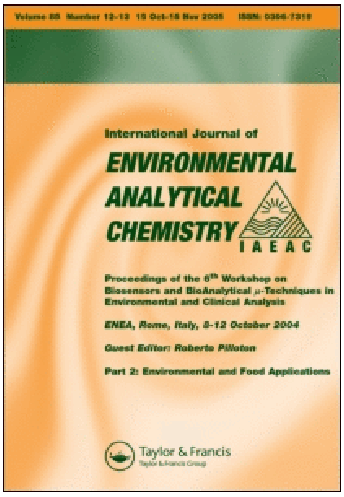

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Comparison Of Analytical Techniques For The Determination Of Trace Elements In Rain Water

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COMPARISON OF ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN RAIN WATER

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Summary—Two methods for the determination of cadmium, copper and lead in EPA reference precipitation sample, corresponding to 1987, 1988, 1989 and 1990 BAPMoN Intercomparison Program, have been compared: graphite furnace atomic absorption spectroscopy (GFAAS) and anodic stripping voltametry (ASV). A relatively good agreement was found between the two techniques and with the reference values. The results for the analysis of Cl and F by spectrophotometry, Ca, Mg, Na, K and Zn by AAS, and Fe, Mn, Cu, Ni, Pb and Cd by GFAAS in the same sample, corresponding to 1988 and 1989, showed good agreement with the stated values. The results of Easter Island rain waters for the years 1990 and 1991 are presented.

KEY WORDS: Trace metals, precipitation, environmental contamination, atomic absorption spectroscopy, voltametry.

INTRODUCTION

Efficient management of environmental pollution requires a reasonable knowledge on the levels, fate and effects of hazardous substances in the different environmental compartments. An important prerequisite in the availability of sufficient data. Their validity and reliability depend strongly on the sensitivity, accuracy and precision of the analytical methods applied in research and control of environmental pollution.

A direct method without any matrix separation or preconcentration is desirable for routine analysis of water for trace elements. The method should be free from interferences over the concentration range of the concomitant species.

The analysis of atmospheric pollutants presents a series of technical difficulties in particular in the determination of trace level elements. This implies an extremely careful handling of laboratory glassware, a good selection of chemicals, and using adequate chemical analysis techniques [1,2]. The most popular instrumental methods for determining trace metals in atmospheric precipitation are the graphite furnace atomic absorption spectroscopy [3-5] and anodic stripping voltametry [6-8].

This work presents the results of the analysis of Mn, Fe, Cd, Cu, Ni and Pb by GFAAS, and Cu, Pb and Cd by ASV in samples of BAPMoN intercomparison rain water from 1987 to 1990. It also shows the flame atomic absorption spectrometry results for Ca, K, Mg, Na and Zn, and the spectrophotometry UV-Vis results for chloride and fluoride in the same samples. Besides, a complete analysis of Easter Island rain waters is presented for the years 1990 and 1991.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer Model 2380 atomic absorption spectrometer with flame and flameless (graphite furnace Model HGA-400 and automatic sample Model AS-40) was used for most determinations. A Priceton Applied Research (PAR) Model 174 A Polarographic Analyzer with mercury drop electrode Model 303 was used for the determination of Cd, Cu and Pb. A Perkin-Elmer Model 551 spectrophotometer was used for the determination of chloride and fluoride.

Reagents

High-purity water supplied from the reagent-grade ion-exchange unit Milli-Q was used. All chemicals used on GFAAS and ASV were of certified suprapure grade (Merck): concentrated nitric acid, hydrochloric acid, potassium chloride. For the preparation of standards, stock solutions (1000mg ml^{-1}) prepared from Merck Titrisol materials were used. All other chemicals used were of analytical reagent-grade.

Glassware cleaning and sample preparation

All glassware was immerse in 10% nitric acid and left overnight (or better during the weekend). Afterwards, the glassware was rinsed 10 times with Milli-Q demineralized water and dried into an oven previously to use.

The reference precipitation sample furnished by EPA was prepared according to the instruction to obtain the simulate pollutant concentration found in rain water. The sample preparation procedure was as follows: An aliquot of 10 ml of sample was diluted to the mark into a 500-ml flask with Milli-Q demineralized water and thoroughly mixed. The resulting solution was treated in the same manner as a sample of natural rain water.

