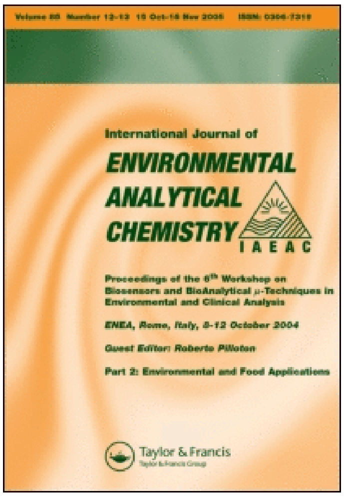

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DETERMINATION OF TRACE ELEMENTS IN RAINWATER BY ICP—AES WITH IONEX PRECONCENTRATION

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Ionex separation and vacuum evaporation were tested as methods of sample pretreatment. Vacuum evaporation enables the detection limit of the whole analysis to be reduced for lead only; for the remaining elements the detection limit is given by background contamination, which could not be eliminated. Ionex separation using Chelex 100 resin was associated with a twentyfold concentration, and in the batch mode in a single polyethylene bottle, the detection limit decreased 10 to 30 times for Cd, Cu and Pb. The effect of contamination remains the limiting factor for Al and Zn, where the decrease in the detection limit of the whole analysis makes half an order of magnitude. The accuracy of the results was tested by comparison analytes and by applying the synthetic sample method.

KEY WORDS : Preconcentration, ICP-AES, rainwater, ionex exchange, heavy metals.

INTRODUCTION

Ecologically important trace metals in rain and snow water are most frequently determined by AAS.[1] This technique features high sensitivity, however, it is time consuming and in cases where a high excess of calcium is present (e.g. in precipitation collected under tree crown in limed forests), suffers from irregular interferences. The aim of the present work was to seek for a procedure of preconcentration of selected metals (Al, Cd, Cu, Mn, Pb, Zn) that would be well suited for ensuring their quantitation by ICP-AES. This method requires analyte preconcentration by a factor of at least one order of magnitude and removal of Ca and alkali metals, whose high excess interferes with the determination in ICP spectrometry,[2] as well as minimization of the background contamination. The overall detection limit is limited not only by the potential of the instrumentation used but - particularly for some metals (e.g. Al, Cd, Zn) - by the variability of the blank (this is even true for the direct ETA-AAS technique).

Preconcentration procedures rely largely on the extraction or ion exchange mechanisms,[3] the latter being used in this work. The preconcentrating effect of chelating ion exchangers depends highly on the analyte species as well as on the competition properties of the other

Table 1 Composition of synthetic sample and recovery from the preconcentration step. The synthetic sample composition was based on data of element contents in rainwater in the Hessen and Boubin regions.[7]

Analyte	*Concentration* [µg/l]	*Found after preconcentration treatment* [µg/l]	*Recovery* [%]
Al	50	50	100
Cd	1	1	100
Cu	25	25	100
Mn	15	13.9	92
Pb	40	36	96
Zn	150	145	97

ions. The fraction of ions chelated by the ion exchanger can be, for instance, reduced by the presence of complexing anions. Fortunately, this is not very significant in the case of rainwater. For a comparison, preconcentration by evaporation,[4] which use to be popular for the determination of low analyte contents, is also studied.

EXPERIMENTAL SECTION

Chemicals and apparatus

A synthetic rainwater sample (Table 1) was made up from standard solutions of the pure metals[4] and other reagent grade chemicals. The resulting pH was 3,45. The samples were prepared and diluted using ultrapure water obtained with a NANOpure apparatus (Barnsted, USA). Nitric acid eluent solution (1 mol/l) was prepared from HNO_3 puriss p.a. (Fluka). Ammonium acetate solution (1 mol/l; pH 6) was prepared from NH_4 OH and CH_3 COOH of reagent grade purity.[5] Chelex-100 type chelating ion exchanger (Bio-Rad, 100-200 mesh, Na^+ - form, 68-76 wt.% moisture content) was purified from metal residues and converted to the H^+ - cycle by washing with 2,5M HNO_3.

All solutions were stored in polyethylene bottles (Plastimat). Prior to use, the glass vessels and polyethylene bottles were cleaned with 6M HCl and 6% H_2 O_2 (1 + 1), hot 20% HNO_3 and deionized water.[6]

The measurements were performed on a PU 7450 ICP-AES (Leeman, USA-Philips, UK) using a procedure reported previously.[4]

Determination by anodic stripping voltametry with an amalgamated graphite electrode was accomplished on a PA-3 instrument (Laboratorní prístroje, Prague). The time of electrolysis was 200 s, and the solution contained 20 ml of rainwater sample, 0.1 ml of 1M CH_3 COOH, 0.1 ml of 1M NaOH and 0.1 ml of 3.8M HNO_3. The polyethylene Emich filter stick equipped with a Nylon screen of 0.09 mm mesh size was manufactured for sucking out the solution. A RVO-64 vacuum rotary evaporator (Labora, Prague) was used for the water evaporation. Actual rainwater samples were taken from the collecting vessel immediately after rain to prevent its contamination from the air.

