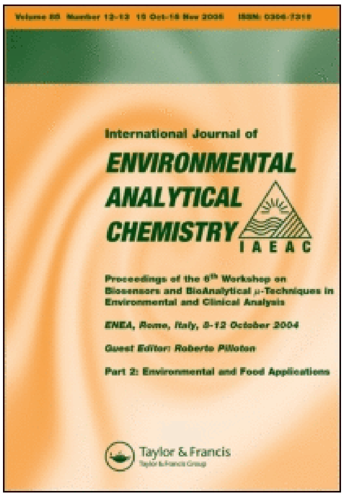

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Practical methodology for the solubility speciation analysis of ambient dust deposits for heavy metals: application to a 6-month measurement campaign

Richard J. C. Brown[a]; Mandy C. Shaw[a]; Matthew R. Roberts[a]
[a] Analytical Science Group, National Physical Laboratory, Teddington TW11 0LW, UK

To cite this Article Brown, Richard J. C. , Shaw, Mandy C. and Roberts, Matthew R.(2006) 'Practical methodology for the solubility speciation analysis of ambient dust deposits for heavy metals: application to a 6-month measurement campaign', International Journal of Environmental Analytical Chemistry, 86: 6, 453 — 460

To link to this Article: DOI: 10.1080/03067310500291627

URL: http://dx.doi.org/10.1080/03067310500291627

Intern. J. Environ. Anal. Chem.
Vol. 86, No. 6, 15 May 2006, 453–460

Taylor & Francis
Taylor & Francis Group

Practical methodology for the solubility speciation analysis of ambient dust deposits for heavy metals: application to a 6-month measurement campaign

RICHARD J. C. BROWN*, MANDY C. SHAW† and MATTHEW R. ROBERTS†

Analytical Science Group, National Physical Laboratory, Teddington TW11 0LW, UK

(*Received 24 May 2005; in final form 26 July 2005*)

A robust and accurate method for the quantitative determination of the water-soluble and water-insoluble, Ni, Cd, Pb and Zn contents of deposited ambient dust is presented. The extraction of the soluble metal phase from deposited ambient dust has been validated using commercially available ambient dust certified reference material. Results from a 6 month measurement campaign, from July to December 2004, are presented. Quantitative analysis of the two fractions, of different aqueous solubility (referred to here as 'solubility speciation analysis'), within deposited ambient dust is reported for the first time. Additionally, the two Bergerhoff dust deposit gauges used in parallel to acquire the dust deposit samples have shown good inter-sampler comparability. The measured total deposition fluxes compare well with those previously reported in urban and semi-rural locations around the UK.

Keywords: Deposition; Heavy metals; Speciation; Solubility; Bergerhoff gauge

1. Introduction

The environment and the general public are exposed to deposited ambient dust containing various classes of hazardous compounds. Important classes of compounds found in ambient air and deposited dust are those containing 'heavy metals' [1], which are considered to be toxic to biological systems and are ubiquitous in the atmosphere. These heavy metals are released through domestic, industrial, and anthropogenic sources [2–4]. Their concentrations in ambient air and deposited dust have been limited by European legislation under the Fourth Air Quality Daughter Directive [5]. Accurate and comparable ambient air measurements of these compounds are therefore increasingly important [6], and standard measurement techniques for metals in ambient air and dust deposits are currently under development by the European Commission for Standardisation (CEN) [7, 8].

---

*Corresponding author. Fax: +44-20-8614 0423. Email: richard.brown@npl.co.uk
†Present address: School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.

International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310500291627

Deposition is the principle pathway for these heavy metals to enter terrestrial and aquatic systems and hence food chains [9, 10], making analysis of their concentration in dust deposits of particular importance [11–13]. It has been determined [14] that ingestion via food and water is the primary source of intake of these metals and their compounds for humans, and they can contribute to cancer of the skin and lung, cardiovascular diseases, and kidney damage. Furthermore, it is recognized that the bio-availability, and therefore the toxicity, of a metal is dependent on its chemical form [15]. Consequently, the development of measurement strategies and analytical techniques for the determination of the various types of compound containing heavy metals in environmental samples is currently of great importance [16–18].

