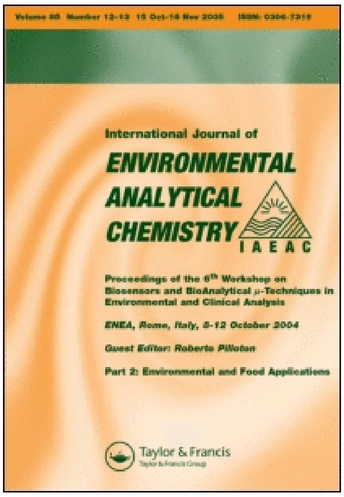

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The Determination of Zinc, Cadmium, Lead and Copper in Precipitation by Computerized Differential Pulse Voltammetry

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A method is described for the determination of metals in rainwater by means of differential pulse anodic stripping voltammetry. Organic interferants are removed by passing the sample over active carbon at pH$\leq$1. A symmetrical, mercury-drop electrode flow through cell is mounted on a PAR 303 electrode stand.

The polarography and the flow injection sample handling system are computer controlled. Results are obtained by means of a calibration graph, standard additions are not necessary. Results for Zn, Cd, Pb and Cu in rainwater are in agreement with results obtained by AAS.

KEY WORDS: Stripping voltammetry, metals, determination, precipitation, rainwater.

INTRODUCTION

In our laboratory, many rainwater samples are analysed as part of a research program on precipitation chemistry.[1,2] For the determination of metals in these samples voltammetric methods using a preconcentration step such as Differential Pulse Stripping Voltammetry (DPSV) and Potentiostatic Stripping Analysis (PSA) have advantages compared to other techniques such as AAS and NAA.

Instrumental cost, the multi-element capability and low detection limits are in favor of Voltammetry. However the application and general acceptance of these methods is seriously hindered because of interferences, caused by the formation of intermetallic complexes and by organic substances in the sample solution.

- The formation of intermetallic complexes is a function of metal concentration within the mercury of the electrode[3] and is therefore of concern mainly if Thin Film Mercury (TFM) electrodes are used.

  The addition of Ga ions[4, 5] only partly solves this problem. Wang and Dewald[6] present an elegant, but rather complicated solution, using a coulometric and a voltammetric cell in series. TFM electrodes must be cleaned and replated frequently, therefore we decided to use a mercury drop electrode in our experiments.
- Organic compounds present a more serious problem. In their presence correct results can be obtained only by standard addition techniques. Even in a relatively pure matrix like rainwater the slopes of calibration curves, obtained by means of standard additions range from almost zero to nearly 100% of the "theoretical" slope, i.e. one obtained in ultra pure water. Organic substances e.g. surface active agents, humic acids etc. are present in all environmental samples. They interfere because they, either are adsorbed on the surface of the mercury electrode so electron transfer is hindered, or form stable complexes[7, 8] with the metals ions. In the latter case reduction is impossible or at best reduction c.q. oxydation potentials are shifted. These phenomena also lead to large variations in sensitivity.

Trying to overcome these problems, we looked for a method to remove effectively organic compounds from the matrix. Prolonged U.V. irradiation[9, 10] with addition of H_2O_2 seems to be the best solution published, this treatment requires however a long time of irradiation. Schlieckman and Umland[11] use a basic carbonate-citrate buffer to determine metals in the presence of humic acids, but in our experience sensitivities are reduced compared to those found in acid media.

We already published[12] a method to eliminate the interference by organic compounds in the U.V. fotometric determination of nitrate in rainwater by the use of active carbon impregnated filters and decided to try the same approach in this case. We studied the absorbtion efficiency and the retention of metal ions for several active carbon filters. Ederol 69K proved to be the best choice: it removed interfering organic compounds from rain water without affecting the metal ion concentrations at $pH \leq 1$. This material is very easily cleaned and gives blanks sufficiently low for the determination of Zn, Cd, Pb and Cu in rainwater.

The analytical system was developed with the aim to analyse rainwater samples which are acidified to preserve the metals. So exchange of the stripping medium must be possible because otherwise the Zn peak will be swamped with the hydrogen peak. Not only the total workload necessitates automation but also the precision and reliability of automated systems is, according to our experience, superior compared to manual methods.

