Heavy metal analysis of rainwaters:
A comparison of TXRF and ASV analytical capabilities

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The aim of this work consisted on the implementation of sufficiently accurate and sensitive analytical procedure for the analysis of metal concentration in rainwater. Different sample preparation procedures were tested to achieve the required concentration prior to direct total reflection X-ray fluorescence (TXRF) analysis. TXRF and anodic stripping voltammetry (ASV) were compared in regard to achieved detection limits, precision and accuracy.

Introduction

The study of regional manifestations of problems in the environmental pollution results of great scientific and practical interest nowadays, and a large number of papers reporting researches carried out on the evaluation of the state of atmospheric pollution have been released during the last decade. A correct estimation of the accuracy and precision when reporting the values obtained for the determined concentrations is one of the basic premises to provide data sets complying the expected fitness for the purposes of evaluation of the implicit impact in the zones under study.

The cycles of the chemicals in the atmosphere are being changed constantly by human beings. The rising of the concentration levels of heavy metals, which often play an important role as nutrients or as toxic elements in the biosphere, is considered as one of the most significant influencing factors in the atmospheric changes.

Different methods have been employed for trace metal analysis in natural waters, such as atomic absorption spectrophotometry (AAS),[1,2] inductively coupled plasma emission spectroscopy (ICP-AES),[2] inductively coupled plasma mass spectrometry (ICP-MS),[3,4] neutron activation analysis (NAA),[5] energy dispersive X-ray fluorescence (EDXRF),[6,7] total reflection X-ray fluorescence (TXRF)[8–10] and anodic stripping voltammetry (ASV),[11–14] among others. The results of a previous study on the factors influencing the fitness of an EDXRF method, preceded by a concentration APDC precipitation procedure were reported before.[15]

TXRF has proved to be a powerful analytical tool during the last years. Its high sensitivity, relatively low costs and simplicity are the features that make it a practically ideal method for the analysis of water samples, involving either direct or pre-concentration steps.[8–10,16–18] ASV has been also used in the analysis of trace concentration levels of several metals in waters.[11–14]

The aim of this work consisted on the implementation and evaluation of TXRF and ASV analytical methods for the heavy metal (Fe, Co, Ni, Cu, Zn, Cd, and Pb) analysis in rainwater samples collected in one selected monitoring station in Cuba.

Experimental

Sampling

Rainwater samples were collected at the Cayo Coco station of the National Network for Atmosphere Monitoring (province of Camaguey, Cuba). Sampling was performed according to the ISO 5667/3-1985 Standard requirements. Samples were passed through $0.27\ \mu m$ nuclear filter to separate suspended matter, and stored in polyethylene bottles (previously treated with diluted HNO_3 and washed with warm organic detergent and distilled water). After filtration, conc. HNO_3 was added to the samples to adjust the pH value to 2, and samples were frozen and kept at $-25\ °C$ until the performance of the analysis.

Instrumental

The employed TXRF spectrometer includes a Mo fine focus tube for excitation and the total reflection module supplied by the International Atomic Energy Agency (Atominstitut/Vienna design).

A voltammetric analyzer (PA4, Laboratorní Pristroje Praha) working in differential pulse mode was used to determine Cd, Pb, Cu and Zn concentrations by anodic stripping voltammetry (ASV). A static mercury drop electrode was used as the working electrode, and saturated calomel as reference electrode.

FAAS (Pye Unicam SP-9) was used to determine Pb content in order to check the accuracy of the results obtained by ASV.

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Sample preparation

Due to the extremely low concentration levels to be determined,[19] several pre-concentration stages were evaluated to allow the use of the total reflection method, which has instrumental sensitivities in the ppb level.

TXRF analysis

Concentration by evaporation procedures: Two variants were tested for sample preparation. The first variant consisted on the evaporation of 100 μl of spiked (with Ga and U) sample using for that purpose specially designed device of PTFE (Fig. 1). The device should allow evaporating large amounts of sample under reduced pressure or heating on to a geometric spot of the minimal achievable area. Volumes above 100 μl were considered unlikely, due to the expected looses by sputtering out during evaporation. The foreseen 20-fold concentration factor should be adequate to lower the detection limits commonly achieved by the measurement of a 5 μl sample under the usual TXRF conditions.

