#### Atmospheric Environment 45 (2011) 3488-3499



Contents lists available at ScienceDirect

### Atmospheric Environment



journal homepage: www.elsevier.com/locate/atmosenv

# Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in $PM_{10}$ in Europe

M. Gerboles <sup>a,\*</sup>, D. Buzica <sup>a</sup>, R.J.C. Brown <sup>b</sup>, R.E. Yardley <sup>b</sup>, A. Hanus-Illnar <sup>c</sup>, M. Salfinger <sup>c</sup>, B. Vallant <sup>c</sup>, E. Adriaenssens <sup>d</sup>, N. Claeys <sup>d</sup>, E. Roekens <sup>d</sup>, K. Sega <sup>e</sup>, J. Jurasović <sup>e</sup>, S. Rychlik <sup>f</sup>, E. Rabinak <sup>f</sup>, G. Tanet <sup>a</sup>, R. Passarella <sup>a</sup>, V. Pedroni <sup>a</sup>, V. Karlsson <sup>g</sup>, L. Alleman <sup>h</sup>, U. Pfeffer <sup>i</sup>, D. Gladtke <sup>i</sup>, A. Olschewski <sup>i</sup>, B. O'Leary <sup>j</sup>, M. O'Dwyer <sup>j</sup>, D. Pockeviciute <sup>k</sup>, J. Biel-Ćwikowska <sup>l</sup>, J. Turšič <sup>m</sup>

<sup>a</sup> European Commission, Directorate General Joint Research Centre, Institute for Environment and Sustainability, Via E. Fermi, I-21027 Ispra VA, Italy

- <sup>b</sup> Analytical Science Division, National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, United Kingdom
- <sup>c</sup> Umweltbundesamt GmbH/Environment Agency Austria, Inorganic Analysis, Spittelauer Lände 5, 1090 Vienna, Austria

<sup>d</sup> Flemish Environment Agency, Kronenburgstraat 45, 2000 Antwerpen, Belgium

<sup>e</sup> Institute for Medical Research and Occupational Health, Ksaverska 2, 10000 Zagreb, Croatia

<sup>f</sup>Czech Hydrometeorological Institute, Na Sabatce 17, 143 06 Prague, Czech Republic

<sup>g</sup> Finnish Meteorological Institute, P.O. Box 503, FI-00101, Finland

h Ecole des Mines de Douai, Département Chimie et Environnement, 941 rue Charles Bourseul, BP 10838, 59508 Douai cedex, France

<sup>1</sup>NRW State Agency for Nature, Environment, and Consumer Protection, Wallneyerstr. 6, 45133 Essen, Germany

<sup>j</sup> Environmental Protection Agency, Richview, Clonskeagh Road, 14 Dublin, Ireland

<sup>k</sup> Environmental Protection Agency, Gostauto Street 9, Vilnius, Lithuania

<sup>1</sup>Voivodship Inspectorate of Environmental Protection in Wroclaw, Laboratory of Jelenia Góra, ul. Warszawska 28, 58-500 Jelenia Góra, Poland

<sup>m</sup> Environmental Agency of the Republic of Slovenia, Vojkova 1b, SI-1000 Ljubljana, Slovenia

#### ARTICLE INFO

Article history: Received 2 March 2010 Received in revised form 6 December 2010 Accepted 9 December 2010

Keywords: Heavy metals PM<sub>10</sub> Particulate matter speciation Air quality legislation Uncertainty of measurement

#### ABSTRACT

This paper presents the results of an intercomparison exercise for the determination of arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb) in PM<sub>10</sub>, which are regulated by the European Directives for ambient air quality. Thirteen laboratories participated, generally using the European reference methods of measurement which consist of a microwave digestion followed by analysis with either ICP-MS or GFAAS. Each participant was asked to analyse five test samples: a liquid Certified Reference Material (CRM), two sub-samples of a NIST dust CRM (one already-digested and one to be digested by the participants) and two loaded filters (one already-digested and one to be digested by the participants).

Participants were able to meet the Data Quality Objectives (DQOs) of the European Directives (expanded uncertainties of 25% for Pb and 40% for As, Cd and Ni) for 93% of all test samples, except for the loaded filter that were digested by the participants. In fact, only 76% of DQOs were met for this test sample, the closest to a routine sample analysis in the laboratory. The difficulties in analysing this test sample came mainly from digestion and contamination processes. Satisfactory results were also obtained using other digestion techniques (Soxhlet extraction and high pressure methods) and analytical methods (ICP-OES for Cd, Ni and Pb, EDXRF for Pb and Ni and Voltammetry for As, Ni, and Pb).

Participants claimed uncertainties of about 10% for Pb and between 15 and 20% for As, Cd and Ni. These uncertainties were confirmed for 77% of results. The reproducibility of the methods of measurement was between 41 and 54% while repeatability remained between 5 and 12% except for the analysis of As on filters which was up to 20%. The majority of participant results showed higher between-day variability (14  $\pm$  11%) than within-day variability (6.0  $\pm$  5.3%).

© 2010 Elsevier Ltd. All rights reserved.

#### 1. Introduction

\* Corresponding author. Tel.: +386 39 0332 785652. *E-mail address*: michel.gerboles@jrc.ec.europa.eu (M. Gerboles). Determination of metals in atmospheric particles is of great interest, due to their harmful effects on human health (Schlesinger et al., 2006; Kampa and Castanas, 2008). In Europe, the monitoring of arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb), in particulate

<sup>1352-2310/\$ –</sup> see front matter  $\odot$  2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.atmosenv.2010.12.020

matter ( $PM_{10}$ ) is regulated by the European Directives for Air Quality (2008/50/EC, 2008) and the 4th European Daughter Directive (2004/107/EC, 2005). The Directives define Limit and Target Values for these heavy metals, and the reference methods for analysis (EN 14902, 2005a) and for sampling (EN 12341, 1998). EN 12341 only allows sampling on quartz filter for 24 h using a low volume sampler with the European PM<sub>10</sub> sampling inlet and an air flow of 38.3 l/min. The Directives also include Data Quality Objectives (DQOs) defining the maximum expanded uncertainty allowed for routine monitoring as 25% for Pb and 40% for As, Cd and Ni. The Directives require that a National Reference Laboratory (NRL) is nominated in each Member State of the European Union (EU) and that these NRLs take part in Intercomparison Exercises (IE) organised at European level.

A limited number of IE for heavy metals on  $PM_{10}$  filters can be found in literature. The major  $PM_{10}$  studies, INTERCOM2000 (Muller et al., 2004), the European Aerosol Phenomenology (Putaud et al., 2004) and the CARB studies (Motallebi et al., 2003), although looking at different aspects of aerosol speciation, did not take heavy metal measurements into account. In the majority of reported IEs for heavy metals, the test samples were not composed of  $PM_{10}$ sampled on 47 mm filters according to EN 12341. In fact, a convenient method to prepare such test samples is still lacking.

Within the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe programme (EMEP), a few IEs are organised for Pb, Cd, copper (Cu), zinc (Zn), As, chromium (Cr) and Ni, although these are based on liquid samples. In one of the last exercises (Uggerud and Hjellbrekke, 2006), four synthetic solutions were prepared using multi-element standards traceable to National Institute of Standards and Technology (NIST). These test samples are easier to analyse than real PM<sub>10</sub> sampled on filters. Nevertheless, up to one third of the participants could not reach the EMEP DQO for low concentration samples, which requires the expanded uncertainty to be 25% or less.

The Workplace Analysis Scheme for Proficiency (WASP), the proficiency scheme organised by Heath and Safety Laboratory (UK) for air monitoring samples (Stacey, 2006), proposes Cd, Cr and Pb spiked on filters but at occupational levels and on 25 mm filters. Another route has been followed by the same laboratory for preparing test samples by using a multiport sampler named the Sputnik sampler (Tylee et al., 2003). It allows preparation of a set of near identical filter samples with homogeneity better than 10%. So far the Sputnik multiport sampler has only been used to prepare 25mm diameter filters at a low flow rate of about 0.11 m<sup>3</sup> h<sup>-1</sup>, making it more appropriate for the level of particulate matter that may be encountered in workplace environment. Two additional proficiency testing schemes are regularly organized. In the first one, organised by International Exercises Laboratories (IELAB - Spain, http://www. ielab.es), Whatman QMA quartz filters are spiked with liquid solutions of As, Cd, cobalt (Co), Cr, Cu, manganese (Mn), Ni, Pb, antimony (Sb), tin (Sn), selenium (Se), thallium (Tl) and Vanadium (V). In the second one, organized by the German Institute for Occupational Safety and Health IFA (http://www.dguv.de/ifa/en/fac/ring/pdf/ ergebnisse/2009\_Metal\_e.pdf), participants receive about 1 g of dust including As, Cr, Cu, molybdenum (Mo), Ni, titanium (Ti) and Zn. Both of these schemes deliver test samples with concentrations of heavy metals that are too high to be appropriate in the field of ambient air quality monitoring.

Alleman and Labaraque (2007) used a commercially available multiport sampler (Rupprecht and Patashnick, model Speciation 2300 – USA) to prepare four sets of test filters by sampling  $PM_{10}$  on 47-mm diameter quartz filters. Only 12 filters could be simultaneously prepared, a small batch for the organization of an IE at a European level. Moreover, the instrument sampled ambient air sequentially onto three groups of four filters thus leading to a possible lack of homogeneity between groups.

