Environ Chem Lett (2006) 3: 186–191
DOI 10.1007/s10311-005-0029-7

ORIGINAL PAPER

**M. L. Astolfi · S. Canepari · M. Catrambone ·
C. Perrino · A. Pietrodangelo**

Improved characterisation of inorganic components in airborne particulate matter

Received: 8 August 2005 / Accepted: 15 November 2005 / Published online: 6 January 2006

Abstract We set up a microanalytical procedure for non-volatile ions by ion chromatography (IC) and for elements by energy-dispersive X-ray fluorescence (ED-XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES). We analysed NO_3, SO_4, NH_4, Na, Mg, Ca, Fe, S, Zn, As, Cd, Cu, Mn, Ni, Pb, Sb, Se, Ti, and V. The use of complementary techniques yields reliable data for both trace and crustal elements, overcoming the analytical restrictions characteristic of the individual techniques. Some elements determined by two or by all three techniques can be used as data quality markers. The application of the procedure to a short $PM_{2.5}$ monitoring campaign is also described, aimed to the identification of fireworks tracers.

Keywords Airborne particulate matter · Fireworks tracers · Metals · Inorganic ions · Sequential leaching · Quality assurance

Introduction

The chemical characterisation of fine airborne particulate matter (PM) has a key role in understanding the adverse effects of particulate matter on human health, ecosystems and materials, in supporting the environmental policies and in improving models for the source apportionment of air pollutants. Among the components of particulate matter, inorganic ions are investigated for their significance in secondary pollution events, whereas trace metals, because of their chemical stability, are used to perform a reliable identification of particulate sources (Goodarzi and Huggins 2001).

The availability, bio-geochemical distribution and toxicity of an element are dictated by its particular chemical form in a given matrix and for this reason the information yielded by the only determination of the total element is insufficient (Templeton et al. 2000). In the past, the application of chemical fractionation by sequential leaching to particulate matter samples, which allows the evaluation of metals mobility, gave poor results because of the difficulties in obtaining a good reproducibility on very low particulate mass amounts.

Sequential leaching methods for 24 h low-volume loaded filters were recently developed by Viksna et al. (2004) following the current need for particulate matter chemical characterisation on routine basis. It is worth stressing that in applying two-step or three-step sequential schemes to small sample amounts (mg) it is necessary to apply a careful control procedure in order to achieve an acceptable level of analytical reproducibility. Furthermore, the leaching is usually performed by means of non-pH-buffered solvents, while the recovery of metals in a sequential extraction is well known to be strongly dependent on the operative conditions (Pueyo et al. 2001).

A two-step microanalytical leaching procedure for the determination of non-volatile ions (Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$, Na^+, Ca^{2+}, Mg^{2+} and $NH_4{}^+$) by ion chromatography (IC) and elements (As, Cd, Cu, Fe, Mg, Mn, Ni, Pb, S, Sb, Se, Ti, V and Zn) by inductively coupled plasma optical emission spectroscopy (ICP-OES) on low-volume 24-h PM_{10} and $PM_{2.5}$ samples was recently validated by the same authors (Canepari et al. 2005a, b). The procedure, consisting of a single extraction in acetate buffer followed by acid digestion of the residual (Canepari et al. 2000), was successfully tested for equivalence with reference methods (EN12341 1998; EMEP/CCC 1996) and, by a proper control of solubility equilibrium, led to well-reproducible results.

In this work, a third step is introduced prior to leaching and acid digestion. It is based on the determination of Al, Fe, Mg, Mn, S and Si by energy-dispersive X-ray fluorescence (ED-XRF), and is aimed to improve the accuracy in the determination of Al and Si, which were scarcely recovered by the two-step method. In addition, the use of

M. L. Astolfi · S. Canepari
Chemistry Department, University of Rome "La Sapienza",
Ple A. Moro 5, Rome, Italy

M. Catrambone · C. Perrino (✉) · A. Pietrodangelo
C.N.R. Institute of Atmospheric Pollution,
Via Salaria km 29,300, C.P.10, 00016, Monterotondo st.
(Rome), Italy
e-mail: perrino@iia.cnr.it
Tel.: +390690672263
Fax: +390690672660

three independent techniques (IC, ICP-OES, ED-XRF) allows the development of an inter-laboratory quality control (QC) scheme to check and quantify, sample-by-sample, systematic errors in the leaching steps. A validation of the ED-XRF-extended procedure, carried out on parallel $PM_{2.5}$ samples to evaluate the contribution of the ED-XRF step to the analytical error, is reported; the application of the procedure to the characterisation of a fireworks event is also discussed.