As a second variant of concentration by evaporation 10 drops (5 μl each) of spiked sample were successively deposited and dried on the reflector surface. The expected concentration factor in this case should be 10.

Chemical pre-concentration: This variant consisted in the digestion with 0.2 ml of conc. HNO_3 of the precipitate obtained with the APDC pre-concentration procedure described in Reference 15. The resulting solution was diluted with twice distilled-deionized water up to 25 ml, achieving a final 40-fold concentration factor from an initial sample volume of 1 liter.

ASV analysis

For the polarographic determination of Cd, Pb, Cu and Zn, 10 ml of water sample was placed into a fussed quartz measuring vessel of the polarographic analyzer. 5 mg of re-crystallized ammonium persulphate were added to remove by oxidation the organic matter and the solution was heated on a sand bath until dryness. The residue was collected with 10 ml of 0.01 mol/l HNO_3, used as supporting electrolyte. The solution was flushed with N_2 for 15 minutes, and afterwards was electrolyzed at the preset potential (Table 1). The influence of the instrument operational settings and the temperature on the Cd peak height, as well as the possible interference of Fe, Co, Ni, Sr and Ca on the resulting sensitivity for Cu, Cd and Pb were studied and the results are presented in the ASV section. Standard solutions of 5 μg/l of Cu, Cd and Pb were measured for this study.

Measurement conditions and quantification

For TXRF the internal standard method is employed to correct for any variations in sample deposition on the sample–reflector surface, which could produce differences in regard to the resulting absolute sensitivity. Ga and U were used as internal standards for the analysis of elements by K and L lines, respectively. The fitting of the TXRF spectra was performed with the AXIL-QXAS package, distributed by the International Atomic Energy Agency (IAEA).[20] The samples were measured for 1000 seconds.

The expression relating the measured diffusion limit current I_d and concentration C_m^0 in ASV are well known,[21] and the quantification was made by both calibration curves and the standard addition method. All calibration curves were elaborated according to the specifications of ISO 8466 standard.
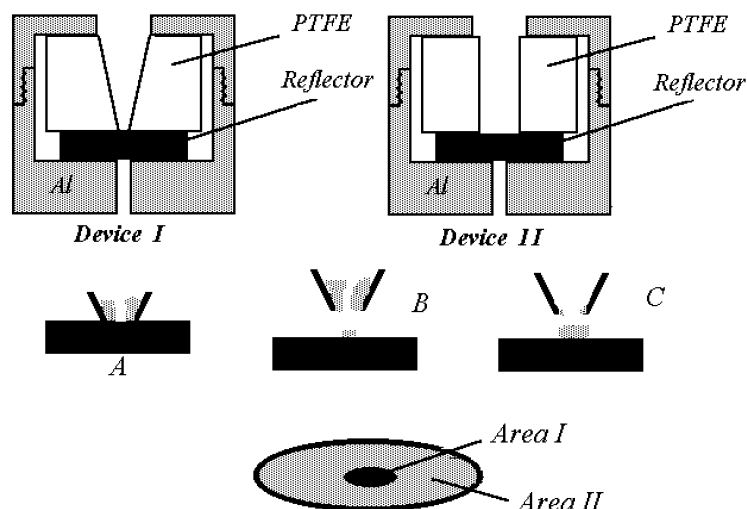

Fig. 1. The evaporation devices

Table 1. The ASV operational parameters

Element	Deposition potential, mV	Working range, mV
Cu	20	−300 to 200
Zn	−985	−1100 to 700
Cd	−565	−700 to −200
Pb	−370	−700 to −200

All potentials are referred to saturated calomel electrode.