Some limited field comparisons using PM<sub>10</sub> sampled on filters have taken place. For example, Mickel (2002) reported the preparation of a set of band strips of 1 by 4 inches cut from a large quartz filter. The samples were used for an IE organised by the US Environmental Protection Agency in which 5 participants analysed bervllium (Be), Cd, Cr, Pb, Mn and Ni, No reference values were available for the test samples. However, the scatter of results was low with typical standard deviations of about 10% for Pb and Cr. and 15% for Cd, Mn and Ni. Another example is given by the INTERREG III study (AREMA et al., 2004). In this project, PM<sub>10</sub> was sampled for two consecutive 3-days periods using two Partisol samplers (Rupprecht and Patashnick, USA). Filters were analysed by three laboratories using either Wavelength Dispersive X-ray Fluorescence (WD-XRF) or graphite furnace atomic absorption spectrometry (GFAAS). Large differences of results were observed between laboratories, for example up to a factor of 3 for Cu.

Due to the lack of IE at a European level, the Joint Research Centre (JRC) of the European Commission (EC) organised in 2007 the first EC exercise for the measurement of heavy metals in PM<sub>10</sub>. The IE focused on the measurement of the heavy metals regulated by the European Directives, namely: Pb, As, Cd and Ni. The elements included in the EMEP programme (Cr, Cu and Zn) were also tested. Other elements of interest, aluminium (Al), Co, iron (Fe), Mn and V, were added as a result of participant requests. However, only the analysis of Pb, As, Cd and Ni was mandatory for participation in the IE and only a few participants reported results for the rest of the elements (Gerboles and Buzica, 2008). Therefore, the data treatment was not carried out on the small data set available for elements other than As, Cd, Ni and Pb.

This IE was designed to study if the DQO of the European Directives were met by the participants and if the uncertainty reported by NRLs was validated by the difference between their results and the reference values of test samples. Furthermore, the repeatability/reproducibility of the methods of measurement and the between-day/within-day variability of each laboratory were estimated. Finally, the test samples were divided into a few types in order to endeavour to distinguish, as far as possible with a limited number of test samples, the sources of analytical discrepancies among the effect of calibration, digestion, matrix effect and method of analysis on the PM<sub>10</sub> measurement of heavy metal in the European Union.

#### 2. Methodology

#### 2.1. Participants and measurement methods

The NRL members of AQUILA (http://ies.jrc.ec.europa.eu/aquilaproject/aquila-homepage.html), the network of the NRLs of the EU Member States and Candidate Countries, were invited to participate in the IE. Table 1 shows the participating laboratories consisting of twelve NRLs and the JRC. The Polish laboratory, Chief Inspectorate of Environmental Protection, was a regional laboratory nominated by the Polish Ministry of Environment to participate in the IE. Two of the NRLs used two different methods of measurements so that 15 different sets of results were obtained in the IE. In order to ensure confidentiality of results, all laboratories were given a number at random for identification.

The 4th Daughter Directive states that the reference methods for the determination of heavy metals in PM<sub>10</sub> shall be based on either Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Graphite Furnace Atomic Absorption Spectrometry (GFAAS). However, any measuring method used by NRLs was accepted in order to assess the whole picture of data quality for heavy metals analysis in the EU. In fact, NRL 0 used Energy Dispersive X-ray Fluorescence (EDXRF) for As, Ni and Pb and WDXRF for Cd, NRL 8 and 11 used

#### Table 1

National Reference Laboratories participating in the Intercomparison Exercise.

Country		NRLs
Belgium	VMM	Flemish Environment Agency
Austria	UBA	Umweltbundesamt GmbH
France	EMD	Ecole des Mines de Douai
Croatia	IMI	Institute for Medical Research
		and Occupational Health
Lithuania	EPA	Environmental Protection Agency
Czech Republic	CHMI	Czech Hydrometeorological Institute
Germany	LANUV	State Agency for Nature, Environment,
		and Consumer Protection
Slovenia	ARSO	Environmental Agency of the Republic of Slovenia
Ireland	EPA	Environmental Protection Agency
Poland	GIOS	Chief Inspectorate of Environmental Protection
Finland	FMI	Finnish Meteorological Institute
United Kingdom	NPL	National Physical Laboratory
European	JRC	Joint Research Centre – Institute for
Commission		Environment and Sustainability

Optical Emission Spectrometry (ICP-OES) and NRL 15 used Voltammetry. Table 2 shows the method of digestion and analysis of each participant, the traceability of their standards and their method of estimation of uncertainty.

#### 2.2. IE protocol and preparation of test samples

Five different types of test samples were prepared in the IE:  $S_1$ , a liquid Certified Reference Material (CRM);  $S_2$ , a digested NIST dust CRM;  $S_3$ , a NIST dust CRM;  $S_4$ , an already-digested PM<sub>10</sub> filter and  $S_5$ , a non-digested PM<sub>10</sub> filter. Participants were required to carry out 6 replicate analyses of all test samples including the digestion of  $S_3$  and  $S_5$ . Furthermore, for  $S_1$  and  $S_5$  the 6 replicate analyses had to be repeated on 3 different days with 3 different calibrations. Reagent blank values had to be subtracted from  $S_1$ ,  $S_2$  and  $S_3$ . The values of a blank filter had to be subtracted from  $S_4$  and  $S_5$ . The blank filter came from the same filter lot as  $S_4$  and  $S_5$ . The PM<sub>10</sub> and element masses of all test samples were consistent with the samples found in routine monitoring. They were set by considering the Limit Values of PM<sub>10</sub>, As, Cd, Ni and Pb, the sampling time (24 h) and sampling flow (38.3 l/min) defined in EN-12341.

It was planned to estimate analytical or calibration bias using  $S_1$ , matrix effect comparing  $S_1$  and  $S_2$ , and the efficiency of digestion using the results of digested and non-digested pairs of dust CRM test samples ( $S_2$  and  $S_3$ ) and filter test samples ( $S_4$  and  $S_5$ ). The within-day and between-day variability of the methods of measurement were estimated by repeating the analysis of selected test samples over several days for  $S_1$  and  $S_5$ .

Full details of the preparation of the test samples, the calculation of their reference/assigned values and their uncertainty estimation can be found in Gerboles and Buzica (2008). The reagents used for the preparation of samples were of ultra pure grade (J.T. Baker). All labware (volumetric flasks, PFA vials, etc) and digestion vessels were thoroughly cleaned before use by soaking in 10% nitric acid overnight, rinsing at least three times, first with 10% nitric acid and second with ultra pure water, then drying at temperatures below 50 °C and finally storing in a dust protected area as mentioned in EN 14902 (2005a). In addition, the temperature programme used for the digestion of test samples (see below) was performed once on the vessels of the microwave oven (Millestone Ethos Touch) after having been filled with 8 ml of nitric acid and 2 ml of hydrogen peroxide. Afterwards, they were rinsed at least three times with ultra pure water and then placed in an oven at 150 °C for 2 h to improve the cleaning process. The temperature controlled digestion programme used for the digestion of all samples consisted of three steps: twenty minutes of linearly increasing temperature between ambient and 220 °C, twenty-five min of constant temperature (220 °C) and twenty minutes of cooling. This process was performed twice to ensure full digestion of all the dust samples. Afterwards, the digestion vessels were gradually opened over 1 h in order to reduce the temperature and slowly release the pressure, avoiding evaporation or liquid loss by any spray of small droplets.

## 2.3. Test sample prepared using a liquid certified reference material $(S_1)$

S<sub>1</sub> consisted of a solution prepared by dilution of liquid CRMs. 100 µl of CRM BY14 (Romil 'PrimAg' ICP calibration mix) and 900 µl of CRM R14 (Romil 'PrimAg' ICP calibration mix) were transferred into a 2 L glass flask using two gravimetrically adjusted pipettes. Subsequently, 10 ml of 70% nitric acid (HNO<sub>3</sub>) was added. Finally, the 2 L flask was filled up with ultra pure water. Aliquots of this solution were then transferred into 50 ml flasks made of perfluoroalkoxy copolymer (PFA). S<sub>1</sub> was prepared in a balance room where the temperature and relative humidity were kept at 20  $^\circ\text{C}\pm1$   $^\circ\text{C}$  and  $50 \pm 5\%$ , respectively. The reference values and uncertainties of As, Cd, Ni and Pb for S<sub>1</sub> are given in Table 3. The uncertainties were calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM, 2008) with two methods of estimation, one using the volumes of BY14 and R14 CRMs and one using their weights. The factors taken into account to estimate the uncertainty of S<sub>1</sub> were the repeatability of weighing, the uncertainty of the balance, the uncertainty of each element given in the certificates of the CRMs, the uncertainty of the volume of the 2 L flask, the temperature expansion of the volume of the flask and the reproducibility of filling the flask. The background blank level arising from the presence of heavy metals in reagents (HNO<sub>3</sub> and ultra pure water), 2 L flask and PFA flask was guantified by analysing 6 samples of a solution of 10 ml of HNO<sub>3</sub> diluted with ultra pure water in a 2 L flask subsequently transferred into a PFA flask. The resulting low blank value was subsequently included in the uncertainty estimation. The reference values determined using the volumetric method were retained because this method allowed lower uncertainty estimates.