The easiest solution to obtain medium exchange is to use a Flow Injection system, so we decided to develop a computerized FIA-DPSVA combination.

EXPERIMENTAL

Equipment

Polarograph: PAR 384; Electrode stand: PAR 303; Peristaltic pump: Gilson minipuls; Sample changer: Gilson escargot (5 ml tubes); Computer: Apple II with 2 floppy disk systems and Epsom MX 82 printer. Polarograph and computer are linked by an RS 232 interface; Tubing: FEP I.D. 0.7 mm; Valves: Flairfitt, pneumatically operated; Filter: EDEROL 69K, Binzer-Hatzfeld, W-Germany. Cut to 20 mm diam.

Reagents

Acetic acid: reagent quality Merck; Sodium acetate: reagent quality Merck; Nitric acid: Suprapure Merck; Mercury: Suprapure Merck; Buffer solution: 0.2 M sodium acetate, 0.1 M acetic acid.

Conditions

Sample loop: 4.0 ml; Deposition time: 100 s; Acetate flush: 30 s;

Equilibration time: 5 s; Deposition potential: -1.6 V vs. Hg/Hg_2SO_4, K_2SO_4 sat.; Scan rate: 13,33 mV/s.

The general set-up and flow scheme are given in Figure 1 and Figure 2.

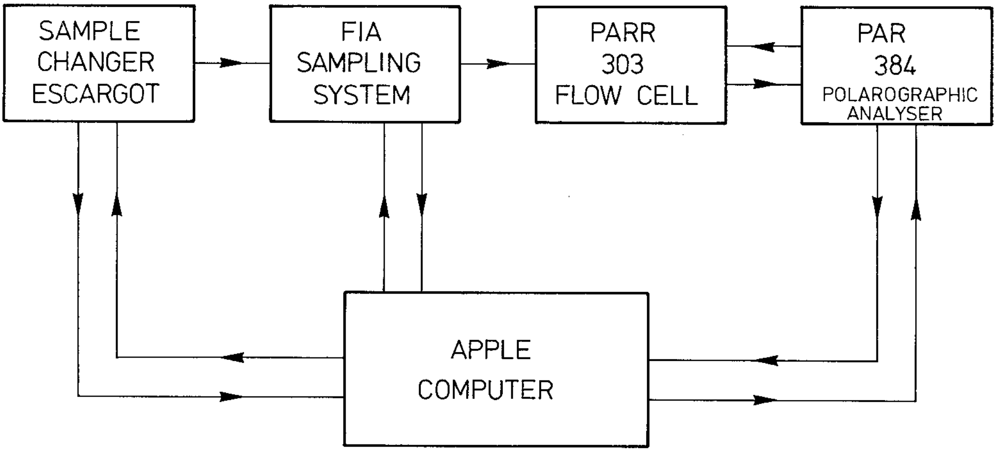

FIGURE 1 General set-up.

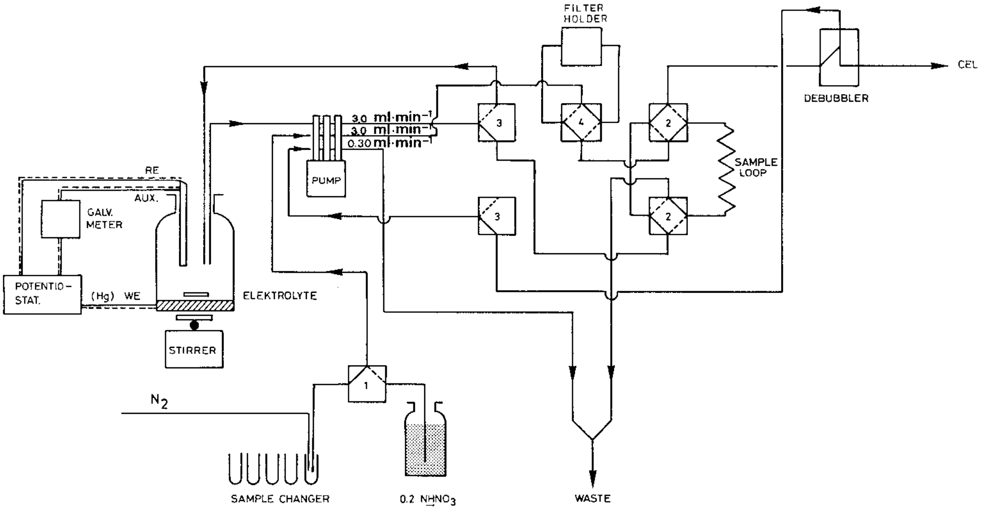

FIGURE 2 Flow scheme.