Experimental

The following reagents were used: MilliQ deionised water (Millipore Corp., Bedford, MA), HNO_3 (65%, RPE, Carlo Erba, Milan, Italy), H_2O_2 (30%, Suprapur, Merck, Darmstadt, Germany), HF (40%, Suprapur, Merck), glacial CH_3COOH (RPE, Carlo Erba), HCl (30%, Suprapur, Merck), CH_3COOK (p.a., Sigma–Aldrich), $NaHCO_3$ and Na_2CO_3 (p.a., Merck), ion chromatography (IC) and inductively coupled plasma (ICP) standards (1000 mg l^{-1}, CertiPUR, Merck).

For the ED-XRF analyses a Spectro X-LAB 2000 spectrometer (Spectro Analytical Instr. GmbH, Kleve) has been used. Four targets have been employed, two secondary (molybdenum and cobalt), a Barkla scatter (aluminium oxide) and an HOPG Bragg crystal; with respect to these targets the spectrometer was operated respectively at 40 kV and 7.5 mA (molybdenum), 49 kV and 6.1 mA (aluminium oxide), 30 kV and 10.0 mA (cobalt), 20 kV and 15 mA (HOPG).

The energy-dispersive Si(Li) detector is cooled by liquid nitrogen and operates at 148 eV; each spectrum was collected for a total time of 900 s. Quantitative analyses of XRF spectra have been performed by using the Turboquant software package.

It was decided to use the ED-XRF technique for the determination of Al, Fe, Mg, Mn, S and Si, whereas the other elements of this study were determined, with higher analytical reproducibility, by the ICP-OES technique. The detection limits for the analyses by ED-XRF of airborne particulate loaded filters are reported in Table 1. LOQs for ICP-OES analyses are reported elsewhere (Canepari et al. 2005a).

Table 1 Detection limits for airborne particulate 24 h-collected on Teflon filters analysed by ED-XRF

Element	Detection limits	
	On filter area (ng cm^{-2})	Concentration in air (ng m^{-3})
Mg	236	120
Al	154	78
Si	110	76
S	49	25
Mn	9.1	4.6
Fe	67	34

These values have been calculated using the three times square root of the number of background counts according to the IUPAC definition (IUPAC 1978; Winefardner and Long 1983)

To calculate element concentrations in the loaded filters, multielement standards were first used to create a calibration method. Afterwards, the calibration was checked and refined by analysing 18 real loaded filters (47 mm Teflon, 1 μm pore size supported by polypropylene ring, Pall Co.) 24-h collected at the site of the Institute for Atmospheric Pollution of CNR (National Research Council of Italy), in the semi-rural area of Montelibretti (Rome), by a low-volume sampler operating at the flow rate of 20 l/min (Ambient Dust Automatic Monitor, OPSIS). After ED-XRF analysis, these filters were re-analysed by ICP-OES (Simultaneous Vista MPX, VARIAN), performing direct dissolution of the samples by HF acid digestion (Bettinelli et al. 2000) in microwave oven (Milestone Ethos Touch Control equipped with HPR 1000/6S rotor). In this case the ICP-OES equipment was arranged with Teflon components. Before analysing real samples, the analytical protocols of both acid digestion and ICP-OES analysis were optimised and checked on the SRM NIST 1648 coarse urban dust; percentage recoveries higher than 95% and RSDs on 12 replicates below 5% have been obtained.

All the other PM samples used in this work were collected at a traffic station in the centre of Rome by using two identical automatic low volume samplers (SWAM 5A, FAI Instruments, Italy) placed side-by-side at about 3 m above ground level. Parallel 24-h $PM_{2.5}$ or PM_{10} samples were collected on Teflon filters from 1 to 8 January 2004, at the flow rate 38 l/min, obtaining 20 pairs of twin samples. $PM_{2.5}$ or PM_{10} masses were automatically determined in situ by ^{14}C beta rays attenuation. Sampled filters were put into separate containers, stored at 5°C in the absence of light and analysed within a few days.