## 2.4. Test samples prepared using a dust certified reference material ( $S_2$ and $S_3$ )

S<sub>2</sub> consisted of a solution of a digested dust CRM. S<sub>2</sub> was prepared with the NIST Standard Reference Material (SRM) 1648 (NIST - USA: Urban Particulate Matter) which was placed over night in an oven at 105 °C for drying and then stored in a desiccator before use. 150 mg of the NIST 1648 was weighed in the balance room directly into a digestion vessel of the microwave oven that was closed immediately after weighing. The digestion was carried out with the temperature programme mentioned before using 8 ml HNO<sub>3</sub> and 2 ml hydrogen peroxide H<sub>2</sub>O<sub>2</sub> plus addition of 0.5 ml hydrofluoric acid (HF) to fully digest the silicate matrix. After digestion, the solution was completely transparent without any solid substrate remaining. It was transferred into a 1 L glass flask and made up to the mark with ultra pure water without filtering. Immediately, aliquots of this solution were then transferred into 25 ml PFA flasks. The reference value of S<sub>2</sub> was computed from the mass of dust CRM, the mass ratio of heavy metals given in the NIST SRM 1648 certificate, the volume of the glass flask and the efficiency of the digestion of S2 carried out by JRC. The presence of traces of heavy metals in the ultra pure water, HNO<sub>3</sub>, HF, flask and vials was neglected since it was found by analysis to be lower than 1% of that in the digest solution. However, a contribution equal to these traces of heavy metals was added to the estimation of uncertainty.

#### Table 2

Digestion and analytical methods, traceability to standards and estimation of measurement uncertainty of all participants.

NRL	Analytical method and calibration	Digestion ( $S_3$ and $S_5$ )	Calibration standards	Uncertainty
0	S <sub>5</sub> : EDXRF for As, Pb and Ni,	No digestion	Calibration curve with filters prepared by aerosol generation	Repeatability only
1	$S_1$ to $S_5$ : GFAAS. Calibration curve	EN 14902 method with 8 ml of HNO <sub>3</sub> and 2 ml of $H_2O_2$	Calibration curve using Merck AAS standards solutions (As, Cd, Pb and Ni 1000 ppm)	Based on precision and reproducibility
3	ICP-MS (PE Elan DRC II) Calibration curve using matrix matched aqueous standards	EN 14902 method with 8 ml sub boiled $HNO_3$ 65% and 2 ml $H_2O_2$ 30% pa, dilution to 50 ml in calibrated quartz flasks with ultra pure water; then filtration through 150 mm folded filters in 50 ml PE flasks	Using Plasma standard, Baker Instra Analyzed ICP standards, traceable to NIST SRM 3103a (As), 3108 (Cd), 3136 (Ni) and 3128 (Pb)	Uncertainty estimated using at least 6 independent analysis and relative standard deviation of measurements of NIST SRM 1643e and 1648. The estimation includes the sample preparation, digestion, dilution
4	ICP-MS (PE Elan 6100 DRC <sup>plus</sup> ) with simple mathematical corrections for interference. Calibration curve with <sup>115</sup> In, <sup>71</sup> Ga as internal standard	EN 14902 method: Microwave digestion (Millestone Ethos) at a temperature of 220 °C with supra pure 8 ml HNO <sub>3</sub> and 2 ml H <sub>2</sub> O <sub>2.,</sub> dilution to 50 ml in PP flasks with Ultra pure water	PlasmaCal (SCPscience) traceable to NIST, PlasmaCal 1000 ppm standard and QC standards are NIST traceable, certified accuracy to within plus or minus 1%	and measurement procedure. GUM method ( $k = 2$ ) combining repeatability and bias of Quality Controls with a tolerance of $\pm 5\%$ and assuming a rectangular distribution
5	GFAAS (AAnalyst 600, Perkin Elmer). Calibration curve using aqueous standard solutions (Cd and Pb) or matrix matched aqueous standards (As and Ni)	S <sub>3</sub> : microwave digestion with 3 ml HNO <sub>3</sub> (65%) and subsequent dilution to 25 ml with DI-H <sub>2</sub> O; S <sub>5</sub> : Soxhlet extraction with 50 ml HNO <sub>3</sub> (65%), extract concentrated and made up to 10 ml with De-H <sub>2</sub> O	MERCK AAS standard solutions (CertiPUR®) traceable to SRM from NIST	No uncertainty reported
6	GFAAS (PerkinElmer Aanalyst 800). Calibration curve for As, Ni, Cd, Pb and V	EN 14902 method with 8 ml HNO <sub>3</sub> and 2 ml $H_2O_2$	Standard solution IV (FLUKA) for calibration curve and ICP multi- element standard solution XVI and VIII (MERCK) for quality control	GUM method combining standard uncertainty of recovery, calibration and laboratory bias
7	ICP-MS (Thermo Elemental with PlasmaLab software). Calibration curve	$S_3$ : quantitatively transferred to a microwave vial for digestion, then evaporated to a droplet and mixed with 10 ml of 3% HNO <sub>3</sub> . $S_5$ : Microwave digestion with 6 ml HNO <sub>3</sub> and 2 m H <sub>2</sub> O <sub>2</sub> , then 5 ml evaporated to a droplet and mixed with 10 ml of 3% HNO <sub>3</sub>	Standard Analytika-Astasol; Merck Certipur and SRM NIST 1648a	GUM method with contribution of calibration (CRM certified uncertainty) and repeatability ( $n = 12$ , 1 day) of CRM analyses.
8	GFAAS for As and ICP-OES for Cd, Ni, Pb, Zn, Cr, Mn, V, Fe, Cu. Calibration curve	High pressure digestion with HNO <sub>3</sub> and $H_2O_2$ and HF for Cr, Fe, Ti. Dilution with 1% HNO <sub>3</sub> to 25 ml. Filtration	CPI international, traceability of the standards safeguarded by certified NIST SRM.	GUM method with contribution of filter blank, sampling volume, digestion, dilution and spectroscopic analyses.
9	ICP-MS. Calibration curve with Rh as internal standard	EN 14902 method with 8 ml HNO <sub>3</sub> and 2 ml $H_2O_2$ microwave digestion with maximum power of 600 W	Perkin Elmer Multi-element ICP-MS Calibration Std. 3, QA/QC ICP Multi XVI PE PurePlus	Repeatability, reproducibility and bias taken into account
10	Perkin Elmer ELAN ICP-MS 6000. Calibration curve by serial dilution using Ge, Rh, Re as internal standards.	EN 14902 method with 8 ml HNO <sub>3</sub> and 2 ml $H_2O_2$ , using a MARS 5 digester.	BDH laboratory supplies. NIST traceable. BDH QC-2	No uncertainty reported
11	GFAAS for all elements and test samples except ICP-OES for Pb on $S_4$ and $S_5$ . Calibration curve	$ \begin{array}{l} S_3{:} 8 \mbox{ ml of HNO}_3 \ (70\%) + 2 \mbox{ ml H}_2O_2 \ (30\%) \\ \mbox{completed with ultra pure water to 25 ml,} \\ S_5{:} \ 0.5 \mbox{ ml HF} \ (49\%) \mbox{ evaporation on a hot plate} \\ \mbox{at } 70{-}80\ ^\circ\mbox{C, then microwave digestion with} \\ 8 \mbox{ ml of HNO}_3 \ (70\%) \mbox{ and } 2 \mbox{ ml H}_2O_2 \ (30\%) \\ \mbox{completed with ultra pure water to 25 ml} \end{array} $	Merck ICP multi-element Standard for calibration IV, Check: SPS-WW1 and WW2 Promochem and NIST 1648	Uncertainty reported but without explanation on the estimation method
				(continued on next page)

(continued)	Analytical	ICP-MS (Pe
Table 2	NRL	12

NRL	Analytical method and calibration	Digestion $(S_3 \text{ and } S_5)$	Calibration standards	Uncertainty
12	ICP-MS (Perkin Elmer Sciex Elan 6000) according to standard ASTM D 5673, Calibration curve	EN 14902 method with 8 ml HNO <sub>3</sub> and 2 ml H <sub>2</sub> O <sub>2</sub>	At least 5 standards, gravimetrically prepared using Merck ICP Multi-element Standard Solution VI CertiPUR, with concentration levels and acidity adjusted to match the analysed samples. Quality Control samples prepared from a different Lot of the same standards. NIES 8 was used to control the efficiency of digestion.	Uncertainty calculated using systematic error and random error
14	ICP-MS (PerkinElmer Elan DRC II). Long tem drift corrected with external standard and short term correction with internal standard (Y, In, Bi). For all sample solutions, 6 replicates were performed. Arsenic was corrected for interference coming from ArCl and for matrix effects. Calibration curve	Digestion using a CEM Mars X microwave oven at a temperature up to $220 ^{\circ}$ C with 8 ml of 70% HNO <sub>3</sub> and 2 ml 30% H <sub>2</sub> O <sub>2</sub> . S <sub>3</sub> was diluted to 500 ml before analysis, with reagent blank.	Calibration standards were gravimetrically prepared using NIST SRMs (3103a, 3108, 3136 and 3128). For calibration of all analyses, at least four gravimetrically-prepared calibration solutions were used	Calculated following the GUM method. The uncertainty estimation comprises contributions from instrument repeatability, internal standard correction, uncertainty in the calibration standards and in sample dilutions.
15	Anodic stripping voltammetry for Cd. Pb, Cu, Zn and As. Adsorptive stripping voltammetry for Ni using Metrohm 797 VA Computrace. Calibration by standard additions	EN 14902 method with 8 ml HNO <sub>3</sub> and 2 ml H <sub>2</sub> O <sub>2</sub>	CRM Romil – PrimAg-xtra and NIST 1648	Expanded uncertainty calculated using the error contribution from the instrument responses and the one from calibration, repeatability, calibration standards and recovery (for 5a, 5a)
16	ICP-MS (Agilent 7500). Long tem drift correction with external standard and short term correction with internal standard (Sc-Y-Re). Correction with a collision cell for Fe and As. For all sample solutions, 3 replicates were performed. Calibration curve	EN 14902 with 8 ml HNO <sub>3</sub> and 2 ml H <sub>2</sub> O <sub>2</sub> , Sub-boiled Ultrapure Nitric Acid 70% was used in all further dilution steps.	Quality Control Standard CSTD solution (2 ng/g) was prepared and used every 11 steps of analysis to correct an eventual instrumental drift. NIST SRM 1648 was used as a second check. BDH Certified Calibration Standard 2 (10 µg/ml), ROMIL Certified Standards (5c, Y, Re)	No uncertainty reported

M. Gerboles et al. / Atmospheric Environment 45 (2011) 3488-3499

Reference values and combined uncertainty of heavy metals in samples $S_1$ , $S_2$ and $S_3$
Assigned values and combined uncertainty for $S_4$ and $S_5$ .

