Chem. Anal. (Warsaw), 41, 419 (1996)

The Analysis of Environmental Samples by ICP–AES

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Key words: environmental analysis, ICP–AES, sampling

The multiple capabilities of inductively coupled plasma–atomic emission spectrometry have been proved by analysis of various samples of environmental importance. The main feature of analysis of airborne particulate, water, drinks and food, soils and human hair are indicated. In the case of non-ferrous metallurgy the elements of toxicological relevance are lead, cadmium, copper and zinc. All determinations were made using the spectrometer-SPECTROFLAME-P (Spectroanalytical Instruments). The results of analysis of various types of samples from Romania are presented.

Przedstawiono wszechstronne możliwości analityczne atomowej spektrometrii emisyjnej ze wzbudzeniem w plaźmie indukcyjnie sprzężonej w zastosowaniu do różnych typów próbek środowiskowych. Omówiono podstawowe zagadnienia związane z analizą pyłów powietrza, wód, napojów i żywności, gleb i włosów ludzkich. W przypadku metalurgii nieżelaznej pierwiastkami o znaczeniu toksykologicznym są ołów, kadm, miedź i cynk. Wszystkie oznaczenia wykonywano stosując spektrometr SPEKTRO--FLAME-P (Spectroanalytical Instruments). Przedstawiono wyniki analiz różnych próbek pobranych w Rumunii.

Environmental analysis has become the number one priority for many laboratories. It is a major requirement for instrumentation and methodology capable of implement the protection laws [1]. One of the main instrumental techniques that plays a leading role in the analysis of environmental samples is ICP–AES [2,3] (Inductively Coupled Plasma–Atomic Emission Spectrometry).

There are a number of characteristics which make ICP–AES suitable for environmental analysis: good sensitivity for many elements, simultaneous multi-element determination, fast analysis, a very wide dynamic calibration range and a few chemical interferences. Utilization of hydride techniques [4,5] can improve the sensitivity and selectivity.

Environmental pollution can be monitored in a number of ways and this has resulted in a wide variety of sample types being supplied for analysis as: airborne particulates, waters (fresh, waste, river, sea), soils and sediments, plant materials, biological samples (serum, urine, tissue). For each type of sample its processing is specific and sampling is essential [6].

This paper wants to prove the multiple capabilities of ICP–AES in the environmental analyses.

EXPERIMENTAL

The determinations were carried out by means of an atomic emission spectrometer with inductively coupled plasma, SPECTROFLAME-P (SPECTRO-Analytical Instruments, Germany) [7].

The instrument has 30 fixed spectral channels that can simultaneously be monitored by the three polychromators and allow one to carry out the background correction, application of internal standard method and other facilities [8].

The argon utilized was of spectral purity (99.998%); the cooling flow rate was 12 l min^{-1}, the auxiliary flow rate 0.8 l min^{-1} and the nebulizer flow rate 1 l min^{-1}; all of them are functions of plasma power and some of them were automatically controlled. The consumption rate of the liquid sample was about 2 ml min^{-1}. The observation height is adjustable; it is usually 12 mm.

Table 1. Analytical data for elements determined

No.	Element	λ, nm	BEC, mg l^{-1}	DL, mg l^{-1}
1	Al	308.215	0.65	0.013
2	B	249.773	0.11	0.002
3	Cd	226.502	0.1	0.002
4	Cr	267.716	0.18	0.0035
5	Cu	324.754	0.079	0.0015
6	Fe	259.940	0.059	0.001
7	Mg	279.079	0.06	0.0011
8	Mn	257.610	0.017	0.0003
9	Mo	203.844	0.012	0.0003
10	Ni	231.603	0.25	0.005
11	P	178.287	0.5	0.01
12	Pb	283.307	1.40	0.027
13	Sb	206.833	0.60	0.014
14	Si	251.611	0.32	0.006
15	Sn	189.989	0.4	0.008
16	Ti	334.940	0.08	0.0015
17	Zn	213.856	0.079	0.0015

BEC – Background Equivalent Concentration.
DL – Detection Limit.