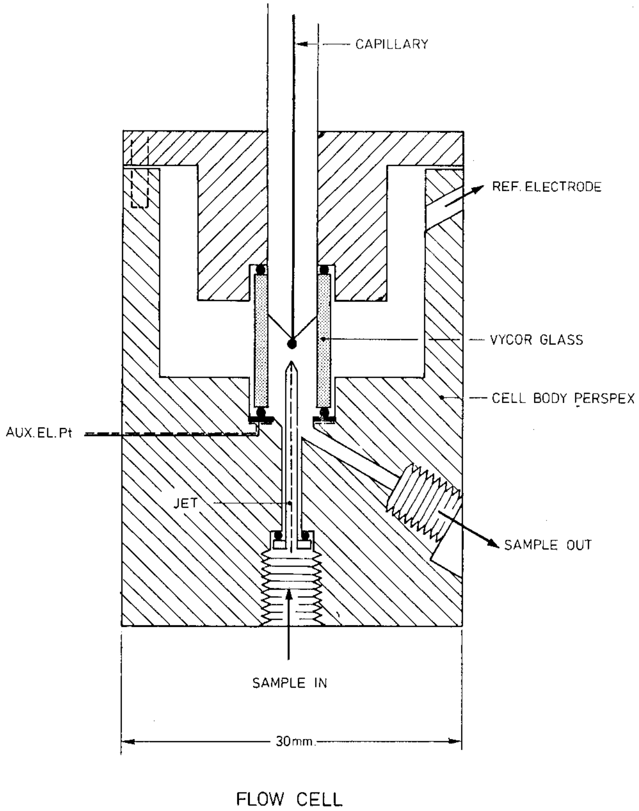

FIGURE 3 Flow cell.

- —The flow through cell is shown in Figure 3. It is constructed to fit directly onto a PAR 303 electrode stand. The electrode configuration is symmetrical, a small piece of porous vycor tube serves as a liquid junction and as the cell wall. The distance between the 0.3 mm diameter jet and the mercurydrop is 0.5 mm. Waste mercury will leave via the sample outlet.
- —It is, in principle, not necessary to remove oxygen from the sample in stripping voltammetry,[13] provided medium exchange is performed with a deaerated solution after the electrolysis step. We tried this approach but were not able to obtain sufficiently low background current levels. Clearly it is rather difficult to remove

the last traces of oxygen from the cell. We prefer to flush the HNO_3 and buffer solutions with nitrogen. The pump, valves and all connecting teflon tubing are, except for short connecting lines to the cell and sample changer, placed in a nitrogen flushed box. The samples are deaerated for 8 minutes in the sample position.

A debubbler is situated close to the cell, so all large gas bubbles are removed. Small bubbles can be formed within the cell because the solutions are (super) saturated with nitrogen. The only way to prevent this formation of bubbles is to make sure that the solutions are undersaturated before they enter the analytical system. A simple way to achieve this is to use 20 cm of 0.3 mm I.D. tubing to aspirate the liquids. The pressure drop over this tube causes part of the nitrogen to leave the liquid phase. This nitrogen is collected at the top of a small vessel (actually an oversized debubbler) and is, together with some liquid, pumped back to the storage vessel. Bubbles present in the sample will be collected in the filter holder, they are removed by reversing the flow for a short time during each analyses, (Figure 2, valve 4). The system has proven to be very reliable with these precautions and it is able to analyse 100 samples overnight. The computer controls the sample changer, the FIA system and the polarograph.

— The operation of the valves and the sample changer is realized with a 16 channel relais interface. One channel is adapted to switch off all apparatus if a hardware or software error is detected.