Detection limits

The limit of detection is defined as the value resulting from a signal corresponding to three times the standard deviation of the noise signal. In EDXRF practice, detection limit for an element i is customarily calculated by using this value, the instrumental sensitivity S_i (counts·s^{-1} w/w^{-1} [mA^{-1}]) and the measuring time t_{meas}. The main noise signal in XRF spectra is the value of the continuum counting under the peak (N_{cont}). As mentioned before, some peaks are also noticed in a measurement performed from a blank sample with a net peak area N_{blank}, or in the absence of sample (instrumental background, net peak area N_{bkgd}). In general, the probability distribution of the results of a series of measurements for any of these signals can be considered as close to a Poisson distribution, and in such case $\sigma_N = \sqrt{N}$. Therefore, the limit of detection must be calculated as:

$$LOD_i = \frac{3\sqrt{N_{cont} + N_{blank} + N_{bkgd}}}{t_{meas}S_i} =$$

$$= \frac{3\sqrt{I_{cont} + I_{blank} + I_{bkgd}}}{\sqrt{t_{meas}}S_i}$$

where I is the respective count rate (s^{-1}).

Detection limits for ASV were calculated as described in the Standard ISO-8466/Part 4.

The performance of the TXRF analytical method as well as the determination of the recovery and reproducibility of the results were evaluated analyzing synthetic solutions and an inter-comparison of the results obtained for 9 rainwater samples from Cayo Coco station. The reproducibility of the ASV procedure was evaluated using rainwater samples.

The reproducibility (R, %) of the methods was calculated as:

$$R = (\sigma/\bar{x}) \times 100$$

where σ is the confidence interval ($\alpha = 0.05$) and $\bar{x}$ the average concentration.

Results and discussion

TXRF

Aqueous solution was prepared from multi-elemental standard solutions. The relative sensitivity curves obtained for K and L lines are shown in Figs 2 and 3.

A PTFE device was built to perform the first variant of evaporation/concentration step mentioned above (Fig. 1). Two devices were tested. When trying to evaporate 100 μl samples with the funnel-shaped device into residues similar to the one resulting from the evaporation of a single 5 μl drop (3-mm diameter spot) the following undesired effects were observed: the deposition of salts takes place mostly in the inner edges (Fig. 1A), the deposited residues are often removed in PTFE parts (Fig. 1B) rather than kept in the reflector surface (Fig. 1C) when dissembling the device to remove the sample reflector.

A second device (Fig. 1II) was built to avoid the effects described above. A lower density of salts and a lower concentration factor are obtained in this case, due to the resulting larger area. This procedure was also discarded because of the contamination frequently observed after evaporation. The successive evaporation (up to 10 drops) offered better results, but the results obtained for Fe, Cu and Zn still presented a consistent bias, suggesting that some contamination occurs during deposition-evaporation. This pre-concentration variant was selected as the most suitable for a relatively simpler analysis. The obtained values for blank measurements (4 replicates), as well as the evaluated metrology parameters (recovery, reproducibility and the detection limits) are shown in the Tables 2 and 3, respectively.

The results obtained for the application of APDC pre-concentration stage (TXRF-APDC) are also summarized in Table 3. The recoveries for all of the elements (both evaporation and APDC pre-concentration procedures) were quantitative (>98%). The detection limits are three or four times better than the values obtained for the case of successive evaporations.

ASV

The changes in the measured peak current while varying the deposition time (t) or the mercury drop radius (r) were evaluated. The obtained results agree with the tendency reported by KEMULA:[22] when the sample volume is sufficiently large, t and r are small, the peak height is independent of the voltage V, and it is directly proportional to t and r (Fig. 4).

The influence of the temperature on the measured Cd peak current height showed an increase of about 1.50% per centigrade (Table 4). As far as the temperature in our laboratory varied between 28 and 32 °C, it was decided to perform the sample measurements and the calibration curves within short time interval. The presence of Ca, Mn, Fe, Co, Ni and Sr in the range of concentrations studied does not significantly interfere the determination of Cu, Cd and Pb (Table 5).

The achieved detection limits are shown in Table 6 and are lower than 0.5 µg/l.

The reproducibility ranged in general from 5 to 20%. The worst results were obtained for metal concentrations near the detection limits.

