters were divided into three parts (controlled by weighing). One quarter was submitted to PIXE and one half
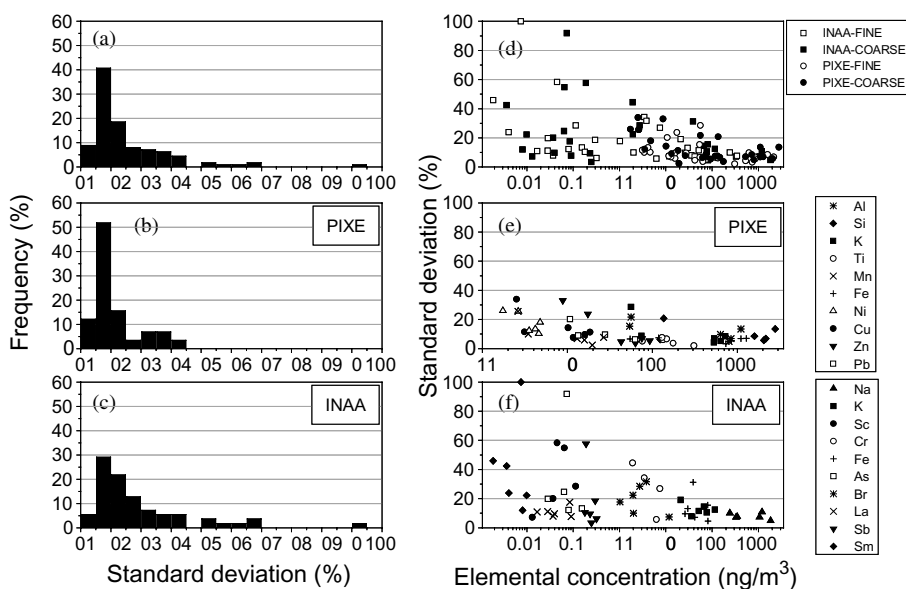


Fig. 6. Differences for all filter fractions. Frequency (%) of SD8c (PIXE) and/or SD4c (INAA) obtained for the comparison between fractions provided by different collectors, for PIXE and INAA (a), PIXE (b) and INAA (c) for both fine and coarse filters. Relation between the SD4p (PIXE) and SD2p (INAA) and the elemental concentration obtained for the comparison between parts of filters providing from different collectors, for INAA and PIXE (d), PIXE (e) and INAA (f) for both fine and coarse filters.
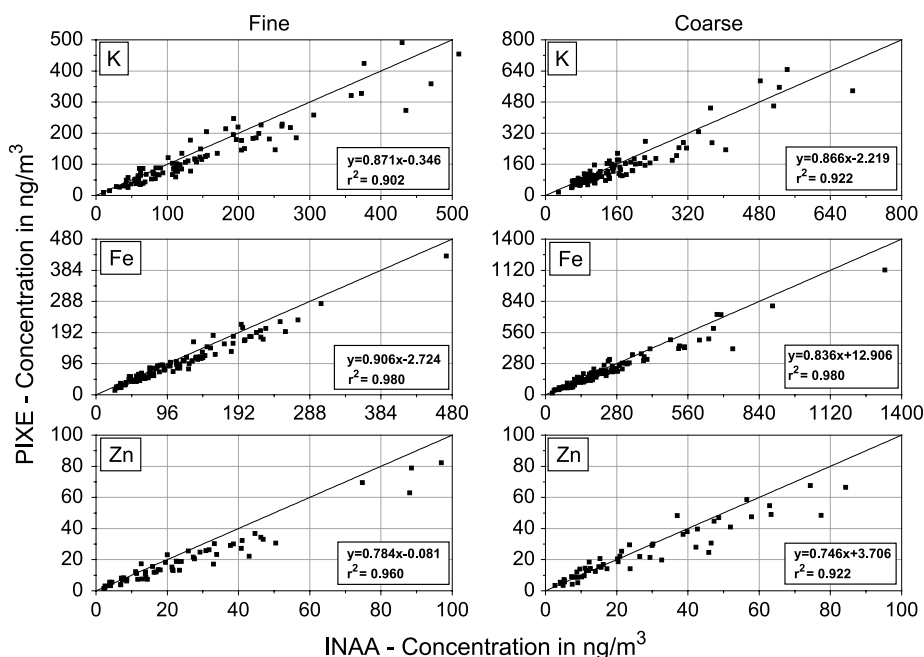
Fig. 7. Correlation between K, Fe and Zn concentrations measured by INAA and PIXE in fine and coarse size fractions.

was submitted to INAA. Fig. 7 shows the comparison between INAA and PIXE measurements for K, Fe and Zn. Each point corresponds to the analysis of the same sample for INAA and PIXE.