'Solubility speciation analysis' is used here to classify pollutants with regard to their solubility in various solvents. Arguably the most important classification of this type, with respect to toxicity and likelihood of entering aquatic and terrestrial biosystems, for ambient dust deposits, is solubility in water [19, 20]. It is assumed that heavy metal-containing compounds that are soluble in water will be more likely to enter food chains and therefore be of a greater hazard to human health than heavy-metal-containing water-insoluble compounds. The water-soluble fraction may then be considered to have a greater 'toxicity weighting' in ambient dust than the water-insoluble fraction. Future legislation is likely to require speciation analysis of pollutants as a more refined method of gauging the impact on human health, and the environment, of ambient dust and particulate matter.

This article describes a simple, quantitative, robust and fully validated methodology for the measurement of the water-soluble, and water-insoluble, deposition fluxes of nickel, cadmium, lead and zinc in ambient air. The methodology has been field-tested over a 6 month period from July to December 2004, with monthly deposition samples being collected using two Bergerhoff gauges operating in parallel at the National Physical Laboratory, Teddington, UK. Similar approaches have been used to investigate the chemical speciation of ambient air particulates [21], usually for Ni [22–24], but also for other metals [25, 26] and, indirectly, for the measurement of heavy metals in 'road-runoff' [27]. Few studies exist on the solubilization of trace metals in ambient aerosols [19, 20, 28–30], and such a procedure has not been described previously in the literature for deposited dust samples. The presentation of validation data for the development of the measurement methodology, and the application of the technique in the field, increase the importance of this study.

2. Experimental

2.1 *Sampling*

Ambient dust deposit samples were collected over monthly periods, from July to December 2004. Two Bergerhoff gauges (with polythene sampling bottles) were used, sampling in parallel, and placed approximately 1.0 m apart. Sampling was in accordance with VDI 2119 [31]. The samplers were located on the western boundary of the National Physical Laboratory's site, next to Bushy Park, in Teddington, south-west London, UK. The polythene sampling bottles were cleaned thoroughly before use with 2% nitric acid solution (Aldrich) followed by thorough rinsing with deionized water (18 MΩ cm, MilliQ, Millipore).

2.2 *Analysis*

At the end of the sampling period, the polythene sampling bottles were collected, any large foreign bodies (such as leaves, insects, etc.) removed, and sealed until analysis. If, after sampling, the bottles were completely dry, a little deionized water (18 MΩ cm, MilliQ, Millipore) was added to the bottles before sealing in order to assist in the dissolution and suspension of the dust deposit.

Following sampling, the deposited dust material in the polythene sampling bottles was subjected to hot water extraction with sonication (see section 2.3). The water-soluble portion was analysed using stripping voltammetry; the water-insoluble portion was analysed using ICP-MS. The water-soluble fraction was further split into two portions; one for the analysis of Cd, Pb, and Zn by anodic stripping voltammetry, and one for the analysis of Ni by adsorptive cathodic stripping voltammetry. All chemicals were used as purchased (Aldrich), and deionized water was used at all times (18 MΩ cm, MilliQ, Millipore).

For Cd, Pb, Zn: ammonium acetate buffer (aqueous solution of 0.5 M sodium acetate and 1.5 M KCl, 1 mL) was added to the water-soluble fraction (10 mL), and analysis was performed using differential pulse anodic stripping at a hanging mercury drop electrode (HMDE) (Metrohm Computrace 757VA). Calibration was performed by addition of a standard solution containing mass fractions of 10.02×10^{-6} Pb, 1.05×10^{-6} Cd and 15.05×10^{-6} Zn.

For Ni: ammonium chloride buffer (aqueous solution of 1 M NH_4Cl and 1 M NH_4OH, 1 mL) and a complexing agent (aqueous solution of 0.1 M dimethylglyoxime sodium salt solution, 1 mL) was added to the water-soluble fraction (10 mL). Calibration was performed by addition of a standard solution of Ni mass fraction 1.16×10^{-6}.

The insoluble fraction was measured using a previously described, fully validated technique for the measurement of particulate phase heavy metals on ambient air filters [32]. Briefly, the water-insoluble portion, and the filter paper on which it had been collected, was added to 70% HNO_3 (8 mL) and 30% H_2O_2 (2 mL) and digested in a Mars X Microwave System (CEM Microwave Technology Ltd). After cooling, all samples were diluted to a minimum of 50 mL with deionized water. Analysis was then performed using an Elan DRC II ICP-MS facility (PerkinElmer SCIEX, UK). Calibration was achieved by the working curve method using multi-element calibration standards.