— The RS 232 interface supports the communication between the Apple and the polarograph. The polarogram (200–500 points) is collected as a large array of ASCII characters. At higher baud rates (>300 bd) synchronisation problems can occur due to memory management time outs, generated by the Applesoft operating system. A good datatransfer at 2400 bd can be obtained by placing a compact conversion routine at the beginning of the program.

— Despite its limited speed we prefer Applesoft-BASIC above computer languages as PASCAL or FORTRAN. Development of new applications can be realized quickly as the interactive nature of the interpreter allows adaption of parameters “on the fly”.

— Although the polarograph generates results itself, we process the polarogram with a peak search routine for reasons of flexibility.

The printer output of each analysis consists of a plot of the voltammogram, a list of detected peaks and results for identified peaks. Results and (optionally) voltammograms are stored on floppy disk.

PROCEDURE

A blank and two standards are placed in the first positions of the sample changer, the rest of the positions are filled with samples and a standard is placed at every 10th position. About 100 samples can be handled overnight.

- —The parameters, to run the PAR 384 in the DPSV mode are entered from the Apple Keyboard by a program called "INIT".
- —A sample volume of 4.5 ml is aspirated (90 sec.), valve 1 is switched and the 0.2 M HNO_3 solution transports the sample over the carbon filter to fill the 4.0 ml loop (30 sec.). The initial situation is as shown in Figure 2, following the full drawn lines.
- —Valves 2 and 4 are switched. The buffered electrolyte now takes the sample to the cell and deposition is started. 0.2 M HNO_3 is backflushed over the filter so any gas bubbles, if present, are expelled. The sample line is flushed with water, a new sample is placed in the sampling position where it is flushed with nitrogen.
- —After 130 s, i.e. 100 s deposition and 30 s to replace the nitric acid medium the pH within the cell is 4.5. Valves 3 and 2 are switched, the flow stops and stripping is started. The electrolyte is now recirculated to its storage vessel where it is permanently electrolyzed at a mercury pool at -1.6 V vs Hg/Hg_2SO_4, K_2SO_4 sat.
- —Switching valves 3, 1 and 4 restores the initial situation. The voltammogram is transferred to the Apple via the RS 232 interface. A new cycle starts when peaks and peak maxima are detected and preliminary results have been calculated and stored. Blanks and standards, analysed at regular intervals within a run provide the information necessary to correct for any drift in sensitivity. After completion of a run all results are recalculated and a final report is prepared.

RESULTS

—Behaviour of the carbon filter.

The filter retains heavy metals as a function of the hydrogen ion concentration of the solution. This variable was studied by passing a precipitation sample over the filter. The sample was acidified with 0.01 to 0.5 M HNO_3. Zn, Cd, Pb and Cu were determined by the procedure as described. The concentrations found in the eluate are plotted in Figure 4. The percentage recovery is given related to the concentrations as determined by A.A.S. It is evident that the metal ions quantitatively pass the filter at H^+ concentrations exceeding 0.1 M. We decided to use 0.2 M HNO_3.