PIXE and INAA comparison was performed in terms of the concentration differences normalised by the average ($D_T$). Such differences were calculated for each sample, per element and per size fraction and obvious outlier differences were excluded. In Fig. 8 the frequency of $D_T$ for K, Fe and Zn is shown.

The correlation of the $D_T$ with the elemental concentration data is insignificant, so the variability in the differences is not concentration dependent. However, PIXE and INAA concentrations for Zn are near the detection limit for some samples.

Figs. 7 and 8 show that there is a good agreement between INAA and PIXE results. However, for these elements there is a systematic difference between INAA and PIXE with values from PIXE lower than values determined by INAA. Freitas et al. [17] obtained similar results and give some explanations for them.

The comparison between INAA and PIXE results for K indicates an average of $D_T$ of −16% and −15% for fine and coarse fractions, respectively. The $D_T$ average for Fe data for fine and coarse fraction, is −14% and −11%. Zeisler et al. [18] determined Fe concentrations by INAA and PIXE and obtained lower concentrations for PIXE especially in the samples with large Fe amounts.

Salma et al. [12] made an equivalent study and obtained an excellent agreement for K and Fe with accurate data to within 5–10%.

Our values from PIXE, for the element Zn in the fine fraction, are about 24% lower than those determined by INAA. For coarse values the average of the $D_T$ is −6.6%. According to IAEA [19] the Zn sensitivity is usually not adequate enough in thermal NAA, which could explain the differences obtained. INAA and PIXE measurements of Zn were also done by Zeisler et al. [18], who obtained PIXE values 20% lower for PIXE. For Toro and Cortés [4], PIXE gave always lower values for Zn and Fe. Salma et al. [12] obtained a Zn ratio PIXE to INAA of 0.84 indicating also that PIXE concentrations are lower comparing with INAA ones.
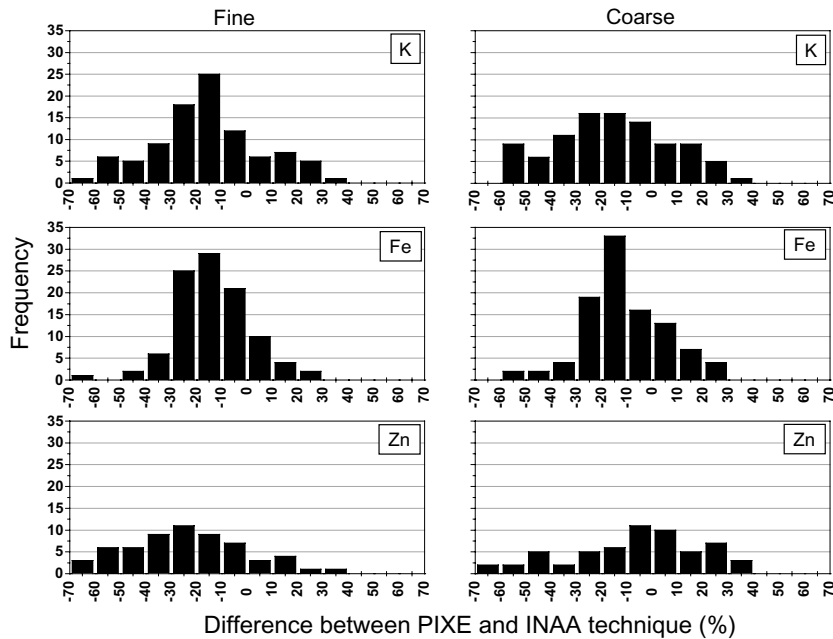
Fig. 8. Frequencies of the difference between PIXE and INAA concentrations normalised by the average (%) for K, Fe and Zn in fine and coarse fractions.

These differences in the techniques could be acceptable for factor analysis and source identification, especially for the constant bias, however care should be taken when emissions of air mass loadings are estimated from such results. To study if the bias is based in the method's calibration, or if it is a load dependent response function a new study is being prepared using the presently available NIST SRM 2783.