Both analysis methods were described by complete measurement equations and fully GUM-compliant uncertainty statements [33].

2.3 *Extraction and method validation*

Water was the solvent used to discriminate the different dust deposit fractions. Although solutions of lower pH could be used in order to mimic the conditions found in the lungs and the stomach, solubility in deionized water was considered to be a better starting-point in assessing the potential for toxic compounds to enter food chains, via aquatic systems and through uptake by terrestrial flora and fauna [34]. It was necessary, therefore, to determine the most effective extraction conditions to recover the maximum amount of all water-soluble material, without unduly complicating the measurement methodology. The test material used was an urban dust-certified reference material (NIST SRM 1648) whose matrix is representative of deposited ambient dust. Extraction methodologies involving combinations of either hot or cold water, with or without sonication of the sample, were employed. A minimum of six replicates was performed for each extraction condition. The different extraction protocols are outlined below:

- Cold-water extraction: deionized water (40 g, 20°C) was added to the CRM (25 mg) in a clean polythene sampling bottle. The mixture was agitated (15 min) then filtered (reduced pressure). A further aliquot of deionized water (40 g, 20°C) was added to the sampling bottle. The mixture was agitated (15 min) and filtered (reduced pressure) again.
- Hot-water extraction: as for 'Cold water extraction', except that hot water (90°C) was used.
- Cold-water extraction with sonication: as for 'Cold water extraction', except that agitation was performed using a sonic bath.
- Hot-water extraction with sonication: as for 'Hot water extraction', except that agitation was performed using a sonic bath.

The extraction procedures resulted in two separate phases of the sample being obtained—the soluble fraction in the filtrate and the insoluble fraction as a solid residue on the filter paper. No significant change in pH of the water used was observed before and (in the soluble fraction) after extraction. The soluble fraction was then analysed using stripping voltammetry (see section 2.2). The results are shown in figure 1. The quoted measurement uncertainties are dominated by the repeatability of the extraction procedure. As can be seen from figure 1, the use of hot water with sonication extracted the largest percentage of water-soluble material from the NIST SRM 1648. As this technique was the most efficient and was not disproportionately complicated, this methodology was used for the extraction of the field samples. The percentage of water-soluble species in the NIST SRM 1648 measured following the hot water extraction with sonication is not inconsistent with a recent speciation study of elements in NIST SRM 1648 [35].

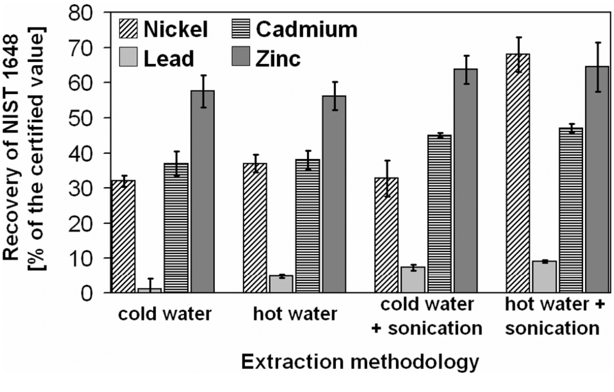

Figure 1. Measured percentage of the certified Ni, Cd, Pd, and Zn content of NIST SRM 1648 extracted into the water-soluble fraction following the application of different extraction methodologies. Measurement uncertainties are quoted at the 95% confidence level.

The residue, after extraction with water, was digested in acid and measured using inductively couple plasma-mass spectrometry (ICP-MS) (see section 2.2) in order to ensure that all the NIST SRM 1648 material had been accounted for, within the uncertainty of the analysis procedure.

3. Results and discussion

The total deposition fluxes (the sum of the water-soluble and water-insoluble phases) measured during the 6 month field measurement campaign are shown in figure 2. The measured values appear to remain relatively constant, within the accuracy of the measurement, over the period of the field measurement campaign with no monthly, or seasonal, trend clearly discernible for any of the analytes. This is, in part, because the relatively large uncertainties associated with the measurements make any trend analysis very difficult. However, the total deposition fluxes measured for these elements are very similar to those previously reported in urban and semi-rural locations around the UK at similar times of year [36, 37].