The analysis of a group of rain water samples showed a good agreement between the results obtained by the different methods (Table 7), and are alike to the values reported in the literature for this kind of samples.[19,23] A few of the TXRF results were significantly higher than those obtained by ASV methods; probably related to contamination effects.
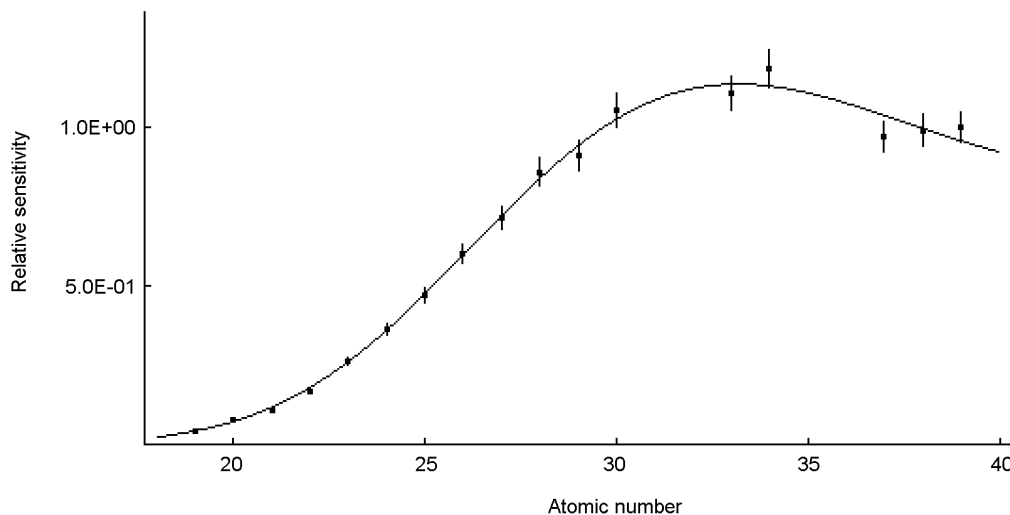

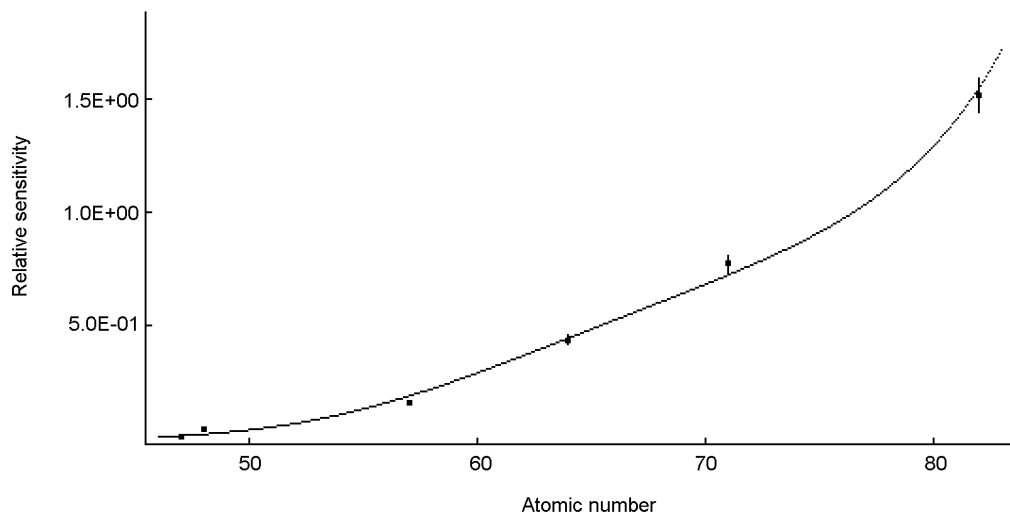*Fig. 2.* Relative sensitivities (Ga) for K lines