After ED-XRF detection, the samples were extracted in acetate buffer solution (0.01 M, pH 4.5) in ultrasonic bath for 15 min; then the extracts were divided into two portions: one was analysed for anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, Ca^{2+}, Mg^{2+} and NH_4^+) by ion chromatography (DX 100 IC, DIONEX Co.) and the other for elemental content (Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sb, Se, Si, Ti, V and Zn) by ICP-OES equipped with a quartz torch and an ultrasonic nebulizer (U 5000 AT+, Cetac Technologies Inc.). After extraction, each filter was put into a PTFE vessel and 4 ml of 65% HNO_3 + 2 ml of 30% H_2O_2 were added; after digestion in microwave oven the mineralised solution was filtered on HNO_3 pre-washed cellulose nitrate filters (25 mm, 0.45 μm Millipore), and analysed by ICP-OES (Canepari et al. 2000). ICP calibration was daily performed by a matrix-matched six-point multi-elemental solution set. The sum of the element content in the extract (e) and in the mineralised residue (r) was considered alike total content in calculations, since, although the mass balance is affected by incomplete dissolution of silicates in the solid residue by HNO_3/H_2O_2 digestion, the mass loss was assessed to be negligible for all the considered elements except Al, Cr and Si (EN12341 1998). Blanks of the two-step method resulted to be lower than 30% of the measured values for all the elements.

Table 2 Average relative error (σ%) and linear regression parameters (R^2, *a*, *b*) of the total element contents (ng) determined as sum e+r by the two-step method (check group c) or by ED-XRF-extended method (test group t)

	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	Mg^{2+}	Ca^{2+}	Mg	Fe	S	Zn	As	Cd	Cu	Mn	Ni	Pb	Sb	Se	Ti	V
σ%																				
c	20	10	6	4	20	22	11	10	3	14	13	31	10	7	26	12	9	15	34	13
t	25	13	10	8	24	22	14	20	5	26	25	25	25	19	24	16	12	36	11	17
R^2																				
c	0.96	0.91	0.78	0.99	0.99	0.81	0.72	0.97	1	0.91	0.99	0.99	0.99	0.99	0.39	0.99	0.99	0.94	0.9	0.98
t	0.92	0.9	0.9	0.93	0.99	0.75	0.96	0.75	0.99	0.98	0.74	0.88	0.9	0.86	0.89	0.94	0.98	0.48	1	0.98
a																				
c	0.99	0.81	0.72	1.02	0.89	1.19	0.65	0.84	0.96	0.73	0.79	0.82	0.91	0.97	0.8	0.8	0.83	0.64	0.9	0.79
t	0.89	0.88	0.86	0.99	0.96	1.23	1	0.85	1.02	0.41	0.86	0.75	1.23	0.91	0.56	1	1.03	1.53	1	1.11
b (ng)																				
c	5602	39991	1514	1008	1281	473	1162	1291	959	1059	44	5	27	−5	49	56	18	15	−26	7
t	4576	42006	987	1234	65	523	−49	0.75	913	643	0.74	0.88	0.9	51	37	−2	−8	1	5	−10
Rg (μg)																				
c	27–643	167–535	6–8	45–218	2–40	7–20	1–27	4–21	49–174	2–6	173–892	30–1313	238–8162	85–454	117–341	403–8197	79–1298	19–95	71–968	30–109
t	20–340	147–685	6–79	59–260	2–85	5–19	1–4	2–15	10–95	0.7–10	14–107	1–36	52–596	50–225	48–620	32–390	15–140	3–43	18–176	22–486

The maximum and minimum values of ions and elements in the collected filters are also reported (Rg)

Results and discussion

Validation of ED-XRF-extended leaching method

To quantify the analytical error introduced in the two-step method by including the new ED-XRF step, a new validation of the overall method was carried out by following a scheme based on pairs of equivalent real loaded filters. Twenty pairs of $PM_{2.5}$ samples were divided into two groups of ten pairs each. One group was used as check group (c), and both filters (A and B) of each pair were treated by the old two-step method previously validated for equivalence with reference methods (EN12341 1998; EMEP/CCC 1996). The second group was used as test group (t), and the filter A of each pair was treated by the EDXRF-extended method whereas the filter B was treated by the old two-step method. In this way if any differences were found between results of groups c and t, these should only be attributed to the possible alteration of the loaded filters due to the EDXRF-step. In both groups, within each pair of twin filters, samples to be treated as filter A or B were randomly chosen. Mean relative per cent differences (σ%) in the determination of each element were calculated as averages of the relative error of each pair:

$$\sigma\%_{i,f} = (|m_{Ai,f} - m_{Bi,f}| \times 2/(m_{Ai,f} + m_{Bi,f})) \times 100$$

where m_A and m_B are the masses (ng) of the element i in the fraction f (extract e, mineralised residue r, sum of the two fractions t) measured on the filters A and B of the ten pairs, respectively. Al, Cr and Si were not included in this part of the study, as it is well known from the literature (EN12341 1998) that they are not quantitatively recovered by HNO_3/H_2O_2 digestion. The results of the validation tests are reported in Table 2. Also, the effect of the wide variability of the real particulate sample concentration on the reliability of the results was assessed by the linear regression $m_{Ai,f} = am_{Bi,f} + b$ (in case of equivalence a=1 and b=0) and outcomes are also reported in Table 2.