A 100-ml portion of Easter Island rain water sample was filtered through a 0.45-μm membrane filter. Then, it was acidified to 0.2% with nitric acid suprapur. The samples were sent from Easter Island by the Chilean Meteorological Direction.

Table 1 Atomic absorption spectrometry instrumental conditions for determination of Na, Ca, K, Mg, and Zn.

	Na	*K*	*Ca*	*Mg*	*Zn*
Lamp	HCL	HCL	HCL	HCL	HCL
Lamp int (mA)	12	12	10	15	15
Wavelength (nm)	589.0	766.5	422.7	285.2	213.9
Slit (nm)	0.2	0.7	0.7	0.7	0.7

PROCEDURES

Atomic absorption spectrometry determination

The elements Na, Ca, K, Mg and Zn were measured in three replicates by atomic absorption spectrometry with an air-acetylene flame. For Na, Ca, K, and Mg determination, a solution of 0.2% Cs and 1% La was previously added to the measuring aliquot. Slight ionization occurs in the air-acetylene flame and can be corrected by the addition of an alkali salt to samples and standards. The instrumented conditions for each element are given in Tables 1–3.

Anodic stripping voltametry determination

An aliquot of the solution (usually 0.5 or 1.0 ml) was placed in a polarographic cell containing 5 or 10 ml of potassium chloride. The heavy metals were preconcentrated simultaneously at the HMDE by deposition as amalgams. This was achieved by adjusting the deposition potential to -1.0 V for 2 min and stirring the solution with a magnetic stirrer to enhance mass transfer to the HMDE. After turning off the stirrer, and a rest period of 30 s, anodic stripping was performed in the differential pulse mode (DPASV) with the following parameters: pulse height, 50 mV; pulse duration, 56 ms; time, 0.5 s; and scan rate, 5 mVs^{-1}. The measurement is repeated once before adding small volumes (20-100 ul) of standard solution.

Spectrophotometric determination

Chloride An aliquot of sample ($\leq$ 20 ml) containing $\leq$ 40 μg of chloride was transferred into a 25-ml standard flask and diluted to 20 ml with demineralized water. Later, 2 ml of 0.25 M ammonium ferric sulfate and 2.5 ml of saturated solution mercuric thiocyanate were added. The mixture was homogenized each time, diluted to the mark with demineralized water and shaken well. The absorbance at 455 nm in a 5-cm cell against a reagent blank, after 15 min, was measured.

Table 2 Graphite-furnace temperature analytical programme for the determination of Cd, Cu, Fe, Mn, Ni and Pb.

Cadmium *step*	*1*	*2*	*3*	*4*	*5*
Temp. (°C)	120	400	2000	2600	50
Ramp (sec.)	20	10	3	1	3
Hold (sec.)	10	10	6	4	3
Read			3		
Internal Ar (ml/min)			40		
Copper *step*	*1*	*2*	*3*	*4*	*5*
Temp. (°C)	120	900	2250	2700	50
Ramp (sec.)	15	15	0	1	10
Hold (sec.)	20	20	5	5	10
Read			ON		
Internal Ar (ml/min)			40		
Iron *step*	*1*	*2*	*3*	*4*	*5*
Temp. (°C)	120	1000	2200	2700	50
Ramp (sec.)	20	20	0	1	10
Hold (sec.)	15	20	5	5	10
Read			ON		
Internal Ar (ml/min)			40		
Manganese *step*	*1*	*2*	*3*	*4*	*5*
Temp. (°C)	120	750	2100	2700	50
Ramp (sec.)	20	20	0	1	10
Hold (sec.)	20	20	6	5	10
Read			ON		
Internal Ar (ml/min)			40		
Nickel *step*	*1*	*2*	*3*	*4*	*5*
Temp. (°C)	120	750	2500	2700	50
Ramp (sec.)	20	25	0	1	10
Hold (sec.)	10	15	6	5	10
Read			ON		
Internal Ar (ml/min)			40		
Lead *step*	*1*	*2*	*3*	*4*	*5*
Temp. (°C)	120	550	2300	2700	50
Ramp (sec.)	20	20	1	2	10
Hold (sec.)	20	15	6	5	10
Read			ON		
Internal Ar (ml/min)			40		

Table 3 Graphite-furnace Instrumental parameters and reading conditions for the determination of Cd, Cu, Fe, Mn, Ni and Pb.