PROCEDURE

Ionex preconcentration

The whole preconcentration procedure was performed in a single 250 ml polyethylene bottle fitted with a screw cap to prevent sample contamination from the environment. To 200 ml of sample were added Chelex-100 in an amount corresponding to 0.2 g of dry matter and 2.5 ml of ammonium acetate solution. A simple polyethylene proportioning device had been manufactured allowing the wet ionex to be proportioned without weighing. The ammonium buffer converted the ionex from the H^+ form to the NH_4^+ form and adjusted the sample pH to 6, which is the optimum for the sorption of the analytes examined.[7] The amount of the buffer added exceeded six times that given by the manufactured for the ionex saturation. This was made to prevent incomplete saturation of the ion exchanger by ammonium ions, which might result in the liberation of H^+ ions into the solutions associated with an unwanted pH change. The mixture was stirred on a shaking machine or on a magnetic stirrer for a minimum of 1 hour.[7] Thereafter, the solution was sucked out by means of the Emich filter stick and the ion exchanger in the flask was washed by adding 10 ml of ammonium acetate solution (pH 6), which then was sucked out.

The use of a higher amount of the buffer results in a partial elution of the retained metals from the exchanger.[5, 7, 8] For desorption of the metals, 10 ml of 1M HNO_3 were added, the whole was stirred repeatedly and the solution was sucked out with the Emich filter stick and submitted to ICP-AES measurement following the method described earlier.[4]

At least five blanks were prepared for each sample series. Ultrapure water was used in place of the sample and all operations were included in the procedure. Correction for the blank was made by substracting the mean blank value when it exceeded the detection limit.

Table 2 Comparison of the detection limit in ICP-AES analysis without and with the preconcentration step.

Analyte	*Detection limit for whole analysis*				
	Direct analysis	*Ionex preconc.*		*Evaporation*	
	[mg/l]	*[mg/l]*	*gain*	*[mg/l]*	*gain*
Al	0.02	0.005	4×	0.01	2×
Cd	0.003	0.0001	30×	0.0012	2.5×
Cu	0.005	0.0003	17×	0.002	2.5×
Mn	0.001	0.0006	1.7×	0.001	1×
Pb	0.1	0.01	10×	0.01	10×
Zn	0.01	0.002	5×	0.012	0.8×

Preconcentration by evaporation

For a comparison, preconcentration on a rotary vacuum evaporator was investigated at the boiling water bath temperature and water pump vacuum. 200 ml of sample acidified with HNO_3 to a concentration of 0.28 mol/l was reduced in volume to about 5 ml. The residue was transferred into a 10 ml volumetric flask, the evaporator vessel was rinsed, the total volume was adjusted with ultrapure water and submitted to ICP-AES measurement.

RESULTS

Preconcentration recovery

Fifteen aliquots of the synthetic sample were worked up in parallel. The results from the preconcentration treatment were processed statistically and compared with the starting heavy metal contents in the sample to obtain the preconcentration recovery data (Table 1). Ionex separation of manganese proved to be rather difficult, the recovery, however, was satisfactory for trace analysis purposes.

Limit of detection

Authentic rainwater samples with very low heavy metal contents were analyzed in eight replicates by ICP-AES applying the above preconcentration procedures. The results were processed statistically using the IUPAC methodology[9] to obtain the detection limit and its ratio to that of the direct determination[10] (Table 2).

Accuracy testing

Rainwater samples were analyzed by ICP-AES following ionex preconcentration, by anodic stripping voltammetry (Cu, Pb and Cd), and—for samples with high Zn contents—by direct ICP AES.[4] The results and their comparison based on the t-test are given in Table 3. A significant difference was only found for Cd, and this was a consequence of the high precision of the two procedures compared. The relative difference was of 3.5% which is

Table 3 Comparison of results with those of the independent method. The t-test results are given to assess the significance of the differences between the results.[5]

	ICP with ionex separation			*Independent method*			
Analyte	*x*	*s*	*n*	*x*	*s*	*n*	*t-test*
Cd	5.57	0.050	4	5.77	0.096	4	0.99
Cu	11.45	0.21	4	11.38	0.43	5	0.92
Pb	23.5	2.38	4	22.00	0.68	4	0.64
Zn	16.1	0.83	4	14.7	2.73	6	0.62

satisfactory. The differences for Cu, Pb and Zn are irrelevant and the agreement satisfies analytical requirements. For Al and Mn, comparison data could not be obtained and so the above accuracy testing. Results obtained with the synthetic sample is the only possibility for accuracy testing, other methods being the standard addition method and the analysis of reference material (e.g. from NIST or BCR).

DISCUSSION

Ionex separation associated with a twentyfold preconcentration, is largely sufficient for the determination of Al, Cd, Cu, Mn, Pb and Zn in rainwater. The detection limit is about one order of magnitude improved for all the elements except for manganese. Due to the high sensitivity, the limit of detection of manganese is given by the level of contamination in the laboratory. Since this also applies to the direct determination by ICP-AES, no significant improvement appeared. As far as the remaining analytes are concerned, the decrease of the detection limit is lower for Al and Zn, which are typical contaminants of water.

From the contamination point of view, the procedure is advantageous because the whole preconcentration takes place in a single closed vessel. This becomes evident if the results are compared with those from the evaporation procedure, where the detection limit was markedly lower for lead only. For the remaining analytes the effect was irrelevant, and for Ca, Fe, Mg and Na the detection limit was even significantly increased.

Apparently, in addition to contamination taking place during the pouring of the samples, sample interaction with the evaporator walls (sorption and desorption) during the long-term contact at elevated temperature plays a major role. This effect is enhanced by the unadequate cleaning of the evaporator after each sample treatment. Some of these problems are eliminated by simple evaporation in a dish in air, but this is unpractical in conventional laboratories with regard to the air contamination.

Ionex preconcentration removes the substantial fraction of interfering macroelements, which is particularly convenient for enabling the analysis by spectral methods. A number of samples can be preconcentrated in parallel, so the method is well suited for routine analyses. The method does not put high demands on the instrumentation but in the accuracy of the work.

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