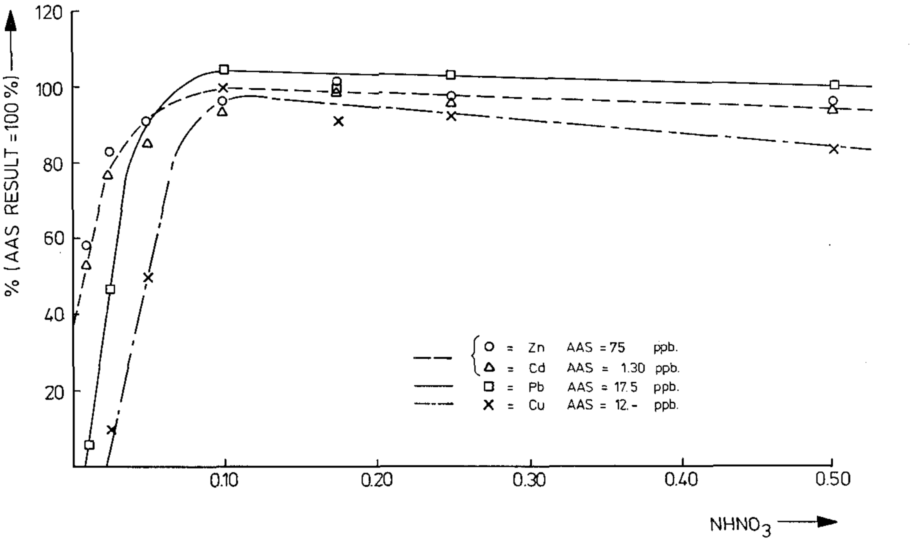

FIGURE 4 Adsorbtion of Zn, Cd, Pb and Cu from precipitation on active carbon as a function of $[H^+]$.

— Blanks.

For the analysis of precipitation samples it is important that blanks are as low as possible. We tested carbon impregnated filter paper from different manufacturers and found a rather large variation in blank values. The filters were tested by placing 4 layers of filter in the filterholder. "Samples" of 0.2 M HNO_3 were analysed. Figure 5 is plot of results obtained with 4 layers of the paper as received. Figure 6 gives the results after the filters were

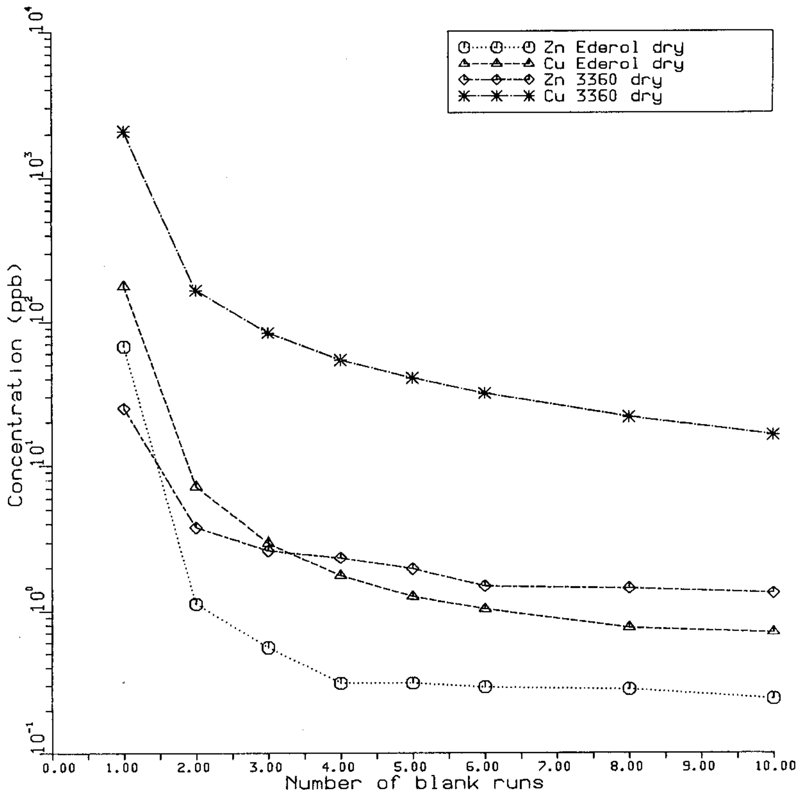

FIGURE 5 Successive blanks with dry filters.

leached for two days in 0.2 M HNO_3. The results are given in ppb for Zn and Cu. Blanks for Lead and Cadmium were very low i.e. $Pb < 0.1$ ppb $Cd < 0.01$ ppb. It will be clear that low blanks are easily obtained if pre-leached filters are used.

We selected the Ederol 69 K filter because of the low and stable blanks and its physical stability which is superior to the other filters tested. Before use the filters are leached for a few days in 0.2 M HNO_3, 4 layers are placed in the filter holder and after 3 to 4 injections of 0.2 M HNO_3 a low and stable blank is obtained. The lifetime will depend on the purity of the samples. In our case 200 rainwater samples could be run with the same filter set.