Instrumental parameters *Element*	*Lamp*	*Wavelength nm*	*Slit nm*	*current lamp*	*D_2 Correc.*
Cadmium	EDL	228.8	0.7	5 w	yes
Copper	HCL	324.5	0.7	15 mA	no
Iron	HCL	248.3	0.2	30 mA	no
Manganese	HCL	279.5	0.2	20 mA	no
Nickel	HCL	232.0	0.2	25 mA	yes
Lead	HCL	283.3	0.7	10 mA	yes

Reading conditions *Elements*	*Read sec.*	*aliq. µl*	*graph. tube*	*sensit. check µg/l*
Cadmium	9	20	Normal	6
Copper	5	30	Normal	32
Iron	5	50	Pirocoated	15
Manganese	6	15	Normal	14
Nickel	6	20	Pirocoated	75
Lead	7	20	Normal	65

Fluoride 20 ml of sample containing < 20 µg of fluoride were placed in a 50-ml standard flask. A drop of phenolphthalein and a few drops of 0.02 M sodium hydroxide were added until a change of colour occurred. The mixture was neutralized by a drop by drop addition of 0.02 N perchloric acid. Then, 25 ml of the chromogenic reagent (for 250 ml:20 ml buffer acetate, 50 ml 0.001 M cerium (III) nitrate, 100 ml acetone, 50 ml 0.001 M alizarin complexone and make up to volume with demineralized water) were added and the absorbance at 617 nm was measured against a blank, in 5.0-cm cells.

RESULTS AND DISCUSSION

The mean values found for the EPA reference precipitation samples are given in Table 4. These samples correspond to the BAPMoN Intercomparison Program of the years 1987, 1988, 1989 and 1990. The results generally showed a close agreement with the stated values for all three elements in the reference materials.

Table 5 displays the regression data and correlation coefficients for the methods comparisons for cadmium, lead and copper. A paired t-test shows no significant differences between the methods.

The comparison of the results for Cd, Pb and Cu by GFAAS and ASV methods is illustrated in Figure 1. Despite a few apparent "fliers", there is, in general, a good agreement between the methods with little bias. The accuracy is further confirmed by the results for the EPA certified samples.

Table 4 Comparison of the results for Cd, Pb and Cu by GFAAS and ASV methods (mg/l).

1987			*4585*			*5705*
Elem	*GFAAS*	*ASV*	*true value*	*GFAA*	*ASV*	*true value*
Cd	0.031 ± 0.004	0.026 ± 0.004	0.032	0.075 ± 0.022	0.071 ± 0.002	0.073
Pb	0.121 ± 0.032	0.100 ± 0.018	0.120	0.278 ± 0.018	0.282 ± 0.028	0.274
Cu	0.053 ± 0.012	0.038 ± 0.004	0.048	0.162 ± 0.008	0.162 ± 0.028	0.149

1988			*4190*			*5539*
Elem	*GFAAS*	*ASV*	*true value*	*GFAAS*	*ASV*	*true value*
Cd	0.023 ± 0.002	0.030 ± 0.002	0.034	0.015 ± 0.002	0.023 ± 0.002	0.019
Pb	0.124 ± 0.014	0.109 ± 0.026	0.110	0.059 ± 0.004	0.061 ± 0.028	0.054
Cu	0.072 ± 0.004	0.072 ± 0.008	0.070	0.032 ± 0.002	0.039 ± 0.006	0.029

1989			*4080*			*5813*
Elem	*GFAAS*	*ASV*	*true value*	*GFAAS*	*ASV*	*true value*
Cd	0.061 ± 0.002	0.030 ± 0.006	0.038	0.015 ± 0.008	–	0.018
Pb	0.123 ± 0.010	0.123 ± 0.021	0.111	0.057 ± 0.001	–	0.060
Cu	0.078 ± 0.010	0.092 ± 0.010	0.076	0.043 ± 0.008	–	0.040

1990			*4110*			*5784*
Elem	*GFAAS*	*ASV*	*true value*	*GFAAS*	*ASV*	*true value*
Cd	0.029 ± 0.004	0.031 ± 0.002	0.031	0.017 ± 0.002	0.017 ± 0.002	0.016
Pb	0.097 ± 0.004	0.112 ± 0.022	0.093	0.054 ± 0.004	0.053 ± 0.006	0.051
Cu	0.073 ± 0.016	0.150 ± 0.030	0.063	0.032 ± 0.002	0.053 ± 0.006	0.029