Table 1 lists the elements analyzed, the wavelenght employed, the detection limits ($DL=2\sigma$) and the equivalent concentration of the background (BEC) obtained by means of SPECTROFLAME-P. One can deduce an empirical relation, frequently tested, between the equivalent concentration of the background and the detection limit $BEC \approx 50 \times DL$.

RESULTS AND DISCUSSION

Airborne particulates analysis

Sampling of air has been carried out by suction; a known volume of air is filtered through glass wool or filter paper with fine pores. The airborne particulates retained are usually brought into the solution by digestion under pressure or, more recently, digestion under pressure by microwaves [9,10].

It is worth mentioning that no sampling is carried during rain, snow or sleet falls; the volume of air filtered should be sufficient to reach the limits desired.

Table 2 presents four samples of air picked up by suction (1–3 through glass wool; 4 through filter paper) and one sample (5) of settled dust (from an IMNR laboratory).

Table 2. Results of airborne particulates analysis

Nr. crt	Sample	Pb	Cd	Cr	Cu	Mn
1	Furnace Air, mg m^{-3}	1.76	<.002	<.005	.03	<.005
2	Air N1, mg m^{-3}	.028	<.002	<.005	.042	<.005
3	Air N2, mg m^{-3}	.075	<.002	<.005	.021	<.005
4	Air IMNR, mg m^{-3}	.13	<.002	<.005	.004	<.005
5	Dust IMNR, %	3.6	.005	.010	.56	.054

Table 2. (continuation)

Nr.	Zn	Al	Mg	Mo	Ni	Sb	Sn	Ti
1	.10	.31	1.50	<.005	.010	.04	<.005	.01
2	.052	.36	1.04	<.005	<.005	<.005	.012	.016
3	.050	.34	.83	<.005	<.005	<.005	.005	.008
4	.020	.085	.008	<.005	<.005	.015	.005	<.005
5	2.84	1.31	.63	.008	.055	.035	.060	.021

The samples were dissolved in HNO_3 and HCl [11]; blank samples of glass wool or filter paper, not used for aspiration, were also taken for correction of results.

The main element sought was lead and the first sampling was carried out in front of a furnace containing molten lead. The allowable concentration of lead in the atmosphere of working areas is 0.05 mg m^{-3} as average throughout a working shift and 0.1 mg m^{-3} the peak value which should never be exceeded. Throughout protected areas the maximum concentration allowed as daily average is 0.0007 mg m^{-3}.

Table 3 shows the results of analyses effected on settled dust from various working sites in the industry of non-ferrous metallurgy. The analysis of settled dust is usually carried out before that of the dust in atmosphere which affords the localization and identification of the metals that can cause disease.

Table 3. Results of analysis of dust from non-ferrous metallurgy area

No.	Ind. area	Al, %	As, %	Cd, %	Cr, %	Cu, %	Fe, %	Mg, %
1	Neferal Cu_1	2.29	0.013	0.023	0.012	12.0	4.29	0.14
2	Neferal Cu_2	4.28	0.009	0.013	0.017	15.2	6.12	0.20
3	Neferal Al_1	19.42	0.008	0.027	0.038	0.57	18.46	1.14
4	Neferal Al_2	22.22	0.006	0.046	0.022	0.72	8.40	1.15
5	Neferal Pb_1	1.55	0.156	0.014	0.0045	1.78	4.39	0.22
6	Neferal Pb_2	0.66	0.47	0.013	0.0037	2.92	2.31	0.17
7	IMNR Al, Cu	3.16	0.026	0.042	0.015	5.54	4.26	0.40
8	IMNR Pb	5.09	0.030	0.0094	0.021	2.90	4.34	0.36
9	IMNR AL	2.64	0.070	0.23	0.0097	3.81	4.19	0.34
10	IMNR Ti	1.32	0.013	0.0057	0.043	0.69	15.44	0.32

Table 3 (continuation)