Fig. 3. Relative sensitivities (U) for L lines

Table 2. Results from blank measurements in TXRF

	Evaporation procedure		Chemical
	PTFE, Variant II	10 drops × 5 μl	pre-concentration (APDC)
Sample volume	1 ml	0.05 ml	1 l
T_{meas}	500 s	500	500
C_{Ga}	200	200	40
C_U	169.6	169.6	33.9
Ti	2.3 ± 0.5	<1.9	N.D.
V	<0.9	<1.2	N.D.
Cr	1.4 ± 0.3	1.5 ± 0.5	N.D.
Mn	1.1 ± 0.2	<1.7	0.21 ± 0.01
Fe	30 ± 10	6.0 ± 0.9	3.1 ± 0.3
Co	<0.8	<0.7	<0.25
Ni	<0.8	<0.8	0.20 ± 0.05
Cu	5 ± 1	4.6 ± 0.5	0.8 ± 0.4
Zn	15 ± 5	5.2 ± 0.6	2.3 ± 0.7
As	<0.8	<1.6	N.D.
Se	<0.8	<1.1	N.D.
Br	<0.8	<1.0	N.D.
Sr	3.8 ± 0.27	3.2 ± 0.4	N.D.
Pb	2.5 ± 0.3	<1.7	0.65 ± 0.15

N.D.: Not determined.
All concentration values are given in μg/ml.

Table 3. Recoveries, precision and detection limits for TXRF

| Technique	Parameter	Element					
		Fe	Co	Ni	Cu	Zn	Pb
10 drops	Initial concentration, μg/l	20.2	20.0	20.0	20.0	20.6	20.2
5 μl	Recovery, %	104.0	102.9	103.1	96.8	103.4	104.0
	Precision, %	8.28	5.73	6.50	8.27	5.85	8.28
	Detection limits, μg/l	2.2	1.2	1.3	1.8	2.0	2.2
APDC	Initial concentration, μg/l	25.0	25.0	25.0	25.0	26.0	25.0
+	Recovery, %	102.8	101.2	101.7	101.6	97.0	102.8
TXRF	Precision, %	4.24	3.01	3.54	4.06	4.37	3.32
C_f=40	Detection limits, μg/l	0.8	0.4	0.4	0.6	0.7	0.7

C_f is the resulting concentration factor.
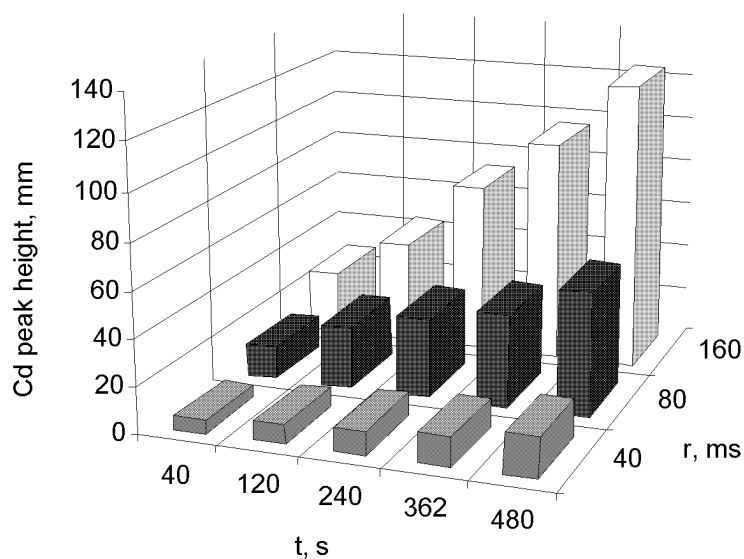
Fig. 4. Variation of the measured Cd peak-current vs. r and t factors

Table 4. Influence of temperature on limit current for Cd (5 µg/l)

Temperature, °C	Peak height, mm	Increasing, %
22 ± 1	18 ± 1	1.58 (22–29 °C)
29 ± 1	20 ± 1	1.36 (29–40 °C)
40 ± 1	23 ± 1	1.54 (22–40 °C)

Table 5. Interferences of Fe, Co, Ni, Sr and Ca on the determination of Cu, Cd and Pb

Solution	Peak height, mm		
	Cd	Pb	Cu
A	23 ± 2	19 ± 2	22 ± 2
B	22 ± 2	20 ± 2	24 ± 2
C	–	–	–

A: Cu, Cd and Pb: 5 µg/l.
B: Cu, Cd and Pb: 5 µg/l; Mn, Fe, Co, Ni, Sr: 100 µg/l; Ca: 4000 µg/l.
C: Mn, Fe, Co, Ni, Sr 100 µg/l; Ca: 4000 µg/l.