The results of the solubility speciation analysis of the samples collected during the field measurement campaign are displayed in table 1. The measured proportions of

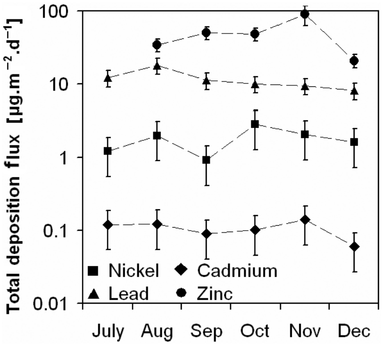

Figure 2. Total deposition fluxes of Ni, Cd, Pb, and Zn measured during the 6 month field measurement campaign. Measurement uncertainties are quoted at the 95% confidence level.

Table 1. Monthly water-soluble (Sol) and water-insoluble (Insol) deposition fluxes for Cd, Ni, Pb, and Zn, recorded during July–December 2004 in the Teddington area.

	Deposition flux (μg/m^2/day)							
	Cd		Ni		Pb		Zn	
Month (2004)	Sol	Insol	Sol	Insol	Sol	Insol	Sol	Insol
Jul	0.05	0.07	0.35	0.87	8.5	3.7	–	13
Aug	0.05	0.08	0.40	1.60	8.5	9.5	23	12
Sep	0.05	0.04	0.18	0.74	5.4	5.8	34	16
Oct	0.06	0.04	1.54	1.29	7.0	3.1	42	6.6
Nov	0.09	0.05	1.10	0.96	6.1	3.3	84	6.1
Dec	0.02	0.04	0.99	0.62	6.3	1.8	15	5.9

water-soluble to water-insoluble fluxes are very similar to the proportions recorded during method validation with NIST SRM 1648 for Cd, and quite similar for Ni and Zn, in most cases. The proportion of Pb in the deposited dust, that is water-soluble, appears to be much higher than that recorded for the NIST SRM 1648. This represents the first reported data of the solubility speciation analysis of heavy metals in ambient dust deposits in the literature. Such data assist in giving an initial indication of 'toxicity weighting' per amount of heavy metal in deposited dust, owing to the different toxicities of water-soluble heavy-metal-containing compounds (such as sulphates, nitrates, and carbonates), and water-insoluble heavy-metal-containing compounds (such as sulphides, oxides, and elemental metal).

The data shown in figure 2 represent an average of the deposition fluxes recorded from the two Bergerhoff gauges sampling in parallel. However, the measured fluxes from each gauge agreed, within the uncertainty of the measurement, in all cases. To illustrate this, figure 3 compares the soluble deposition fluxes of Ni, Cd, Pb and Zn measured from the two Bergerhoff gauges, sampling in parallel, during the field-measurement campaign. As can be seen, agreement between the values is extremely good. This is the expected result since the Bergerhoff gauges, unlike active ambient air samplers with size-selective heads, should have little possibility of suffering from inter-sampler bias. This is provided, of course, that they are close enough to each other to sample the same environment, without being too close and therefore disturbing each other's sampling characteristics, and that results are not dominated by a small number of large particles.

As shown in figure 2, the uncertainties of these measurements can often be quite large: between 60 and 15% (relative), at the 95% confidence level. The contribution of individual sources to the overall measurement uncertainty is detailed in figure 4. Because the mass fractions being measured are so low, the uncertainty in the blank measurement (here corresponding to the metals content of the deionized water (for the water-soluble fraction) and the filter paper (for the water-insoluble fraction)) has a large contributory factor to the final measurement uncertainty. Low analyte

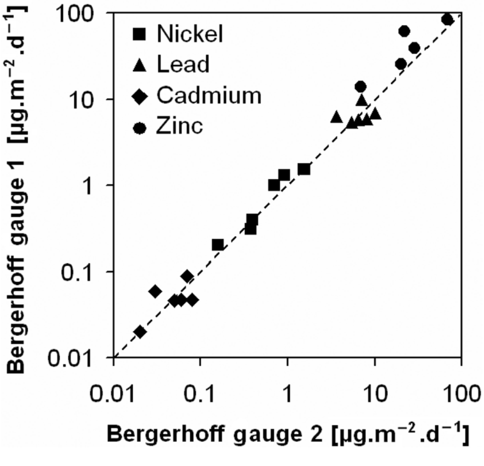

Figure 3. Comparison of the soluble deposition fluxes of Ni, Cd, Pb, and Zn measured from the two Bergerhoff gauges, sampling in parallel, during the field measurement campaign. Measurement uncertainties for the data range between 60 and 15% (relative), at the 95% confidence level.