Table 5 Regression data for method comparison

Element	*degrees of freedom*	*t-test*	*slope*	*intercept*	*correl. coeff.*
cadmium	7	0.001	0.849	0.006	0.98
lead	7	0.042	1.006	-0.003	0.99
copper	7	0.232	0.93	0.007	0.97

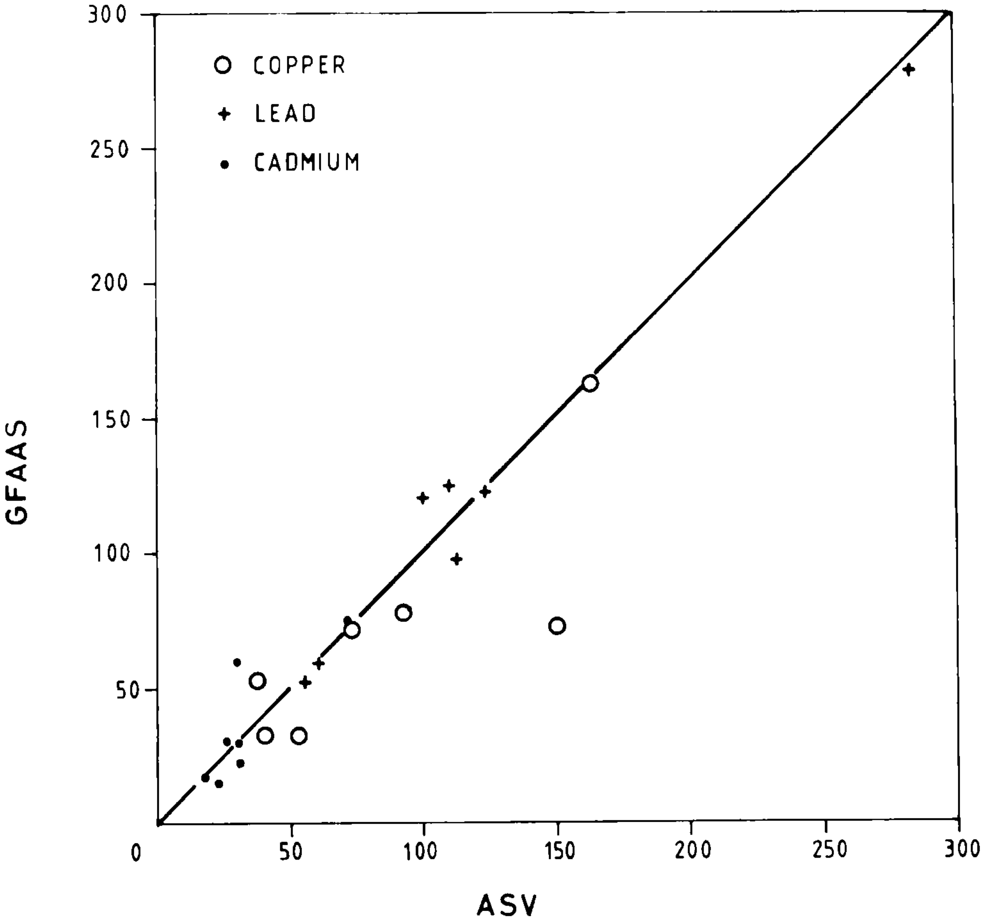

Figure 1 Comparison of methods

Table 6 compiles the GFAAS results obtained for Mn, Fe, Cd, Cu, Ni and Pb, the flame atomic absorption spectrometry results for Ca, K, Mg, Na and Zn, and the spectrophotometry UV-Vis results for chloride and fluoride, in EPA reference precipitation samples corresponding to the BAPMoN Intercomparison Program of the years 1988 and 1989.

In general, a relatively good agreement was found between the laboratory results and true value when the three named techniques were used. However, contamination during the analytical determination could be present despite of the extremely careful handling of laboratory glassware, and the good selection of chemicals. Excluding these obvious cases, a good agreement can be seen. The GFAAS values were also probably affected by the blank.

The results of the analysis of Easter Island rain water corresponding to different months of the years 1990 and 1991 are summarized in Table 7. The same techniques used for the analysis of EPA reference precipitation samples (Table 6) were used in the determination of all elements.