No.	Mn, %	Mo, %	Ni, %	Pb, %	Sb, %	Sn, %	Ti, %	Zn, %
1	0.17	0.0021	0.032	2.64	0.027	0.47	0.055	28.5
2	0.25	0.0034	0.051	3.46	0.046	0.67	0.045	17.5
3	0.22	0.0027	0.030	1.29	0.032	0.096	0.062	1.19
4	0.17	0.0026	0.029	1.36	0.042	0.13	0.087	3.10
5	0.047	<0.001	0.058	32.7	14.30	0.79	0.0063	5.18
6	0.018	<0.001	0.10	52	9.12	1.77	0.011	3.05
7	0.13	0.013	0.20	4.75	0.12	0.23	0.040	3.78
8	0.033	0.0030	2.21	58	0.26	0.45	0.037	2.17
9	0.089	0.012	0.52	3.42	2.37	0.89	0.055	2.65
10	0.11	0.67	0.18	4.65	0.052	0.094	0.61	3.05

Water analysis

Analysis of water may seem, at first sight, an easy task, because distilled water is, in general, the basic medium of all samples determined by plasma atomic emission spectrometry and, besides, the performance of the method in this medium is best.

The analysis of the following fresh water samples was performed: nine samples (1–9) from the running drinking water system of city Bucharest, one sample from the water available at IMNR Institute (10), a sample of well water from commune Branesti (11). Sampling was carried out twice at different times (10.04.94 and 03.16.95). Two types of mineral water (12,13) were also analyzed for comparison.

Care was taken to contain the representative samples in clean flasks, to utilize only decontaminated laboratory glassware and acids of advanced purity.

Because the total concentration of pollutants in water was sought, the samples were acidified shortly after sampling [12] with nitric acid at $pH \leq 2$ and were not filtered.

Equal amounts (500 ml) of each sample were taken in adequate beakers and 4 ml of concentrated HNO_3 were added to each sample; they were evaporated to wet salts, without reaching the boiling point or dry residuum. After cooling other 4 ml of concentrated HNO_3 were added to each sample to dissolve the residuum. Then 4 ml HCl (1:1) were added to each sample (if it was necessary the insoluble materials were filtered); samples were then transferred into 25 ml volumetric flasks, giving a 20 time concentration of analytes.

Table 4 lists the elements determined, the maximum allowable concentrations (MAC), the exceptional maximum allowable concentrations (EMAC), according to STAS 1342-91, for some of the elements and the results obtained by averaging the two samplings, because the values were generally constant in time.

Table 4. Results of water analysis [concentration in mg l^{-1} (ppm)]

No.	Cd	Cr	Ni	Pb	Al	Cu	Fe	P	Mg	Mn	Zn
MAC	.005	.05	.01	.05	.05	.05	.1	PO_4.1	50	.05	5
EMAC					.2	.1	.3	PO_4.5	80	3	7
1	<.001	.001	.001	.025	.016	.003	.08	.015	5.1	.020	.020
2	<.001	.001	.001	.030	.045	.003	.12	.022	5.1	.030	.020
3	<.001	.001	.002	.025	.033	.003	.12	.015	5.2	.020	.020
4	<.001	.002	.004	.040	.044	.005	.15	.020	5.4	.020	.020
5	<.001	.001	.002	.020	.016	.003	.03	.010	5.6	.010	.020
6	<.001	<.001	.001	.015	.017	.002	.02	.010	5.5	.010	.020
7	<.001	.001	.002	.020	.017	.004	.14	.015	5.0	.020	.020
8	<.001	.001	.002	.040	.015	.006	.10	.014	5.0	.010	.050
9	<.001	.001	.002	.030	.030	.005	.19	.022	4.8	.030	.050
10	<.001	<.001	.001	.025	.002	.006	.12	.16	12.5	.020	.400
11	<.001	.007	.001	.020	.002	.005	.025	.030	158.	.01	1.00
12	<.001	<.001	<.001	.025	.020	.013	.019	.21	73.	.140	.040
13	<.001	<.001	.002	.050	.030	.010	.094	.07	69.	.120	.080

1–9 drinking water from some quarters of city Bucharest: 1 – Colentina, 2 – Pantelimon, 3 – Balta Alba, 4 – Berceni, 5 – Giurgiului, 6 – Dr. Taberei, 7 – Militari, 8 – 1Mai, 9 – Kogalniceanu.
10 – potable water in IMNR.
11 – well water from commune Branesti.