Results of Table 2 show that a general worsening of the reproducibility is observed when the ED-XRF step is added to the procedure. Nevertheless, with few exceptions (i.e. Se and Zn in the test group), σ% values were lower than 25%.

Linear regression parameters (Table 2) are also affected by the environmental variability of real samples, reflecting the dependence of the analytical data reliability on the broadness of the concentration ranges (Rg). It is worth noting that samples in the t group show narrower Rg than those in the c group, because of the natural variability of real samples. For example, taking into account the high value of Rg, the reliability of Cd results in the check group can be considered as satisfactory despite the high σ% value; a similar situation is found for Zn in the test group.

As and Se contents were in all cases close to their DLs, mainly in the r fraction, strongly affecting the reproducibility of these two elements. The analytical reproducibility of the ion content in the buffer acetate extract e was assessed in the same way, and σ% values were found to be below 30% in both sample groups.

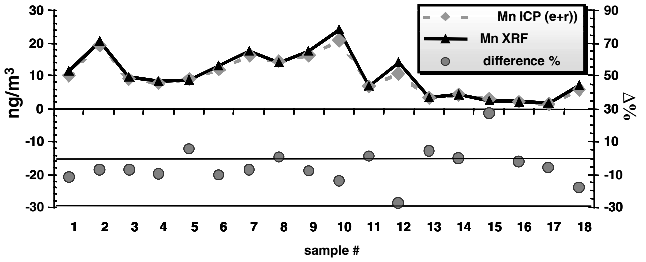

Fig. 1 Comparison of Mn total content determined by ED-XRF or obtained as sum of Mn contents in the e and r fractions by ICP-OES.

These results show that the worsening in the reproducibility due to the introduction of the ED-XRF step may be considered as negligible and that the method is suitable for application to monitoring campaigns. In addition, since most of the 17 elements can be detected by at least two of the three analytical techniques, we could design an inter-laboratory data quality control (QC) scheme, described in the next section, that can be of help in the application of the method to real samples.

Inter-laboratory quality control scheme

The uncertainty levels of the measurements are a critical point mainly in destructive analytical methods like sequential leaching, where real samples are analysed and the determinations cannot be repeated. A quality control system able to perform a cross-check of both the preparative and the detection step, either in real time or after the analyses, is thus required, particularly for the sequential leaching of small airborne particulate matter amounts, in order to ensure that the assessment of accuracy and reproducibility is supported by the identification and quantification of the analytical errors.

Seventeen elements were investigated as possible quality control candidates for assessing the reliability and quality of the analytical detection by ICP-OES and ED-XRF, or by ICP-OES and IC or by the three techniques. On the basis of the analytical quality of data some elements have been selected as quality tracers. Particularly, Fe and Mn could be accurately determined by ICP-OES and ED-XRF, Mg was well detected by both ICP-OES and IC, and S could be determined by all the three techniques. From the intercomparison of the results obtained with different techniques, a scheme was designed for controlling the main analytical errors.

The application of this scheme to determination of Mn in the 20 twin samples is shown in Fig. 1 and Table 3. ED-XRF results are compared with the sum of the Mn contents of the e and the r fractions analysed by ICP-OES. The excellent correspondence between the results yielded by the two techniques (Fig. 1) is confirmed by the low values of the per cent differences reported in Table 3:

$$\Delta\% = ((X_{\text{technique A}} - X_{\text{technique B}}) \times 2/(X_{\text{technique A}} + X_{\text{technique B}})) \times 100$$

where X is the analytical result given by the technique A or B.

This good agreement between the ED-XRF and the ICP analyses of Mn confirms the high accuracy of this determination. Moreover, it allows the sample-by-sample check of possible errors due to sample manipulation, since the two techniques are applied during different steps of the analytical procedure.