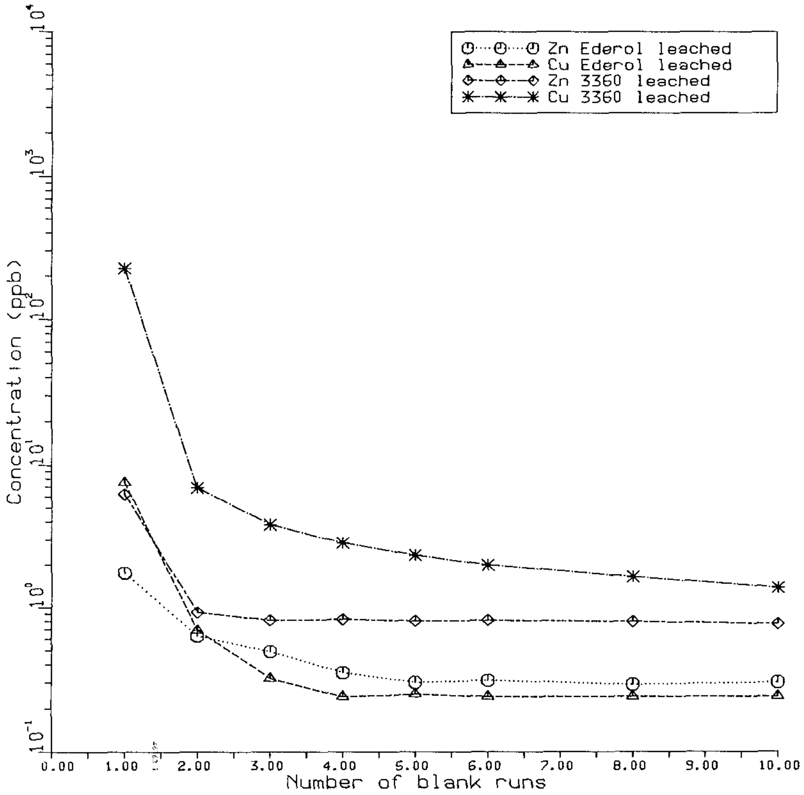

FIGURE 6 Successive blanks with pre-leached filters.

— Carry-over.

In our system carry-over will depend largely on the memory effect of the filter. Values found for blanks and standards, analyzed in random order indicated that carry-over is negligible.

— Minimum oxygen level.

The lowest oxygen level obtainable with our instrument was determined by injecting the buffer as sample. As the buffer is permanently electrolyzed the copper content should be very low. We were not able to distinguish whether the small residual peaks were due to oxygen or to copper so the blanks give an upper limit for the residual current by oxygen.

The results for this sum of oxygen and copper peaks, obtained in succession were: 4.13, 3.79, 3.43, 3.36, 3.47, 3.21, 3.02, 3.28 nA. Mean: 3.46 nA($\equiv$0.12 ppb Cu).

Standard deviation: 0.35 nA ($\equiv$0.01 ppb Cu).

— Rainwater samples.

Table I gives a few typical examples out of a large series of results obtained on precipitation samples acidified to 0.2 M by the addition of HNO_3. For each element the first column contains

TABLE 1

Effect of carbon filter on analytical results.

	Zn (ppb)				Cd (ppb)			
Sample	DPSV			AAS	DPSV			AAS
	without filter		filter		without filter		filter	
	dir.	st.add	dir.		dir.	st.add	dir.	
1	3.7	59	56.6	60	0.46	0.54	0.57	0.60
	2.5		56.6		0.43		0.57	
2	14	51	47.7	50	0.37	0.42	0.56	0.60
	13		47.8		0.37		0.58	
3	6.9	11	12.0	15	0.21	0.12	0.18	0.20
	6.8		12.4		0.20		0.20	
4	7	52	53.1	60	0.45	0.59	0.77	0.80
	6		55.0		—		0.76	

	Pb (ppb)				Cu (ppb)			
Sample	DPSV			AAS	DPSV			AAS
	without filter		filter		without filter		filter	
	dir.	st.add	dir.		dir.	st.add	dir.	
1	12.9	19.5	16.5	15.5	9.7	16.0	7.3	7.4
	13.1		15.9		12.7		7.3	
2	10.9	14.9	15.6	15.0	1.7	4.7	2.3	3.0
	11.3		16.5		1.7		2.2	
3	4.8	5.2	4.9	5.5	2.2	4.3	0.8	0.6
	4.8		5.0		2.4		0.8	
4	24	34.1	32.7	29	8.2	13.2	5.9	7.0
	24		32.2		9.1		7.9	

dir. = result obtained from calibration curve
st.add = result calculated from addition to sample

duplicate results of direct analyses without filter. The peak heights were referred to a calibration graph prepared from standards in milli-Q water acidified to 0.2 M HNO_3. Especially for Zn the results are low compared to AAS results shown in the last column.