Samples/elements	As	Cd	Ni	Pb
$S_1$ , ng ml <sup>-1</sup> , volume	$7.03\pm0.09$	$5.01\pm0.15$	$27.6\pm0.5$	$50.1\pm0.85$
S <sub>1</sub> , ng ml <sup>-1</sup> , gravimetry	$\textbf{7.04} \pm \textbf{0.25}$	$5.00\pm0.23$	$\textbf{27.6} \pm \textbf{0.7}$	$50.1\pm1.1$
$S_2$ , ng ml <sup>-1</sup>	$17.5 \pm 2.2$	$11.4\pm0.60$	$12.5\pm0.6$	$996 \pm 15$
$S_3$ , mg kg <sup>-1</sup>	$116\pm5$	$75\pm3.5$	$82\pm1.5$	$6550\pm40$
$S_4$ , ng ml <sup>-1</sup>	$5.1\pm0.24$	$\textbf{3.1} \pm \textbf{0.15}$	$\textbf{35.9} \pm \textbf{2.6}$	$168.1\pm3.6$
S <sub>5</sub> , ng	$120.2\pm6.4$	$95.6\pm6.2$	$469\pm35$	$3841 \pm 117$

For  $S_1$ , two determinations are given, one using the volume of micropipette and one with the mass of CRMs (both gave equivalent reference values).

The best estimations of the efficiency of digestion, given in Table 4, were obtained by computing the average of the ratios of  $S_2$ NRLs values to the S<sub>2</sub> reference values and then dividing by the ratio of S1 NRLs values to the S1 reference values, with outliers and stragglers being discarded using the Grubbs' test (ISO 5725, 1994) for the largest and smallest ratios. The division by the ratio of S<sub>1</sub> values allowed the subtraction of participants' calibration errors from the estimation of the efficiency of digestion. In the estimation of the efficiency of digestion, it was not possible to deconvolute the contributions of digestion and of potential matrix effect. However Karanasiou et al., 2005, showed that only for As and V a significant matrix effect might take place. The efficiency of digestion was found to be in agreement with figures already reported in literature (Robache et al., 2000a) i.e., close to 100% for all elements except for As whose analysis might have suffered from matrix effect as previously mentioned. The efficiency of digestion was set to 100% for the estimation of S2 reference values while a contribution corresponding to the estimated digestion efficiencies was added to the uncertainty of S<sub>2</sub>.

The other factors contributing to the uncertainty of S<sub>2</sub> were the uncertainty of each NIST-certified mass ratio, the uncertainty of weighing the NIST 1648, the uncertainty of the flask volume and the uncertainty of the traces of heavy metals in the reagents and labware. The reference values of S<sub>2</sub> and their expanded uncertainty are given in Table 3. Before sending the test samples to participants, the reference values of S<sub>2</sub> were confirmed by voltammetric analysis for Zn, Cd, Pb and Cu. The relative bias between analytical values and calculated values were less than 1.5%, except for Cd where this was 6%, a value still well within the uncertainty of the voltammetric method (Buzica et al., 2006).

For S<sub>3</sub>, cleaned PFA vials were dried with zero air and stored for several days in the balance room at 20 °C and 50% relative humidity before being weighed. This was necessary to reach the equilibrium of water vapour exchange between ambient air and the walls of the vials that in turn allowed precise and accurate weighing. About 10 mg of the NIST 1648 was placed in the vial, which was then immediately closed with a lid and weighed. A check was made that the balance came back to its initial value when removing the filled vial to be sure that no dust had fallen on the pan of the balance. Before dispatching the S<sub>3</sub> samples, each vial was sealed with Parafilm (M-Parafilm, American National Can, USA) for which no As, Cd,

#### Table 4

Mean ratios and standard deviations of NRLs results out of reference values for S1, S2 and S<sub>3</sub>. The quoted values correspond to the standard deviations of the ratios.

Samples, elements	As	Cd	Ni	Pb
S <sub>1</sub> ratio	$1.04\pm0.08$	$1.05\pm0.11$	$1.01\pm0.07$	$1.00\pm0.06$
S <sub>2</sub> ratio	$1.17\pm0.13$	$1.04\pm0.10$	$0.99\pm0.09$	$1.00\pm0.05$
S <sub>2</sub> ratio/S <sub>1</sub> ratio	$1.12\pm0.06$	$0.99\pm0.03$	$0.98\pm0.07$	$0.99 \pm 0.04$
S <sub>3</sub> ratio	$1.03 \pm 0.13$	$0.99\pm0.09$	$0.95 \pm 0.10$	$\textbf{0.96} \pm \textbf{0.11}$
S <sub>3</sub> ratio/S <sub>2</sub> ratio	$0.92 \pm 0.10$	$0.96\pm0.09$	$0.93 \pm 0.10$	$\textbf{0.98} \pm \textbf{0.06}$
S <sub>5</sub> ratio/S <sub>4</sub> ratio	$1.00 \pm 0.68$	$\textbf{0.98} \pm \textbf{0.07}$	$1.04\pm0.26$	$1.03 \pm 0.09$

Ni and Pb contamination could be evidenced by ICP-MS analysis. All participants received a procedure describing how to transfer the whole sample into the digestion cell of their microwave oven (Gerboles and Buzica, 2008, page 14).

For S<sub>3</sub>, the mass of heavy metals determined by each participant was divided by the mass of NIST 1648 dust in each vial previously weighed by IRC at the time of preparation. This allowed the NISTcertified mass ratios to be used for the S<sub>3</sub> reference values (see Table 3). As before, it was verified by analysis that the traces of heavy metals in the PFA vial were small enough to be neglected. Before sending the S<sub>3</sub> samples to the participants, the recovery of 6 of the samples was determined by voltammetric analysis. The differences between the voltammetric analysis and the NISTcertified values were small enough (around 5%) and well within the uncertainty of voltammetry, apart for Cd which was around 20%. Nevertheless, considering the preparation method for S<sub>3</sub>, it was unlikely that a negative bias would have occurred only for Cd and not for Zn, Pb and Cu. The high deviation of Cd was therefore neglected for purpose of further calculation and it will be discussed later in the data treatment.

#### 2.5. $PM_{10}$ air filters (S<sub>4</sub> and S<sub>5</sub>)

Seventeen low volume samplers (LVSs, Derenda 3.1 samplers – G) operated according to EN 12341 were used to prepare sets of 17  $PM_{10}$  filters. All the LVSs sampling inlets were cleaned and greased before sampling. The flow of the LVSs was adjusted to have less than 2% of deviation by comparison to a certified gas counter (Ritter – G, certificate with a Deutscher Kalibrierdienst DKD stamp) in the laboratory before sampling. The relative humidity, pressure and temperature sensors were also checked in the laboratory. Before each field test, the flow of all LVS was again checked using an adjusted flow meter (Rota – USA, model L 63/2400 – 14 952).

The sampling site was placed in Milan (Italy), at an urban background monitoring station operated by the "Agenzia Regionale per la Protezione dell'Ambiente della Lombardia" (ARPA Lombardia – I) inside the Politecnico University of Milan, in winter, during a highly polluted period. The monitoring station was located in a park. The traffic around the site was generally moderate with an increase in the late afternoon until the evening.

All filters were conditioned for at least 48 h in the balance room at 20 °C and 50% relative humidity as required in EN 12341. The filters were weighed on two consecutive days to check that their mass remained stable as mentioned in EN 14907 (2005b). If stability was not reached over these 48 h, the conditioning was continued. Most of the filters were Whatman QMA quartz 47 mm, chosen for their low blank level of heavy metals (Robache et al., 2000b). NRL 14 asked for specific filters made of ester of cellulose: 47 mm PALL GN-4 Metricel Membrane filters (Pall Corporation – USA, porosity 0.8  $\mu$ m) that generally resulted in 5% lower PM<sub>10</sub> mass concentration compared to the rest of filters (Gerboles and Buzica, 2008). After sampling, all filters were stored in Petri dishes. They were later conditioned again in the balance room before weighing. For this part of the test, a set of blank filters was also prepared by the JRC.

 $S_4$  consisted of a solution prepared by digestion of an exposed filter. After digestion with 8 ml HNO<sub>3</sub> and 2 ml H<sub>2</sub>O<sub>2</sub>, the solution was transferred to a 25 ml PFA-volumetric flask and diluted with ultra pure water.  $S_5$  was composed of one blank filter and one exposed filter that had to be digested and analysed by the participants according to their standard operating procedure.