Besides identification of casual errors, the temporal trends of the per cent differences, Δ%, also give the possibility of monitoring instrumental drifts. The calibration of the ICP-OES instrument is, indeed, performed daily, and is checked by using control charts obtained by reading a multi-standard solution every ten samples analysed. Therefore, the linear regression of ED-XRF vs. ICP (X_{XRF}=slope(X_{ICP})), whose results are shown in Fig. 1 and Table 3 (last two columns on the right side), can be used as check for possible drifts of the ED-XRF technique by evaluating the slope values (1 for perfect equivalence). These considerations can be easily extended to other elements, like Cu, Ti and Zn, which can be determined with good reliability by more than one analytical technique allowing an accurate sample-by-sample monitoring of the analytical quality of data.

Moreover, the identification of systematic errors is also possible, making it possible to apply a proper correction during the data processing. The optimised method has been applied to real samples, as reported in the following section.

Application to real samples

The optimised ED-XRF-extended extraction procedure was applied to real samples with the aim of investigating the element distribution between the e and the r fractions and their possible employment for the study of source contributions. Particularly, a short field PM_{10} campaign was run over the period of New Year 2004. Twenty-four-hour samples collected at a traffic station in Rome were analysed by applying the above-described procedure with the purpose of investigating the influence of the fireworks of 1 January. The obtained results are shown in Fig. 2, as the ratio between the concentration of each element

Table 3 Average differences and linear regression parameters related to other elements identified as tracers for QC

	Technique A	Technique B	(Δ±SD)%	R^2	Slope
Mn (tot)	ICP-OES$_{(\text{ext+res})}$	ED-XRF	5±11	0.98	1.09
Fe (tot)	ICP-OES$_{(\text{ext+res})}$	ED-XRF	0±19	0.97	1.04
S (tot)	ICP-OES$_{(\text{ext+res})}$	ED-XRF	3±20	0.92	1.09
S (ext)	ICP-OES$_{(\text{ext})}$	IC anions	1±22	0.91	0.91
Mg (ext)	ICP-OES$_{(\text{ext})}$	IC cations	8±20	0.96	1.04

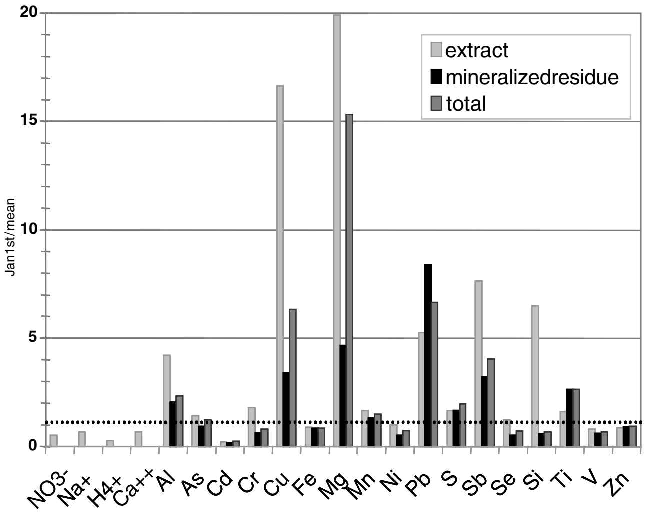

Fig. 2 $X_{\mathrm{Jan\ 1}}/X_{\mathrm{mean}}$ ratio of the mass concentration on 1 January 2004 (fireworks event) to the mean value calculated over the sampling period for the 17 elements: comparison between e and r fractions and the total. For Al and Si the total is obtained by ED-XRF analysis; for the other elements the total is calculated as the sum of the extract and mineralised residue fractions ($e+r$)

in the PM_{10} mass (ng/mg) obtained on 1 January ($X_{\mathrm{Jan\ 1}}$) and its average mass concentration during the overall sampling period (X_{mean}). Data are presented as ng/mg with the purpose of making them independent of the dilution properties of the lower atmosphere (Perrino et al. 2001).

For some elements, i.e. Al, Cu, Mg, Pb and Sb, the $X_{\mathrm{Jan\ 1}}/X_{\mathrm{mean}}$ ratio resulted significantly above 1 for the total concentration, indicating that these elements can be seen as tracers of fireworks events. Data in Fig. 2 show, indeed, very diverse distributions of Al, Cu, Mg, Pb and Sb between the extract and residue fractions. Particularly, the fireworks event strongly contributed mainly to soluble species of Cu, Mg and Sb, whereas Pb was augmented for its scarcely soluble species. For many of the investigated elements the concentration increase was mainly observed either in the e or in the r fraction depending on the different solubility of the element. On 1 January, for example, the increase in Cu and Mg concentration was mainly observed in the extract. The information on total Si cannot be considered a good indicator of fireworks, since the additional contribution to Si coming from this type of event may be considered negligible with respect to the Si background concentrations. However, when the sole soluble fraction of Si is examined, a significant contribution is recognised. The analysis of the solubility distribution gives thus the possibility of identifying new tracers, as the soluble fraction of Si, or of increasing the sensitivity of identified source-selective tracers. In the case of Cu, for example, a sensitivity of the soluble fraction three times enhanced with respect to total was observed.