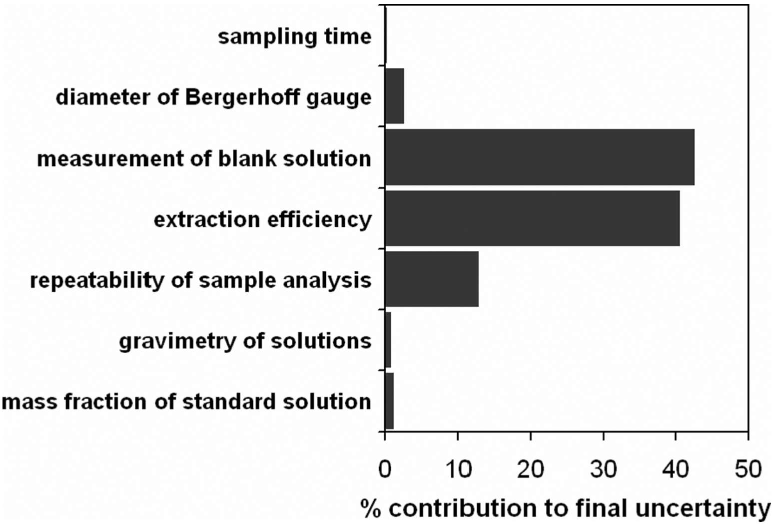

Figure 4. Contribution of individual sources to the overall measurement uncertainty of the solubility speciation analysis of deposited ambient dust samples.

concentrations also mean that the relative repeatability of the analytical measurement is a significant contributing source. The repeatability of the extraction procedure is the other major source of measurement uncertainty.

4. Conclusions

A simple, validated methodology for measuring the heavy metals content of the water-soluble and water-insoluble fractions of deposited ambient dust has been presented for the first time. This has been referred to as 'solubility speciation analysis'.

The aqueous extraction methodology used to separate the two fractions has been validated and optimized in the laboratory using a suitable certified reference material. Analysis of the water-soluble and water-insoluble phases was performed using stripping voltammetry and ICP-MS, respectively.

This methodology has been field-tested during a 6 month measurement campaign that has produced the first reported data for the solubility speciation analysis of Ni, Pb, Cd, and Zn in ambient dust deposits. The total deposition fluxes recorded were consistent with previously reported levels at urban background and rural locations in the UK. The two Bergerhoff gauges, sampling in parallel, showed excellent inter-sampler comparability.

Speciation analysis is being increasingly recognized as a valuable method of determining the actual chemical composition of environmental samples, and therefore a more detailed toxicity analysis. For dust deposits, the most important characteristic affecting the likelihood of their absorption into both aquatic and terrestrial systems is solubility in water. Therefore, solubility speciation analysis, as shown here, is a valuable first step in more robustly determining the actual toxicity of heavy metals in ambient dust deposits.

Acknowledgements

This work was funded by the Department of Trade and Industry's Valid Analytical Measurement Programme. Grateful thanks are proffered to Dr Paul G. Quincey (NPL) for very useful input during the preparation of this manuscript.

References

[1] J.H. Duffus. *Pure Appl. Chem.*, **74**, 793 (2002).

[2] European Commission. *Economic Evaluation of Air Quality Targets for Heavy Metals*, Final report, Entec UK Ltd, January 2001. Available online at http://europa.eu.int/comm/environment/air/ambient.htm (accessed October 2005).

[3] C. Migon, J. Caccia. *Atmos. Environ.*, **24A**, 399 (1990).

[4] G. Le Roux, D. Weiss, A. Cheburkin, N. Rausch, J. Grattan, B. Kober, M. Krachler, W. Shotyk. *J. Phys. IV France*, **107**, 739 (2003).

[5] 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. Available online at: http://europa.eu.int/comm/environment/air/ambient.htm (accessed July 2005).

[6] V. Desauziers. *TrAC*, **23**, 252 (2004).

[7] R.H. Brown. *J. Environ. Monit.*, **4**, 88N (2002).

[8] CEN/TC 264-standard under development. Available online at: www.cenorm.be (accessed July 2005).

[9] S.M. Charlesworth, J.A. Lees. *Sci. Total Environ.*, **235**, 351 (1999).