Since no certified values were available for S<sub>4</sub> and S<sub>5</sub>, assigned values were computed based on the participant results following the algorithm given in annex C of ISO 13528 (2005). The assigned values and their robust standard deviation s<sup>\*</sup> were derived by an iterative calculation in which outliers were discarded and both

these figures were repeatedly recalculated with the modified data, until the process converged. Then, the standard uncertainties  $u_X$  of the assigned values were calculated using equation (1) where p is the number of laboratories. The assigned values of S<sub>4</sub> and S<sub>5</sub> and their uncertainties are given in Table 3.

$$u_X = 1.25 \, s^* / \sqrt{p} \tag{1}$$

The lack of homogeneity in the simultaneously sampled PM<sub>10</sub> filters could have been a major contributor to the uncertainty of the S<sub>4</sub> and S<sub>5</sub> test samples. For this reason, special care was paid to the cleaning of the LVS's inlet, to the initial calibration of relative humidity, temperature and pressure sensors and to the calibration of flow before each sampling period. Moreover, several sets of filters were prepared and weighed to determine the variability caused by the sampling method. Fig. 1 shows the relative standard deviations (RSDs) versus mass concentration collected on the PM<sub>10</sub> Whatman Quartz QMA filters. It includes the RSDs of the S<sub>4</sub> and S<sub>5</sub> sets of test filters at 120 and 55  $\mu$ g m<sup>-3</sup> of PM<sub>10</sub>, respectively. Voltammetric analyses of Cd, Cu, Ni and Pb on the 17 Whatman QMA filters with 40  $\mu g~m^{-3}$  of  $PM_{10}$  were performed. This showed no significant difference between the variability of the elemental content and the one of PM<sub>10</sub> mass concentrations, which therefore may be used as a surrogate for the sampling variability of heavy metals in PM<sub>10</sub>. Moreover, within the set of 17 filters, the filters with high mass concentrations of  $PM_{10}$  were not associated with high heavy metal concentrations ( $R^2$  of 0.028, 0.2173, 0.065 and 0.0201 for Cd, Pb, Ni and Cu respectively). Consequently, the sampling variability could not simply be eliminated by normalizing the S<sub>4</sub> and  $S_5$  reference values with respect to the corresponding  $PM_{10}$ mass concentration of each filter.

#### 2.6. Data treatment

The *z*'-score method (ISO 13528, 2005) was used to demonstrate the capacity of NRLs to comply with the DQO of the European Directives. The normalized deviation ( $E_n$ ) method (ISO Guide 43-1, 2001) was used to check whether the difference between the NRL values and the assigned/reference values remained within the uncertainties given. The  $E_n$  values were only calculated for laboratories that reported their uncertainties of measurement. The repeatability and reproducibility of the method of analysis were determined according to ISO 5725-2 (1994). For each laboratory the within-day repeatability and between-day reproducibility were evaluated using the same ISO standard.



**Fig. 1.** Trend of relative standard deviation of mass concentration of  $PM_{10}$  against the mass concentration of  $PM_{10}$  sampled on Whatman QMA quartz filters with 14–17 Low Volume Samplers Derenda LVS 3.3.

z'-scores were calculated using equation (2) where x represents NRLs' result, X is the reference/assigned value,  $\sigma_p$  is the "fitness-forpurpose-based standard deviation for proficiency assessment" and  $u_x$  is the combined uncertainty of the reference/assigned value. The z'-score evaluation allows the following criteria to be used for the assessment of the results:  $|z'| \leq 2$  are designated satisfactory,  $2 < |z'| \leq 3$  are designated questionable and |z'| > 3 are designated unsatisfactory.

$$z' = x - X / \sqrt{\sigma_p^2 + u_X^2}$$
<sup>(2)</sup>

The relative fitness-for-purpose-based standard deviation,  $\sigma_{p,r}$ , was estimated according to equation (3) using the DQOs (25% for Pb and 40% for As, Cd and Ni), the estimated contributions of sampling  $(u_{s,r})$ , digestion  $(u_{e,r})$  and interference/matrix effects  $(u_{m,r})$ .

Since S<sub>3</sub> and S<sub>5</sub> had to be analysed and digested by each participant,  $\sigma_{p,r}$  was estimated by only subtracting  $u_{s,r}$  (4.7%) from the DQO.  $u_{s,r}$  was estimated using the repeatability of the 17 LVS (RSD: 4%), the interval of tolerance of the flow calibration of the LVS (2%) and the uncertainty of the balance used to weigh the filters (1%). All these contributions were added in quadrature. The basis for relying on the mass scatter to estimate the heavy metal sampling errors is that both parameters should be highly correlated since heavy metals on filters are not expected to undergo volatilisation when stored at ambient temperature before analysis.

For S<sub>2</sub> and S<sub>4</sub>,  $\sigma_{p,r}$  was estimated by subtracting the relative standard uncertainty of digestion  $u_{e,r}$  from  $\sigma_{p,r}$  for S<sub>3</sub> and S<sub>5</sub>.  $u_{e,r}$  was estimated by computing the average of the ratios of S<sub>3</sub> NRLs values to S<sub>3</sub> reference values divided by the ratio of S<sub>2</sub> NRLs values to S<sub>2</sub> reference values for all participants, and after discarding outliers (Table 4).

Finally, for S<sub>1</sub>,  $\sigma_{p,r}$  was estimated by subtracting the relative standard uncertainty due to matrix effects ( $u_{m,r}$ ) from  $\sigma_{p,r}$  for S<sub>2</sub> and S<sub>4</sub>.  $u_{m,r}$  was estimated by computing the average of the ratios of participant values from the reference value for S<sub>2</sub> divided by the same ratio for S<sub>1</sub> (see Table 4). As already mentioned, the JRC-determined efficiency of digestion of S<sub>2</sub> and the matrix effect could not be deconvoluted. Overestimating  $u_{m,r}$  as a result of overestimating the efficiency of digestion might have decreased  $\sigma_{p,r}$  thus slightly increasing  $E_n$  values resulting in a more stringent  $E_n$  test. However, the figures given in Table 4 are close to 1 except for As, the only element expected to have suffered from a matrix effect (Karanasiou et al., 2005). All  $\sigma_{p,r}$  values for all test samples are given in Table 5.

For S5 and S3: 
$$\sigma_{p,r} = \left(DQO^2/4 - u_{s,r}^2\right)^{\frac{1}{2}}$$
  
For S4 and S2:  $\sigma_{p,r} = \left(DQO^2/4 - u_{s,r}^2 - u_{e,r}^2\right)^{\frac{1}{2}}$   
For S1:  $\sigma_{p,r} = \left(DQO^2/4 - u_{s,r}^2 - u_{e,r}^2 - u_{m,r}^2\right)^{\frac{1}{2}}$  (3)

Normalised deviations,  $E_n$ , were calculated using equation (4) where *x* is a participant value with claimed expanded uncertainty  $U_x$  (given in Table 6) while *X* is the reference/assigned value with expanded uncertainty  $U_X$  (given in Table 3).  $|E_n|$  numbers smaller than 1 indicate that the difference between NRLs value and reference or assigned values are within the assigned uncertainties.

$$E_n = x - X / \sqrt{U_x^2 + U_X^2} \tag{4}$$

The repeatability (r) and reproducibility (R) of the method of analysis and the within-day/between-days variability were

#### Table 5

Relative fitness-for-purpose-based standard deviation  $\sigma_{p,r}$  used in the calculation of z'-scores for S<sub>1</sub> to S<sub>5</sub> calculated using the relative standard uncertainty of sampling  $(u_{s,r})$ , digestion  $(u_{e,r})$  and interference/matrix effect  $(u_{m,r})$ .

	DQO	u <sub>s,r</sub>	$\sigma_{\rm p,r}$ for S_5,S_3	u <sub>e,r</sub>	$\sigma_{\rm p,r}$ for S4,S2	u <sub>m,r</sub>	$\sigma_{\rm p,r}$ for S <sub>1</sub>
As	40%	4.7%	19.4%	12.9%	14.6%	12.9%	6.7%
Cd	40%	4.7%	19.4%	9.9%	16.7%	2.9%	16.5%
Ni	40%	4.7%	19.4%	12.3%	15.1%	6.9%	13.4%
Pb	25%	4.7%	11.6%	6.7%	9.5%	3.8%	8.6%

determined according to ISO 5725 (1994). They were calculated using equations (5) and (6), respectively, where p is the number of participants after discarding outliers (see Gerboles and Buzica, 2008),  $s_i$  is the standard deviation of the 6 measurements of each participant for each test sample,  $y_m$  is the mean of the 6 measurements of each participant, m is the reference value of each test sample and n is the number of repeated measurements.

$$r = 2.8\sqrt{\frac{\sum_{p} s_i^2}{p}}$$
(5)

$$R = 2.8 \sqrt{\frac{1}{p-1} \sum_{p} (y_m - m)^2 + \frac{n-1}{n} \frac{\sum_{p} s_i^2}{p}}$$
(6)

#### 3. Results and discussions

#### 3.1. Data quality objective of the European directives

The *z*'-scores for As, Cd, Ni and Pb are given in Fig. 2a. *z*'-scores are evidenced by the colour and direction of the horizontal triangles while the background colour indicates the analytical method used by each participant. The participants showed the following pattern of results: satisfactory *z*'-scores for all test samples and elements for NRL 4, 5, 9 and 14; satisfactory *z*'-scores with all test samples except for As and partly for Cd with the liquid CRM (S<sub>1</sub>) and already-digested dust CRM (S<sub>2</sub>) for NRL 3; satisfactory *z*'-scores with the liquid CRM and dust CRMs (S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>) and questionable or unsatisfactory *z*'-scores for As and Pb with the filter test samples digested by the participants (S<sub>5</sub>) for NRL 1 and 12; questionable or unsatisfactory *z*'-scores for As and on occasion for Cd in S<sub>5</sub> for NRL 0; mainly satisfactory *z*'-scores except for As, Ni and Pb in S<sub>5</sub> for NRL 11; high *z*'-scores values for Cd with S<sub>4</sub> and S<sub>5</sub> for NRL 15.