## 4. Conclusions

This work has generated data that illustrate some difficulties as well as some excellent quality features of INAA and PIXE used for the measurement of elemental composition in air pollution studies.

Results from APM total mass concentrations collected with two Gent collectors working side-by-side indicate that the two samples are working in a reproducible way. Comparisons of elemental concentration between different parts of the same filter show that the reproducibility varies from sample to sample and element to element. An inverse relation between reproducibility and elemental concentration in different parts of the same filter was observed, especially for PIXE analysis. However, generally the results are reproducible to within 5–15% providing a strong support for the validity of the analytical techniques.

The combination of INAA and PIXE is advantageously used in aerosol studies, to enlarge the number of environmental important elements measured and to evaluate and check the accuracy of the analytical procedures. Results obtained by PIXE and INAA techniques identify systematic differences for co-analysed elements. For K, Fe and Zn concentrations determined with PIXE are lower by 7–25% than concentrations determined with INAA.

## References

[1] H.J.M. Bowen, D. Gibbons, Radioactivation Analysis, Clarendon, Oxford, 1963.
[2] R. Cornelis, J. Hoste, A. Speecke, C. Vandecasteele, J. Versieck, R. Gijbels, Activation Analysis, Part 2, 1976.

[3] S.A.E. Johansson, J.L. Campbell, K.G. Malmqvist, Particle-Induced X-ray Emission Spectrometry (PIXE), John Wiley & Sons, 1995.

[4] P. Toro, E. Cortés, J. Radioanal. Nucl. Chem. 221 (1997) 127.

[5] W. Maenhaut, F. François, J. Cafmeyer, O. Okunade, Applied Research on Air Pollution Using Nuclear-related Analytical Techniques, Appendix 4, IAEA, Australia, 1995, 4.1.

[6] J. Kučera, J. Šantroch, J. Faltejsek, J. Horáková, V. Hnatowicz, V. Voseček, V. Havránek, Applied Research on Air Pollution Using Nuclear-related Analytical Techniques, Appendix 8, IAEA, Australia, 1995, 8.1.

[7] S.R. Biegalski, Elemental Analysis of Airborne Particles, Gordon and Breach Science Publishers, USA, 1999, Chapter 7, p. 255.

[8] P.K. Hopke, Y. Xien, T. Raunemaa, S. Biegalski, S. Landsberger, W. Maenhaut, P. Artaxo, D. Cohen, Aerosol Sci. Technol. 27 (1997) 726.

[9] S.M. Almeida, M.C. Freitas, M.A. Reis, C.A. Pio, J. Radioanal. Nucl. Chem., in press.

[10] P. Artaxo, W.E. Castro, M. De Freitas, K.M. Longo, Applied Research on Air Pollution Using Nuclear-related Analytical Techniques, Appendix 5, IAEA, Australia, 1995, 5.

[11] R. Zeisler, N. Haselberger, M. Makarewicz, R. Ogris, R.M. Parr, S.F. Stone, O. Valkovic, V. Valkovic, E. Wehrstein, J. Radioanal. Nucl. Chem. 217 (1997) 5.

[12] I. Salma, W. Maenhaut, H.J. Annegarn, M.O. Andreae, F.X. Meixner, M. Garstang, J. Radioanal. Nucl. Chem. 216 (1997) 143.

[13] W. Maenhaut, J. Cafmeyer, X-Ray Spectrom. 27 (1998) 236.

[14] E. Bombelka, F.W. Richter, H. Ries, U. Wätjen, Nucl. Instr. and Meth. B 3 (1984) 296.

[15] W. Maenhaut, Co-ordinated Research Program: CRP E4.10.08, IAEA, Belgium, 1992.

[16] F. De Corte, The $K_0$-Standardization Method – A Move to the Optimization of Neutron Activation Analysis, Agregé thesis, Gent, 1987.

[17] M.C. Freitas, S.M. Almeida, M.A. Reis, O.R. Oliveira, Nucl. Instr. and Meth. A 505 (2003) 430.

[18] R. Zeisler, S.F. Heller-Zeisler, A. Fajgelj, J. Radioanal. Nucl. Chem. 233 (1998) 15.

[19] IAEA, Training Course Series No. 4, IAEA, Vienna, 1992.