The higher aluminium concentration in the drinking water from the supply network of the city, compared with water from other sources is assigned to utilization of $Al_2(SO_4)_3$ in purification of drinkable water. Aluminium has lately been suspected to be harmful for the central nervous system [2].

Analyses were also carried out on liquids that are ingested by people to determine their content of metals. The liquids studied were: concentrated juices of fruits, various qualities of coffee beans or instant coffee and teas made from plants.

At concentrated juices only accidentally we found Fe, Pb, Cu in higher concentration.

In the case of coffee beans and instant coffee it is worth mentioning the concentration of phosphorus which is considerably higher than in water, reaching tens of mg ml^{-1}; perhaps there is a relationship between the strength of coffee and the concentration of phosphorous. Phosphorous is also present in the teas but in ten times smaller concentration.

The analysis of soil

Evaluation of the quality of water and air is a simple problem compared with the determination of the quality of soil, because the wide variety of soils composition influences their chemical, physical and biological properties. The adverse effects of soil pollution do not show up immediately; they appear after some time and are irreversible. On the other hand no maximum limits allowable for toxic elements were issued or, if there are some, they are not unanimously accepted (standardized). In Romania it was established that the 7th class of soil defines the maximum allowable values of pollutant. Moreover, there is no standardized method of determination of the toxic elements in the soil.

Attention is generally focused on soluble compounds of toxic elements in the soil which carried away by precipitations, eventually acid rains, penetrate into the natural circuit of water and are encountered in ground water and plants. Bonding and retention of heavy metals in plants depends to a great extent on the pH.

Extraction of soil for analyses is carried out in various ways: with acetic acid [13], Na_2EDTA, aqua regia [14] or mixture of various acids.

We analyzed soils in the neighbourhood of non-ferrous metallurgical works from Zlatna, Copşa Mică and Neferal. Samples were taken from depths of 0–10 cm and 10–30 cm from the four cardinal points, over various zones depending on the distance from the source. Sampling was effected in spring time and autumn seeking Pb, Cu, Zn and Cd. Maps were drawn showing the plume of pollution for each element.

The digestion [15] intended to afford a total content and not only that of soluble compounds, was carried out as follows: 1.000 g of soil sample was finely ground and transferred in a teflon evaporating dish; 8 ml of HF were added and the dish heated on a sand bath to remove silica and break the complexes. Then 2.5 ml $HClO_4$, 15 ml HCl and 6 ml HNO_3 were added, the filtrate was transferred to a 50 ml volumetric flask; the residuum left on the filter was subjected to alkaline melting in a nickel crucible whith NaOH and Na_2O_2 (1:2). The melt was poured from the crucible with 10 ml HCl and 2 ml HNO_3 and the sample was brought to a 50 ml volumetric flask.

The blank samples of the reagents employed for the acid attack and the alkaline melt were effected in order to deduct their values from the values of samples, if necessary.

Spectral measurements took account of the spectral background correction.

Tables 5 and 6 list the results of the analyses carried out on soils picked up in the neighbourhood of two non-ferrous metal processing works.

Cadmium MAC (maximum allowable concentration) amounts to 3 ppm while NC (normal concentration) to 0.5–1 ppm; in case of copper, lead and zinc the corresponding values are 100 ppm and 12 ppm; 100 ppm and 15 ppm; 300 ppm and 50 ppm, respectively.

Table 5. Results of analysis of soil, Zone 1

Sample	Season	Zone	Dist. km	Depth cm	Cd ppm	Cu ppm	Pb ppm	Zn ppm
P_1	Spring	Aval	0.5	0–10	6	1400	1300	1300
P_2			0.5	10–30	7	1500	1500	1500
P_3			1.5	0–10	12	10500	1380	2500
P_4			1.5	10–30	11	8600	1600	3200
P_5		Amont	1.5	0–10	5	1400	640	700
P_6			1.5	10–30	7	2800	1500	1650
P_7			0.5	0–10	5	740	730	1080
P_8			0.5	10–30	6	1050	1240	1380
P_9	Autumn	Aval	0.5	0–10	16	10100	2100	3100
P_{10}			0.5	10–30	16	7200	2500	4100
P_{11}			1.0	0–10	4	750	750	630
P_{12}			1.0	10–30	4	1370	2840	960
P_{13}		Amont	1.0	0–10	3	540	780	580
P_{14}			1.0	10–30	3	190	320	270
P_{15}			0.5	0–10	8	1470	3150	1220
P_{16}			0.5	10–30	3	150	410	310