Regarding the DQO for  $S_5$ , nearly 85% of z'-scores were satisfactory for Cd and Ni while this figure decreased to 64 and 73% for As and Pb, respectively. In fact, 22 and 20% of z'-scores were found to be unsatisfactory for As and Pb and strong outliers were observed. Some participants explained that they encountered difficulties with the digestion of sample S<sub>5</sub>. An explosion occurred in the microwave vessel during the digestion of sample S<sub>5</sub> for NRL1 and NRL12, leading to spilling of liquids and incomplete digestion. Nevertheless, both participants analysed the remaining solution, which gave lower results than the assigned value (one third of the assigned value for As, two thirds for Cd and Ni and half to two thirds for Pb). One of the explosions was explained by the lack of temperature control in the digestion vessel. For the other explosion, the temperature or power of the microwave digestion program specified in EN 14902 was questioned by the NRL as being more extreme than necessary. Satisfactory results were also obtained using other digestion methods: e.g., Soxhlet extraction (NRL 5) and high pressure methods (NRL 8).

Table 6	
Relative expanded uncertainties $(U_{x,r})$ claimed by the NRLs for As, Cd, Ni and Pb.	

As	S1	S2	S3	S4	S5	Cd	S1	S2	S3	S4	S5
NRL 1	4.9%	4.9%	4.9%	4.9%	4.9%	NRL 1	5.9%	5.9%	5.9%	5.9%	5.9%
NRL 3	10.3%	10.3%	10.3%	10.3%	10.3%	NRL 3	9.2%	9.2%	9.2%	9.2%	9.2%
NRL 4	10.3%	8.1%	15.7%	7.7%	14.4%	NRL 4	7.9%	6.3%	14.6%	7.2%	14.4%
NRL 6		18.3%	14.1%	52.0%	15.5%	NRL 6		9.7%	14.0%	15.6%	6.9%
NRL 7	20.0%	20.0%	20.0%	20.0%	20.0%	NRL 7	20.0%	20.0%	20.0%	20.0%	20.0%
NRL 8	18.1%	18.1%	18.1%	18.1%	18.1%	NRL 8	5.4%	5.4%	5.4%	5.4%	5.4%
NRL 9	16.0%	16.1%	16.6%	16.0%	16.0%	NRL 9	16.0%	16.2%	16.6%	16.0%	16.0%
NRL 11	20.4%	20.4%	20.4%	20.4%	20.4%	NRL 11	24.8%	25.0%	25.0%	25.0%	25.0%
NRL 12	20.0%	20.0%	30.0%	20.0%	30.0%	NRL 12	20.0%	20.0%	30.0%	20.0%	30.0%
NRL 14	15.9%		10.2%	26.2%	31.2%	NRL 14	11.2%		4.7%	14.8%	7.9%
NRL 15	11.0%	6.1%	6.4%	17.5%		NRL 15	8.5%	8.5%	7.4%	23.8%	31.8%
Ni	S1	S2	S3	S4	S5	Pb	S1	S2	S3	S4	S5
NRL 1	9.1%	9.1%	9.1%	9.1%	9.1%	NRL 1	7.3%	7.3%	7.3%	7.3%	7.3%
NRL 3	9.5%	9.5%	9.5%	9.5%	9.5%	NRL 3	7.7%	7.7%	7.7%	7.7%	7.7%
NRL 4	7.0%	6.5%	14.2%	6.4%	12.1%	NRL 4	6.8%	6.0%	11.7%	6.1%	11.7%
NRL 6		21.3%	15.1%	25.6%	20.9%	NRL 6		7.6%	7.1%	6.5%	8.3%
NRL 7	46.0%	46.0%	46.0%	46.0%	46.0%	NRL 7	6.0%	6.0%	6.0%	6.0%	6.0%
NRL 8	11.9%	11.9%	11.9%	11.9%	11.9%	NRL 8	5.0%	5.0%	5.0%	5.0%	5.0%
NRL 9	18.0%	17.9%	18.4%	18.0%	18.0%	NRL 9	18.0%	18.1%	18.0%	18.0%	18.0%
NRL 11	10.4%	10.4%	15.8%	10.4%	30.4%	NRL 11	7.2%	7.2%	7.2%	7.2%	7.2%
NRL 12	25.0%	25.0%	30.0%	25.0%	30.0%	NRL 12	20.0%	20.0%	30.0%	20.0%	30.0%
NRL 14	4.6%		5.4%	4.8%	6.6%	NRL 14	5.1%		5.1%	2.4%	5.2%
NRL 15	8.2%	14.9%	11.4%	12.8%	21.7%	NRL 15	7.9%	1.7%	1.8%	5.4%	7.3%

NRL 1 and 8 reported their uncertainty once the results were distributed. The uncertainty of NRL 15 for S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> are given for information only as the laboratory knew the reference values before analysis.

NRL 3 showed high z'-score values for Cd and As in S<sub>1</sub> and S<sub>2</sub>. These discrepancies were produced by the difference in acidity between the laboratory's internal calibration standards and the S<sub>1</sub> and S<sub>2</sub> test samples, a fact demonstrated by NRL 3 with further laboratory experiments.

To explain the differences between their results and the reference values, NRL 7 pointed out that the acidity of the  $S_1$ ,  $S_2$  and  $S_4$ samples that were prepared by JRC and by their laboratory procedure were different. The presence of HF in sample  $S_2$ , thus modifying the sample matrix, was raised as a potential source of interference. Moreover, the 10 mg of dust used to prepare the  $S_3$ samples (when compared to the 100 mg recommendations of NIST) was also questioned on grounds of yielding a non-homogenous sample. As the majority of participants returned correct values for sample  $S_3$ , it is doubtful that there was a lack of homogeneity in the 10 mg of NIST 1648 that NRL7 received. This was also confirmed by other studies (Robache et al., 2000a). NRL7 did not subtract any laboratory blank from  $S_1$  and  $S_2$  because its analytical system automatically subtracted a calibration blank from the test samples.

NRL10 reported a mistake on the dilution factor used to compute their results that should have been the double of what was reported. They would have obtained satisfactory z'-scores by using the correct dilution factor.

NRL11 reported very high values for Ni and Pb on  $S_5$  that were associated with high blank values for these elements. The absence of several analysis of blank filters did not allow determining the real cause and relationship between the high filter and blank values of NRL11. NRL11 was the only laboratories presenting such high blank values which are given in Gerboles and Buzica, 2008.

#### 3.2. Uncertainty reported by participant

In general, participants claimed uncertainties (see Table 6) that were consistent with the DQOs: about 10% for Pb (while the DQO was 25%) and between 15 and 20% for As, Cd and Ni (DQO of 40%) even though the uncertainty induced by sampling was not considered in this IE. However the claimed uncertainties were highly scattered with the highest value being 7 times higher than the smallest one for  $S_5$ . More than half of the participants who

reported their measurement uncertainty did not make a specific evaluation according to the type of test sample.

The  $E_n$  values for As, Cd, Ni and Pb are given in Fig. 2b.  $E_n$  values are evidenced by the colour and direction of the horizontal triangles while the background colour indicates the digestion method used by each participant. About 75% of the  $E_n$  numbers ranged between -1 and 1 showing that the estimation of uncertainty of measurements was consistent with the differences between the participant results and the reference values of the test samples.

The pattern of satisfactory and unsatisfactory  $E_n$  was consistent with the one observed for the *z*'-score. Differences between the  $E_n$ and the *z*'-score patterns occurred when participants underestimated their uncertainty, for example for NRL 7, 8 and 14. The NRLs showed the following results: nearly all satisfactory  $E_n$  values for NRL 4 and 9; questionable or unsatisfactory  $E_n$  values for NRL 1 and 12 especially on the filter that the laboratory had to digest (S<sub>5</sub>); unsatisfactory  $E_n$  values for NRL 3 only for As and Cd with the liquid CRM (S<sub>1</sub>) and already-digested CRM (S<sub>2</sub>); unsatisfactory  $E_n$  values for NRL11 mainly for As, Ni and Pb with filter test sample S<sub>5</sub>; unsatisfactory results for NRL 15 only for Cd with the filters test samples (S<sub>4</sub> and S<sub>5</sub>).

#### 3.3. Repeatability and reproducibility

If all the results were taken into account high reproducibility values would have been estimated: up to 100% for Pb, up to 200% for As and Cd and up to 600% for Ni. However, these values were influenced by the outliers already described for the *z*'-score and  $E_n$  values data treatment. These had to be discarded to correctly estimate repeatability and reproducibility by applying the outlier tests detailed in ISO 5725-2. Fig. 3 gives repeatability and reproducibility values for the measurement method after discarding these outliers. Repeatability remained between 5 and 10% except for the analysis of As on S<sub>4</sub> and S<sub>5</sub> which gave values between 10 and 20%. On average for all test samples, the repeatability of As was higher (11.1 ± 8.6%) than the one of Cd and Ni (6.3 ± 3.8% and 6.2 ± 3.7%, respectively) and the one of Pb (4.7 ± 2.2%). The repeatability for S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> was about 6% (6.5 ± 3.0%, 5.1 ± 1.6% and 5.6 ± 2.1%, respectively) while it increased to 8.1 ± 4.6% for S<sub>4</sub> and to



**Fig. 2.** a) *z'*-scores of all participants (NRLs) for all elements (As, Cd, Ni and Pb in all test samples). The size and direction of the triangles indicate the *z'*-score value. The background colour gives the analytical method. b) En numbers of all participants (NRLs) for the same elements and test samples. The size and direction of the triangles indicate the En numbers. The background colour gives the digestion method of all participants. For S<sub>4</sub> and S<sub>5</sub>, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter.