Column 2 shows results without filter but calculated from a standard addition made to the sample solution. In this case copper tends to be high.

Column 3 contains duplicate results after the sample was passed over the active-carbon filter. Here again peak heights were related to a calibration curve prepared in acidified milli-Q water. As can be seen the results are very close to those obtained by AAS and duplicates are acceptable.

The fact that Zn and Cd show the largest deviations at $pH = 2$ without filter is probably due to adsorbance effects on the electrode surface, which cannot be compensated by a more negative deposition potential. The strong interaction we found for Zn is in agreement with the results found by Plotrowics e.a.[7]

Table II gives some representative examples of duplicate results obtained by Flow Injection Differential Pulse Anodic Stripping

TABLE II

Typical results in ppb for rainwater samples. AAS results in parenthesis.

Code	Zn	Cd	Pb	Cu
9–2	10.5 (10	0.22 (0.30)	5.9 (5.5)	1.4 (1.4)
	10.6	0.22	5.7	1.4
11–2	10.5 (10)	0.16 (0.25)	4.0 (4.0)	1.0 (0.6)
	10.0	0.16	3.8	0.8
13–2	43.6 (40)	0.65 (0.60)	6.3 (4.0)	6.4 (4.8)
	43.0	0.65	6.5	6.0
15–2	10.4 (5)	0.23 (0.30)	5.3 (5.0)	7.7 (8.4)
	10.4	0.22	5.1	7.8
16–2	24.6 (25)	0.67 (0.75)	8.3 (6.5)	3.2 (2.4)
	25.2	0.66	8.7	2.9
10–3	21.0 (15)	0.30 (0.40)	12.4 (10)	3.5 (3.0)
	21.2	0.33	12.5	3.5
12–3	25.2 (25)	0.29 (0.40)	11.3 (11.0)	2.5 (2.4)
	24.9	0.32	10.9	2.0
14–3	53.6 (40)	0.40 (0.45)	15.2 (13.5)	3.7 (3.6)
	52.9	0.39	15.2	3.4

Voltammetry (FI-DPASV). Results obtained by AAS are given in parenthesis.

The results of the analyses of 150 rainwater samples obtained by FI-DPASV and AAS were compared by means of regression analysis. The results are given in Table III.

TABLE III
Regression analysis of results.

	Zn	Cd	Pb	Cu	
n	152	150	152	164	
corr.coeff.	0.9310	0.9685	0.9607	0.9454	
slope	0.9382	1.0248	1.0605	0.8635	
intercept	0.57	−0.05	−0.80	0.18	(ppb)

Typical blanks and corresponding standard deviations obtained by overnight runs of samples, standards and blanks are for Copper: 0.4 ± 0.1 ppb, for Lead: 0.1 ± 0.06 ppb for Cadmium 0.00 ± 0.00 ppb and for Zinc 0.3 ± 0.1 ppb.

Normal sensitivities are: Zn and Cu 30 nA/ppb, Cd 21 nA/ppb and Pb 9 nA/ppb, measured with a 4.0 ml sample loop. The gradual change in sensitivity, because of wear of pump tubing is compensated for by standard solutions, analysed at regular intervals.

The results warrant the conclusion that FI-DPASV is a reliable and fast method to measure heavy metals in precipitation samples. The application of the method to other samples is under investigation.

CONCLUSION

Active carbon impregnated filterpaper was successfully applied in stripping voltammetry of rainwater. Results are more reliable and analysis time is shortened because no standard additions are needed. The method described in this paper can probably be applied also to e.g. seawater, surfacewater and to acid digests of biological samples, these samples always contain a small amount of organic substances after destruction.

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