Table 6 Results of EPA reference precipitation sample corresponding to BAPMoN Intercomparation Program of the years 1988 and 1989 (mg/l) (Ca, Mg, Na, K and Zn by flame-AAS. Fe, Mn, Cu, Ni, Pb and Cd by GFAAS and Cl and F by Spec. UV-vis).

1988

	1044		*2426*		*3812*	
Elem	*lab. value*	*true value*	*lab. value*	*true value*	*lab. value*	*true value*
Cl	0.271 ± 0.002	0.280	2.749 ± 0.162	2.738	1.270 ± 0.028	1.254
F	0.037 ± 0.002	0.051	0.476 ± 0.050	0.474	0.162 ± 0.068	0.167
Ca	0.049 ± 0.014	0.047	0.356 ± 0.022	0.388	0.054 ± 0.002	0.038
Mg	0.021 ± 0.003	0.021	0.063 ± 0.002	0.063	0.043 ± 0.002	0.042
Na	0.195 ± 0.002	0.186	1.744 ± 0.114	1.771	0.399 ± 0.028	0.393
K	0.076 ± 0.002	0.084	0.752 ± 0.006	0.798	0.076 ± 0.001	0.078

	4190		*5539*	
Elem	*lab. value*	*true value*	*lab. value*	*true value*
Fe	0.085 ± 0.007	0.082	0.053 ± 0.003	0.049
Mn	0.033 ± 0.002	0.034	0.017 ± 0.001	0.019
Cu	0.072 ± 0.006	0.070	0.032 ± 0.003	0.029
Ni	0.023 ± 0.002	0.022	0.015 ± 0.001	0.014
Pb	0.124 ± 0.014	0.110	0.059 ± 0.004	0.054
Cd	0.023 ± 0.002	0.034	0.015 ± 0.001	0.019
Zn	0.581 ± 0.060	0.610	0.140 ± 0.014	0.142

1989

	1105		*2435*		*3718*	
Elem	*lab. value*	*true value*	*lab. value*	*true value*	*lab. value*	*true value*
Cl	0.284 ± 0.040	0.295	0.334 ± 0.015	0.358	0.249 ± 0.008	0.232
F	0.034 ± 0.010	0.038	0.082 ± 0.005	0.086	0.177 ± 0.005	0.197
Ca	0.048 ± 0.004	0.045	0.053 ± 0.006	0.044	0.113 ± 0.012	0.125
Mg	0.032 ± 0.004	0.033	0.018 ± 0.003	0.016	0.076 ± 0.007	0.075
Na	0.186 ± 0.014	0.166	0.249 ± 0.006	0.228	1.285 ± 0.004	1.219
K	0.075 ± 0.005	0.064	0.078 ± 0.006	0.070	0.534 ± 0.026	0.508

	4080		*5813*	
lab. Elem	*lab. value*	*true value*	*lab. value*	*true value*
Fe	0.085 ± 0.015	0.088	0.057 ± 0.001	0.054
Mn	0.040 ± 0.004	0.041	0.021 ± 0.001	0.020
Cu	0.078 ± 0.010	0.076	0.043 ± 0.008	0.040
Ni	0.024 ± 0.001	0.027	0.014 ± 0.002	0.016
Pb	0.123 ± 0.012	0.111	0.057 ± 0.001	0.060
Cd	0.061 ± 0.002	0.038	0.015 ± 0.008	0.018
Zn	0.708 ± 0.040	0.696	0.236 ± 0.008	0.240

Table 7 Analysis of Easter Island rain water of different month of the years 1990 and 1991.