 $10.2 \pm 6.7\%$  for S<sub>5</sub>. On average, the reproducibility of As, Cd and Ni were 43, 35 and 48% respectively while it decreased to 24% for Pb. Reproducibility increased with the type of test samples as the difficulty to digest and analyse these samples also increased: 23% for  $S_1$ , 34% for  $S_2$ , 38% for  $S_3$ , 43% for  $S_4$  and 53% for  $S_5$ . On average, the reproducibility of the method of measurements is higher than its repeatability, demonstrating the presence of significant differences between participant results. The ratios of reproducibility to repeatability were 3.3 for S<sub>1</sub>, 6.5 for S<sub>2</sub>, 7.1 for S<sub>3</sub>, 5.4 for S<sub>4</sub> and 6.3 for S<sub>5</sub>. Looking at individual elements, the analogous ratio was 4.2 for As, 5.5 for Cd and 5.1 for Pb and up to 8 for Ni. These large figures evidenced the presence of significant differences between the results of the participants. These differences could not just be explained by the use of the different methods of measurements in the IE. In fact, if only the results of the ICP-MS method are taken into account, only slightly smaller repeatabilities, reproducibilites and ratios of reproducibility/repeatability would be obtained.

#### 3.4. Within-day and between-day variability

Fig. 4 gives the mean within-day and between-day variations of all participants for the  $S_1$  and  $S_5$  test samples for As, Cd, Ni and Pb.

They were calculated using the results of the analyses carried out on three different days using three different calibrations. The within-day variability was calculated using equation (5) and the between-day variability was calculated using equation (6) without discarding outliers.

The within-day variability depended first on the element and second on the type of test sample while the between-day variation depended on the element but was found to be independent of the sample type. Contrary to expectation, the within-day variability was higher for  $S_1$  (7.2  $\pm$  1.4%) than for  $S_5$  (3.9  $\pm$  1.0%) while the between-day variability was similar for S<sub>1</sub> (12.7  $\pm$  10.2%) and S<sub>5</sub>  $(14.3 \pm 11.2\%)$  though higher than the within-day variability. As for repeatability, the within-day variation decreased in the order: 9.6  $\pm$  2.5% for As, 6.0  $\pm$  1.3% for Cd, 4.0  $\pm$  1.3% for Ni and 2.9  $\pm$  1.0% for Pb. The same decreasing pattern occurred for the between-day variability when compared to the within-day variability: 19.4  $\pm$  14.9% for As, 12.8  $\pm$  8.9% for Cd, 13.0  $\pm$  8.6% for Ni and  $8.8 \pm 6.6\%$  for Pb. Although not significant, NRL 4 had higher within-day variation, NRL 7, 12 and 16 had higher between-day variations while the NRL14 between-day variations was slightly lower than the rest of participants. The ratio of between-day to within-day variability was much lower for  $S_1$  (2.0  $\pm$  1.6%) than for



Fig. 3. Relative repeatability (r) and reproducibility (R) for As, Cd, Ni and Pb for each test samples.

 $S_5$  (7.0  $\pm$  4.5%). Looking at individual elements in  $S_1$  and  $S_5$ , the ratio of between-day to within-day variability was lower for As (2.5  $\pm$  1.9%) and Cd (2.2  $\pm$  1.6%) as compared to Ni (6.2  $\pm$  2.1%) and Pb (7.2  $\pm$  3.8%). The high ratios found for Ni and Pb came from the low within-day variability, with substantial between-day variability in the analysis of these elements. The between-day variability of the participants should be better controlled for the analysis of Ni and Pb on filters.

#### 3.5. Main sources of uncertainty and analytical deviations

The mean of the absolute deviations between participant values and reference values were 8.5% for  $S_1$ , 10.5% for  $S_2$ , 9.7% for  $S_3$ , 25.8% for  $S_4$  and 58.9% for  $S_5$ . These figures characterise the scatter of participant results, which clearly increased with the complexity of the digestion and analysis of samples. The lowest deviation was found for sample  $S_1$ , thus suggesting that calibration may not be the main analytical difficulty. The element with the highest bias was As, with 8.5% of relative deviation to the reference value for  $S_1$ . One can also notice in the first row of Table 4 that the mean ratio of participant values out the reference values for  $S_1$  was not significantly different from 1 showing the lack of influence of the calibration on the quality of measurements.

The deviations that were observed for the digested NIST dust CRM (10.5% for  $S_2$ ) were similar to the ones of the same dust CRM that participants had to digest (9.7% for  $S_3$ ). This shows that the digestion of the dust CRM for As, Cd, Ni and Pb did not add further analytical difficulty. Again, this observation is confirmed in Table 4 since the mean ratios of participant values out the reference values for  $S_3/S_2$  were not significantly different from 1.

Both deviations of  $S_4$  and  $S_5$  were much higher than for the other test samples. The filter test samples were more difficult to analyse than the liquid or dust test samples most likely because of the necessary digestion ( $S_5$ ), possible matrix effects ( $S_4$  and  $S_5$ ) and low content of heavy metals in  $S_4$  and  $S_5$  as compared to  $S_3$ . Moreover, the digestion of the filter test sample ( $S_5$ ) by the NRLs resulted in an



Fig. 4. Mean relative within-day and between-day variation of all participants for As, Cd, Ni and Pb in S1 and S5 samples.

increase of the scattering of participant results compared to the already-digested filter test sample ( $S_4$ ). This showed that if the same digestion (here performed by JRC on  $S_4$ ) was carried out on a set of identical filters then the participant results improved. In fact the main source of analytical deviation came from the digestion of the filter test sample ( $S_5$ ) for As.

One may perform a direct comparison of the methods of analvsis of participants by looking at the background colour of Fig. 2a. It can be noted that for EDXRF (NRL 0), the DQO of As could not be met with this technique since its z'-score exceeded 3. Voltammetry was found inappropriate for Cd, as this method experienced a strong interference for this element. In fact, after standard addition of Cd in sample S5, the electrochemical potential of Cd in acetate buffer was at -0.620 V while before the standard addition, the voltammogram of  $S_5$  gave a peak at -0.590 V. This difference of potential was likely caused by a mixture of Cd and another interfering element or compound. By observing the peak value at the two potentials, one could estimate that an increase of measured Cd by a factor two to three was caused by the interference. Tl, having an electrochemical potential of -0.445 V is known to interfere with the determination of Pb (potential of -0.470 V) and Cd (Metrohm,  $n^{\circ}$ . 231/2 e). Initially, it was thought that Tl interfered with Pb and disturbed the determination of the small Cd peak next to Pb. However, by comparing the voltammogram of S<sub>5</sub> with and without addition of Tl, it became evident that the peak of Cd would disappear in presence of Tl. Morever no Tl could be observed on the EDXRF spectra of S<sub>5</sub>. It is thought instead that an unknown organic substance that was still present after digestion strongly interfered with the voltammetric determination of Cd. This point is supported by the correct values that NRL 15 gave for S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> (Gerboles and Buzica, 2008). The results of NRL15 for S1, S2 and S3 are not reported here because NRL15 knew their reference values before reporting its results. In addition, NRL15 did not report As results for sample S<sub>5</sub> as voltammetry repeatedly needed a time consuming regeneration procedure for the As electrode.

Good results were observed using ICP-OES for Cd, Ni and Pb. A few discrepancies were observed for GFAAS and ICP-MS. They were associated with the explosions in the digestion vessel, wrong dilution factors being used, contamination, analytical interference and acidity problems, as mentioned before.

The bias between ICP-MS and references values were compared to the bias between GFAAS and reference values for As, Cd, Ni and Pb in S<sub>1</sub>, S<sub>2</sub> and S<sub>4</sub> after discarding outliers. S<sub>3</sub> and S<sub>5</sub> were not selected since the digestions of participants could have influenced the conclusions. Applying a Student's *t*-test at the 0.01 error level, the t'values showed that no significant bias between ICP-MS and GFAAS could be evidenced. At the 0.05 error level, 2 out of 3 biases for Ni and 1 out of 3 biases for Pb in S<sub>1</sub> were found to be significant. It is unlikely that the Ni and Pb stragglers came from an effect of the measurement method because no significant biases were observed for S<sub>2</sub> and S<sub>4</sub>. Since the same decreasing pattern occurred for Ni and Pb over the three days of S<sub>1</sub> analysis, it is more likely that the between-day variation on S<sub>1</sub> analysis was responsible for these stragglers.

#### 3.6. Preparation of test samples for intercomparison exercises

Several techniques can be used to prepare test samples for heavy metals: using certified liquid solutions or certified dust samples, the preparation of loaded filters with a multiport sampler or with a set of low volume samplers, or by cutting punches from the filter of a high volume sampler.

The preparation of test samples using certified liquid solutions and certified dust (CRMs) was carried out in previous exercises. However, the results of the current intercomparison exercise showed that participants found little difficulty in analysing such types of test samples. On the contrary, the highest discrepancies were associated with the filter test samples digested by participants due to a more complex matrix and lower concentrations than in CRMs. Following this observation, it is doubtful that CRM test samples are sufficient to correctly assess the quality of heavy metal analysis, although they are clearly necessary for estimating the recovery rates.