[10] H.T. Chon, J.S. Ahn, M.C. Jung. *Environ. Geochem. Health*, **20**, 77 (1998).

[11] H-J. Yun, S-M. Yi, Y.P. Kim. *Atmos. Environ.*, **36**, 5449 (2002).

[12] V.N. Smirnioudi, N.S. Thomadis, E.A. Piperaki, P.A. Siskos. *Fresenius Envir. Bull.*, **7**, 85 (1998).

[13] G-C. Fang, Y-S. Wu, C-C. Chu, S-H. Huang, J-Y. Rau. *Toxicol. Ind. Health*, **19**, 25 (2003).

[14] Ambient Air Pollution by As, Cd and Ni compounds, Position paper, Working group on As, Cd and Ni compounds, DG Environment, European Commission (2000).

[15] I.Y.R. Adamson, H. Prieditis, C. Hedgecock, R. Vincent. *Toxicol. Appl. Pharm.*, **166**, 111 (2000).

[16] A. Ruhling. *Environ. Pollut.*, **120**, 23 (2002).

[17] R.A. Sutherland, F.M.G. Tack, A.D. Ziegler, J.O. Bussen. *Appl. Geochem.*, **19**, 947 (2004).

[18] S. Tokalioglu, S. Kartal, G. Birol. *J. Environ. Monitor.*, **5**, 468 (2003).

[19] K.V. Desboeufs, A. Sofikitis, R. Losno, J.L. Colin, P. Ausset. *Chemosphere*, **58**, 195 (2005).

[20] S.C. Hsu, F.J. Lin, W.L. Jeng. *Atmos. Environ.*, **39**, 3989 (2005).

[21] A. Tessier, P.G.C. Campbell, M. Bisson. *Anal. Chem.*, **51**, 844 (1979).

[22] L. Fuchtjohann, N. Jakubowski, D. Gladtke, D. Klockow, J.A.C. Broekart. *J. Environ. Monitor.*, **3**, 681 (2001).

[23] L. Fuchtjohann, N. Jakubowski, D. Gladtke, C. Barnowski, D. Klockow, J.A.C. Broekart. *Fresenius J. Anal. Chem.*, **366**, 142 (2000).

[24] V.J. Zatka, J.S. Warner, D. Maskery. *Environ. Sci. Technol.*, **26**, 138 (1992).

[25] E. Dabek-Zlotorzynska, M. Kelly, H. Chen, C.L. Chakrabarti. *Anal. Chim. Acta*, **498**, 175 (2003).

[26] S. Charlesworth, M. Everett, R. McCarthy, A. Ordonez, E. de Miguel. *Environ. Int.*, **29**, 563 (2003).

[27] M. Backstrom, U. Nilsson, K. Hakansson, B. Allard, S. Karlsson. *Water Air Soil Pollut.*, **147**, 343 (2003).

[28] L.J. Spokes, T.D. Jickells. *Geochim. Cosmochim. Acta*, **58**, 3281 (1994).

[29] B. Lim, R. Losno, T.D. Jickells, J.L. Colin. *Global Biogeochem. Cycles*, **8**, 349 (1994).

[30] L. Morselli, P. Olivieri, B. Brusori, F. Passarini. *Environ. Pollut.*, **124**, 457 (2003).

[31] VDI 2119. *Determination of Dust Precipitation with Collecting Pots Made of Glass (Bergerhoff Method) or Plastic*, VDI, Dusseldorf, 1996.

[32] R.J.C. Brown, R.E. Yardley, A.S. Brown, M.J.T. Milton. *J. Anal. Atom. Spec.*, **19**, 703 (2004).

[33] EN(ISO) 13005: 1998. *Guide to the Expression of Uncertainty in Measurement*, 2nd edn, ISO, Geneva (1995).

[34] R. Chester, F.J. Lin, K.J.T. Murphy. *Environ. Tech. Lett.*, **10**, 887 (1989).

[35] F.E. Huggins, G.P. Huffman, J.D. Robertson. *J. Hazard. Mater.*, **74**, 1 (2000).

[36] S.J. Baker. *AEAT Report AEAT/R/ENV/0264, Issue 2* (2001).

[37] N.J. Pattenden, J.R. Branson, E.M.R. Fisher. In *Deposition of Atmospheric Pollutants*, H.W. Georgii, J. Pankrath (Eds), pp. 173–184, UKAEA Culham, UK (1982).