Table 6. Results of analysis of soil. Zone 2

Sample	Month	Dist. km	Cd ppm	Cu ppm	Pb ppm	Zn ppm
PI_1	June	>5	6	100	510	870
PI_2		1–5	7	54	260	730
PI_3		0–1	13	72	410	1250
PJ_1	July	>5	5	40	270	330
PJ_2		1–5	18	81	390	1550
PJ_3		0–1	26	550	1050	4600
PA_1	August	>5	4	31	130	310
PA_2		1–5	6	42	270	610
PA_3		0–1	12	65	330	1080
PS_1	September	>5	3	31	130	420
PS_2		1–5	5	27	180	640
PS_3		0–1	11	63	360	1070

Table 6 (continuation)

PO_1	October	>5	4	56	340	640
PO_2		1–5	7	50	310	810
PO_3		0–1	11	70	370	1190
PN_1	November	>5	4	50	190	470
PN_2		1–5	9	48	310	820
PN_3		0–1	12	69	380	1020

The analysis of hair

Biological samples [16] as blood and urine are frequently analized to estimate the exposure of personnel to toxic substances and evaluate the conditions of the environment.

Other studies deal with the microelements present in various organs or liquids in the body: brain, bones, teeth, kidney calculuses, finger nails or hair.

However the hair on the scalp is a preferred biological indicator; it is very important and extensively studied because sampling is very comfortable and storage without problems.

The analysis of hair was carried out as follows; 2.500 g of hair were placed in a 250 ml beaker, 15 ml of concentrated HNO_3 were added and the beaker was placed on a sand bath. When the liquid cleared up, 3 ml $HClO_4$ were added to it and after evaporation at wet salts were added 1.5 ml HNO_3 and 1 ml HCl, then the final content was transferred to a 25 ml volumetric flask ready for analysis.

The values obtained for four subjects are listed in Table 7 which also mentions age and sex; the data are compared with data from literature [17].

Table 7. Results of analysis of human hair (Concentration in ppm)

No.	Age year-sex	P	Zn	Mg	Cu	Fe	Al	Pb	Ti
1	44-m	146	147	34	8.4	26	29	28	2.8
2	14-f	81	132	114	9.0	20	35	26	2.1
3	12-m	123	173	24	8.1	46	33	12	2.8
4	44-m	147	158	79	10.0	43	25	13	2.1
Reference [17] ≤ 15		187	144	26	22.0	18	12	8.1	1.1

Table 7 (continuation)

No.	Ni	Cr	Mo	Mn	Cd	Si	B	Sb	Sn
1	.72	.75	15.0	.75	.57	9.2	3.2	.15	< .1
2	.60	.50	.10	1.3	.71	8.2	1.9	.41	< .1
3	.42	.93	< .10	.87	.25	12.0	3.5	1.3	< .1
4	.63	1.5	.24	1.4	.50	30.0	3.7	5.1	< .1
Ref.	.97	.67	.44	.41	.20	–	–	–	–

Conclusions

Atomic emission spectrometry with plasma is most adequate to environmental analyses because it possesses rather low detection limits, takes short time and affords simultaneous multielement analyses.

Special attention should be awarded to sampling because it requires the indications or supervision of the analyst who is aware of the evolution of the analysis.

Analysis and quality evaluation of water and air is simpler than in soil samples whose quality is difficult to evaluate because of the wide variety of soils.

In case of non-ferrous metallurgy the elements of toxicologic relevance most studied were Pb, Cd, Cu, Zn.

Because ICP–AES method is not standardized yet as a method of environmental analysis the results obtained have to be verified with standards corresponding to the medium analyzed.

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Received September 1995
Accepted January 1996