Conclusion

The described microanalytical procedure allows a complete inorganic characterisation of small amounts of filter-collected airborne particles (24-h low volume) by using complementary non-destructive and destructive analytical techniques. This also allowed the design of an efficient quality control scheme based on sample-by-sample cross-check of the data. The information obtained on the total metal content is supplemented by that on the solubility distribution. The choice of evaluating separately the metal contributions in the fraction extracted under weak acid buffered conditions and in the fraction digested under strong acid-oxidising conditions confirmed to be useful either for the identification or for the sensitivity enhancement of tracers which are selective of a specific source like fireworks. In fact, since on 1 January the PM_{10} mass was higher (3.1 mg) than in the following days (2.5 mg on average), elements showing a $X_{\mathrm{Jan\ 1}}/X_{\mathrm{mean}}$ ratio above 1 could have been significantly augmented by the fireworks, whereas, conversely, this event contributed negligibly to elements with $X_{\mathrm{Jan\ 1}}/X_{\mathrm{mean}}$ ratio below 1. These potentials will be further investigated in the next future by application to larger field campaigns.

Acknowledgements This study has been co-financed by the Italian Ministry of Education, University and Research (MIUR). Thanks are due also to Sorgenti Tesorino Spa for the financial contribution. The authors are indebted to Tiziana Sargolini for her valuable technical assistance.

References

Bettinelli M, Beone GM, Spezia S, Baffi C (2000) Determination of heavy metals in soils and sediments by microwave assisted digestion and inductively coupled plasma emission spectrometry analysis. Anal Chim Acta 424:289–296

Canepari S, Bruno P, Cardarelli E, Del Cavaliere C, Ghighi S (2000) Determination of metals in thoracic fraction of ambient particulate matter. Ann Chim 90:645–652

Canepari S, Cardarelli E, Pietrodangelo A, Giuliano A (2005a) Determination of soluble ions and metals in airborne particulate matter by a new two-step sequential leaching procedure. Part A: Experimental design and optimisation. Talanta, 2005, in press

Canepari S, Cardarelli E, Pietrodangelo A, Strincone M (2005b) Determination of soluble ions and metals in airborne particulate matter by a new two-step sequential leaching procedure. Part B: Validation on twin field samples. Talanta, 2005, in press

EMEP/CCC Report 1/95NILU ref. O-7726 (1996) Manual for sampling and chemical analysis. Norwegian Institute for Air Research (NILU), Oslo, Norway

EN12341 (1998) Air quality. Determination of the PM10 fraction of suspended particulate matter—Reference method and field test procedure to demonstrate reference equivalence of measurement methods. CEN, Brussels

Goodarzi F, Huggins FE (2001) Monitoring the species of arsenic, chromium and nickel in milled coal, bottom ash and fly ash from a pulverized coal-fired power plant in Western Canada. J Environ Monit 3:1–6

IUPAC (1978) Nomenclature, symbols, units and their usage in spectrochemical analysis-II. Spectrochim Actab 33B:242

Perrino C, Pietrodangelo A, Febo A (2001) Development of an Atmospheric Stability Index for the evaluation of primary urban pollution. Atmos Environ 35:5235–5244

Pueyo M, Rauret G, Luck D, Yli-Halla M, Muntau H, Quevauviller P, Lόpez-Sànchez JF (2001) Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. J Environ Monit 3(2):243–250

Templeton DM, Ariese F, Cornelis R, Danielsson LG, Muntau H, van Leeuwen HP, Lobinski R (2000) IUPAC Recommendations 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects and methodological approaches. Pure Appl Chem 72(8):1453–1470

Viksna A, Lindgren ES, Standzenieks P, Jacobsson J (2004) EDXRF and TXRF analysis of elemental size distribution and environmental mobility of airborne particles in the city of Riga, Latvia. X-Ray Spectrom 33:414–420

Winefordner JD, Long JL (1983) Limits of detection. A closer look at the IUPAC definition. Anal Chem 55(7):712A–724A