Table 6. Achieved detection limits in ASV

Element	D. L., µg/l
Cu	0.42
Zn	0.31
Pb	0.31
Cd	0.23

Table 7. Comparison of the results obtained by the different methods (in µg/l)

Sample No.	Fe		Ni		Cu		Cd	
	TXRF-EP	TXRF-APDC	TXRF-EP	TXRF-APDC	TXRF-EP	TXRF-APDC	ASV	ASV
1	14 ± 1	12 ± 0.9	<1.3	1.0 ± 0.5	<1.80	2.2 ± 0.5[+]	1.1 ± 0.2[+]	0.37 ± 0.09
2	10 ± 1	8.4 ± 0.8	<1.3	1.8 ± 0.6	22 ± 2	19 ± 1	14.4 ± 0.6	<0.20
3	24 ± 2+	19 ± 1[+]	<1.3	1.2 ± 0.5	14 ± 1	12 ± 1	12.9 ± 0.5	<0.20
4	15 ± 1	13.1 ± 0.9	<1.3	1.0 ± 0.5	6 ± 1	4.8 ± 0.7	5.2 ± 0.3	<0.20
7	9 ± 1	7.1 ± 1.0	<1.3	0.6 ± 0.4	5 ± 1	4.6 ± 0.6	4.1 ± 0.2	<0.20
8	3.8 ± 0.8	3.3 ± 0.6	<1.3	0.8 ± 0.4	6 ± 1	4.4 ± 0.6	3.7 ± 0.2	<0.20
9	3.4 ± 0.8	3.4 ± 0.6	<1.3	2.0 ± 0.6	5 ± 1	4.6 ± 0.6	4.2 ± 0.2	<0.20

Sample No.	Co		Zn			Pb		
	TXRF-EP	TXRF-APDC	TXRF-EP	TXRF-APDC	ASV	TXRF-EP	TXRF-APDC	ASV
1	<1.2	<0.4	6.3 ± 0.9	6.1 ± 0.8	5.6 ± 0.3	<2.2	1.5 ± 0.5	1.0 ± 0.2
2	<1.2	<0.4	13 ± 2	13 ± 1	11.9 ± 0.6	4.3 ± 0.9	2.5 ± 0.5	3.2 ± 0.2
3	<1.2	<0.4	17.8 ± 2	13 ± 1	13.4 ± 0.6	<2.2	2.0 ± 0.5	1.6 ± 0.2
4	<1.2	<0.4	13.2 ± 2	7 ± 0.9	12.1 ± 0.6	<2.2	ND	1.4 ± 0.2
7	<1.2	<0.4	6 ± 1	3.4 ± 0.6	3.9 ± 0.2	<2.2	ND	1.4 ± 0.2
8	<1.2	<0.4	2.9 ± 0.8	3.4 ± 0.6	2.6 ± 0.2	<2.2	1.2 ± 0.2	1.0 ± 0.2
9	<1.2	<0.4	N.D.	1.9 ± 0.6	1.4 ± 0.2	<2.2	<0.70.	0.9 ± 0.2

[+] Results statistically different ($\alpha = 0.05$).
Result statistically differing from the rest of the results are underlined ($\alpha = 0.05$).
N.D.: Not determined.

Conclusions

The TXRF module commonly supplied by IAEA allows to perform the direct analysis of trace elements in water samples in concentration levels as low as tenths µg/l for the elements determined with higher sensitivity. The contamination with traces of Fe, Cu, Zn (10–100 pg) becomes relevant when dealing with evaporation-concentration procedures. Hence, the detection limits for such elements can be seriously affected.

The interfering processes mentioned above do not affect the determination when a chemical pre-concentration procedure is applied, such as APDC-precipitation, and detection limits of tenths of µg/l can be achieved with good reproducibility and recovery.

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