The preparation of large sets of test samples using a multiport sampler or cutting punches from a large filter of a high volume sampler have not been yet implemented for the preparation of test samples for the analysis of heavy metals in PM<sub>10</sub> in ambient air. The homogeneity of the test samples prepared with multiport samplers (i.e. Sputnik or the model Speciation 2300 of Ruppercht and Patashnick) must first be decreased to lower values than the current reported ones (about 10% in the case of Sputnik sampler). In the case of the high volume sampler, the lack of homogeneity of the punches cut from the whole surface of filter may also decrease the homogeneity of the test sample (Pöykiö et al., 2003).

Conversely, the simultaneous preparation of a set of loaded filters with low volume samplers gave satisfactory results in this intercomparison exercises. The homogeneity of the test samples expressed as a relative standard deviation started at 6% for  $PM_{10}$  lower than 20 µg m<sup>-3</sup> and decreased to about 2% for  $PM_{10}$  higher than 50 µg m<sup>-3</sup>. However, a substantial quality control effort was required for the low volume samplers and filters in order to obtain such a good homogeneity.

#### 4. Conclusions

Keeping in mind that only a snapshot of the quality of measurements can be drawn from an intercomparison exercise with limited test samples, extrapolating its results to general rules may be questionable. Nevertheless, this exercise showed generally good results from participants. The Data Quality Objectives (DQO) of the European Directive (25% for Pb and 40% for As, Cd and Ni) were generally met. In general, the uncertainty of measurements was correctly estimated by the majority of participants who declared lower figures than the DQOs of the European Directives. However, some participants did not report any uncertainty.

As expected, the reproducibility of the method of measurements was always higher than its repeatability. Furthermore, for a majority of participants the between-day variability was higher than the within-day variability of measurements. These two observations suggest that it should still be possible to improve the quality of measurements by improving the internal quality control procedures. Arsenic appeared to be the most difficult element to determine whatever the type of sample and the analytical procedure employed.

The main sources of analytical discrepancies were found to be the digestion of filters and the matrix effect between calibration standards and digested filters for As. Calibration errors only had a limited effect. Generally, ICP-MS and GFAAS methods did not give significant different results. Other methods (ICP-OES for Cd, Ni and Pb, EDXRF for Pb and Ni and Voltammetry for As, Ni and Pb) were found satisfactory even though it was not possible to analyse As, Cd, Ni and Pb altogether with any of them. Apart from microwave digestion, Soxhlet extraction and high pressure methods were shown to produce satisfying results. However, seen the small number of test samples, the conclusions regarding the analytical artefacts attributed to calibration, digestion, matrix effect and method of analysis could be driven from the discarding of outliers, the fact that these effects may have been obfuscated by the between days variability or correlated preventing to accurately distinguish between them. Typical correlation could have been between the efficiency of digestion and the matrix effect, the calibration effect may have been correlated with the chosen measurement methods and with the between-day variability and the estimation of the efficiency of digestion may have been unclear because of calibration effects.

#### Acknowledgements

The authors are grateful to Dr. Vorne Gianella of ARPA Lombardia for the availability of the monitoring station in Milan.

#### References

- Alleman L. and Labaraque G., 2007. Sampling and analysis of metals in particulate matter in ambient air. Laboratoire Central de Surveillance de la Pollution de l'Air, report ½, Convention: 000653, http://www.lcsqa.org.
- AQUILA, Network of National References Air Quality Laboratories, http://ies.jrc.ec. europa.eu/aquila-homepage.html.
- AREMA Lille Métropole, Air quality network around Lille, Flemish Environmental Agency, University of Antwerp, Measurement campaigns in the Euroregion, 2002 – 2004, Study realised with the help of the European program, INTERREG III. http://www.vliz.be/imisdocs/publications/132899.pdf.
- American Society for Testing and Materials, 1998. Inductively Coupled Plasma-Mass Spectrometry. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959, USA.
- Buzica, D., Gerboles, M., Borowiak, A., Trincherini, P., Passarella, R., Pedroni, V., 2006. Comparison of voltammetry and inductively coupled plasma-mass spectrometry for the determination of heavy metals in PM<sub>10</sub> airborne particulate matter. Atmospheric Environment 40, 4703–4710.
- Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Official Journal L 23, 26/01/2005. http:// eur-lex.europa.eu.
- Directive 2008/50/EC of the European Parliament and the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European Union L 152/1 of 11.6.2008. http://eur-lex.europa.eu.
- European Standard, 1998. Air quality determination of the PM<sub>10</sub> fraction of suspended particulate matter reference method and field test procedure to demonstrate reference equivalence of measurement methods. EN 12341. Brussels, Belgium. http://www.CEN.eu.
- European Standard, 2005a. Ambient air quality standard method for the measurement of Pb, Cd, As and Ni in the PM<sub>10</sub> fraction of suspended particulate matter. EN 14902. Brussels, Belgium. http://www.CEN.eu.
- European Standard, 2005b. Ambient air quality standard gravimetric measurement method for the determination of the PM2,5 mass fraction of suspended particulate matter – reference method and field test procedure to demonstrate reference equivalence of measurement methods. EN 14907. Brussels, Belgium. http://www.CEN.eu.
- Gerboles, M., Buzica, D., 2008. Intercomparison Exercise for Heavy Metals in PM10. EUR 23219 EN. Office for Official Publications of the European Communities, Luxembourg. DOI:10.2788.63349. http://publications.europa.eu/.
- International Standards, 1994. Accuracy (trueness and precision) of measurement methods and results – Part 2: basic method for the determination of repeatability and reproducibility of a standard measurement method. ISO 5725-2, Geneva, Switzerland. http://www.iso.org.

- International Standards, Guide 98-3:2008. Uncertainty of measurement Part 3: guide to the expression of uncertainty in measurement (GUM:1995). Geneva, Switzerland. http://www.iso.org.
- International Standards, 2001. Gas analysis determination of the composition of calibration gas mixtures comparison methods. ISO 6143 Geneva, Switzerland. http://www.iso.org.
- International Standards, 2005. Statistical methods for use in proficiency testing by interlaboratory comparisons. ISO 13528, Geneva, Switzerland. http://www.iso.org. Kampa, M., Castanas, E., 2008. Human health effects of air pollution. Environmental
- Pollution 151, 362–367.
   Karanasiou, A.A., Thomaidis, N.S., Eleftheriadis, K., Siskos, P.A., 2005. Comparative study of pre-treatment methods for the determination of metals in atmospheric aerosol by electrothermal atomic absorption spectrometry. Talanta 65, 1196–1202
- Metrohm, No. 231/2 e, Application Bulletin, Voltammetric determination of zinc, cadmium, lead, copper, thallium, nickel, and cobalt in water samples according to DIN 38406 Part 16, http://products.metrohm.com/
- Mickel, D., 2002. Air Toxics Pilot Study Laboratory Intercomparison Quality Assurance Report. Environmental Protection Agency. EPA-454/R-02–004.
- Motallebi, N., Taylor Jr., C.A., Turkiewicz, K., Croes, B.E., 2003. Particulate matter in California – intercomparison of several PM<sub>2.5</sub>, PM<sub>10-2.5</sub> and PM<sub>10</sub> monitoring networks. Journal of the Air and Waste Management Association 53 (12), 1509–1516.
- Muller, K., Spindler, G., Maenhaut, W., Hitzenberger, R., Wieprecht, W., Baltensperger, U., ten Brink, H., 2004. INTERCOMP 2000, a campaign to assess the comparability of methods use in Europe for measuring aerosol composition. Atmospheric Environment 38, 6459–6466.
- Pöykiö, R., Perämäki, P., Rönkkömäki, H., 2003. The homogeneity of heavy metal deposition on glass fibre filters collected using a high-volume sampler in the vicinity of an opencast chrome mine complex at Kemi: Northern Finland. Analytical and Bioanalytical Chemistry 375, 476–481.
- Putaud, J.-P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchinic, M.-C., Decesari, S., Fuzzi, S., Gehrig, R., Huglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Muller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Torseth, K., Wiedensohler, A., 2004. A European aerosol phenomenology—2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. Atmospheric Environment 38, 2579–2595.
- Robache, A., Mathé, F., Galloo, J.C., Guillermo, R., 2000a. Multi-element analysis by inductively coupled plasma optical emission spectrometry of airborne particulate matter collected with a low-pressure cascade impactor. Analyst 125, 1855–1859.
- Robache, A., Mathé, F., Galloo, J.C., Herbin, M., Malet, B., 2000b. Conditions de Prélèvements des Particules en Vue de l'analyse des Métaux. Ecole des mines de Douai, Département Chimie et Environnement. http://www.lcsqa.org/system/ files/Etude3\_0.pdf.
- Schlesinger, R.B., Kunzli, N., Hidy, G.M., Gotschi, T., Jerrett, M., 2006. The health relevance of ambient particulate matter characteristics:coherence of toxicological and epidemiologicaliInferences. Inhalation Toxicology 18 (2), 95–125.
- Stacey, P., 2006. The performance of laboratories analysing heavy metals in the workplace analysis scheme for proficiency (WASP). The Annals of Occupational Hygiene 50, 417–425.
- Tylee B., Renli M.A., Butler O., 2003. Metals in ambient air: a new sample type for the WASP QA scheme", in Proceedings of the International Conference in Prague, 21-23 May 2003, QA/QC in the Field of Emission and Air Quality Measurements, Office for Official Publications of the European Communities, Luxembourg, EUR 20973 EN, pp. 88–96, ISBN 92-894-6523-9. http:// publications.europa.eu/
- Uggerud H.T., Hjellbrekke A.G., 2005 and 2006. Analytical intercomparison of heavy metals in precipitation. EMEP/CCC-Report 4/2007, O-7729, August 2008, NILU, Norway.