1990										
Element	*Jan*	*Apr*	*May*	*Jun*	*Jul*	*Aug*	*Sep*	*Oct*	*Nov*	*Dec*
Cl (mg/l)	10.5	12.4	13.4	13.4	4.8	7.6	11.3	24.4	29.8	12.2
F (mg/l)	0.18	0.29	0.29	0.28	0.18	0.18	0.27	0.13	0.22	0.22
Ca (mg/l)	1.90	0.50	1.30	1.30	0.40	0.34	0.39	0.94	1.50	0.70
Mg (mg/l)	0.86	0.74	0.85	0.85	0.35	0.50	0.84	1.61	1.80	0.83
Na (mg/l)	3.1	6.2	7.7	7.7	3.3	4.7	7.4	14.0	17.9	7.4
K (mg/l)	0.49	0.40	0.50	0.50	0.19	0.22	0.42	0.65	1.10	0.41
Fe (μg/l)	3.3	11.2	1.3	1.3	1.0	7.5	4.4	6.8	10.1	13.9
Mn (μg/l)	14.0	16.3	13.7	13.7	<1.0	2.7	35.2	28.5	70.7	27.9
Cu (μg/l)	7.4	2.6	3.3	3.3	2.0	<1.0	<1.0	6.6	5.2	6.0
Ni (μg/l)	<2.0	3.0	1.5	1.5	1.6	<1.0	1.8	<1.0	-	-
Pb (μg/l)	<2.0	<2.0	<2.0	<2.0	<2.0	-	-	-	<2.0	<2.0
Cd (μg/l)	<0.2	0.13	0.33	0.33	0.17	<0.1	0.36	<0.1	0.17	0.11
Zn (mg/l)	4.1	3.0	4.9	4.9	1.8	2.6	3.3	1.3	4.4	4.6

1991								
Elem	*Feb*	*Apr*	*May*	*Jun*	*Aug*	*Sep*	*Oct*	*Nov*
Cl (mg/l)	7.7	3.4	5.2	8.4	5.2	6.7	6.4	7.3
F (mg/l)	0.2	0.2	<0.1	<0.1	0.3	0.2	0.2	<0.1
Ca (mg/l)	0.36	0.18	0.23	0.35	0.30	0.40	0.37	0.52
Mg (mg/l)	0.23	0.25	0.31	0.51	0.33	0.83	0.39	1.10
Na (mg/l)	4.24	2.08	3.08	4.60	3.10	3.70	3.80	4.80
K (mg/l)	0.18	0.23	0.13	0.32	0.09	0.19	0.15	0.17
Fe (μg/l)	<5.0	<5.0	<5.0	<5.0	1.9	3.2	3.2	3.1
Mn (μg/l)	<2.0	<2.0	<2.0	<2.0	1.1	1.1	<1.0	3.5
Cu (μg/l)	2.5	<1.0	<1.0	<1.0	1.7	1.4	0.6	2.0
Ni (μg/l)	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Pb (μg/l)	<2.0	<2.0	<2.0	<2.0	1.4	<1.0	<1.0	<1.0
Cd (μg/l)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn (mg/l)	1.29	1.33	0.32	0.60	3.40	2.00	1.70	3.20

CONCLUSION

Using GFAAS and ASV a number of elements in atmospheric precipitation, at relatively low concentrations, can be determined. For other elements the potential of these techniques is large, because considerable improvements in detection limit can be achieved by decreasing elemental content in the blank. GFAAS and ASV show good precision for the elements investigated. A comparison of the results from ASV and the detection limits for GFAAS indicates that the determination of Cd, Pb and Cu does not require preconcentration.

The results obtained for Cd, Pb and Cu in the reference materials show close agreement with the stated values. The results also demonstrate that there are no significant differences between GFAAS and ASV.

It is possible to conclude that the two methods give accurate results, but all require care during the determination of the elements.

References

1. M. Zief and J. W. Mitchell, *Contamination Control in Trace Element Analysis* (John Wiley & Sons, USA, 1976).
2. L. Mart, *Fresenius Z. Anal. Chem.*, **296**, 350–357 (1979).
3. W. Slavin, D. C. Manning and G. R. Caenrick, *At. Spectrosc.*, **2**, 137–145 (1981).
4. H. Hansson, A. P. Ekholm and H. B. Ross, *Environ. Sci. Technol.*, **22**, 527–531 (1988).
5. G. Bozsal, G. Schlemmer and Z. Grobenski, *Talanta*, **37**, 545–553 (1990).
6. H. W. Nürnberg, *Pure & Appl. Chem.*, **54**, 853–878 (1982).
7. H. W. Nürnberg, P. Valenta, V. D. Nguyen, M. Gödde, and E. Urano de Carvalho, *Fresenius Z. Anal. Chem.*, **317**, 314–323.
8. P. Ostapczuk, P. Valenta, H. Rützel and H. W. Nürnberg *Sci. Tot. Environ.*, **60**, 1–6 (1987).