

MONITORING OF SOILS CHARGED WITH HEAVY METALS

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abstract: Following the world wide most evident interests about environment protection, the present paper deals with the analysis of several Romanian areas contaminated – within the legally accepted limits, though – with heavy metals. Analytical techniques like energy dispersive X-ray fluorescence (EDXRF) spectrometry and inductively coupled plasma atomic emission spectroscopy (ICP-AES) are applied for the analysis of soil composition, as well as the use of both techniques in tandem.

key words: EDXRF, ICP-AES, heavy metals, soil pollution

Introduction

The world wide preoccupations, and especially the European ones, are mainly focused on environment protection. It is why the present paper proposes a method to study the heavy metal contamination of soils, and discusses it within a study case for several soils sampled from different geographical areas of Romania that appealed for solution to the presence of such contaminants.

Soil is a component subsystem of the terrestrial ecosystems, which resulted from numerous physical, chemical and biological processes. Soil and living organisms form an inseparable unity inside the biosphere. Soil is supporting and creating environment for terrestrial plants, the main way to produce vegetation and forestry. Because of such important role the soil is playing it is our duty to try to keep it in best possible conditions [1].

The pollution of soil with heavy metals is so serious problem also because, through the natural cycle, these heavy metals can reach human body and cause irremediable damage.

The two techniques involved in soil analysis are the energy dispersive X-ray fluorescence (EDXRF) spectrometry and the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The latter one, in conventional way, is a destructive method, requiring sample disaggregation, while XRF is a non-destructive technique [2,3].

EDXRF is simple and cheap alternative to other techniques. Generally speaking, the lightest element accessible through this method is Beryllium ($Z=4$) but, due to technological

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limitations and to the weakness of the X-ray response, it is often difficult to analyse elements lighter than Sodium ($Z=11$).

The X-ray fluorescence is based on the effect the high energy X-ray is having, through the excitation of the element mixture sample with specific low energetic lines, on the comprised elements [4]. The field of X-ray fluorescence is very provocative. While its first designation was the analysis of geological samples, the advances in technology and computer science allowed the use of this technique for analytical purposes.

Exhibiting multiple advantages like easy sampling, rapid multielement analysis, non-destructive analysis, and the ability to provide an overall information about samples of unknown origin, buried in various matrix environments (liquids, solids, slurries, powder, thin films, air filters, and so on) XFR is the perfect complementary analysis method to other analytical equipments designed for laboratory use, the technique being also appropriate for research, industry, and quality assurance.

Inductive coupled plasma is a source of atomic emission that could be used, in principle, to identify all of the elements, with exception of Argon. The plasma source is used to dissociate the sample in its constituents – atoms or ions – and to excite them to a superior energetic level. They will return to the initial state through the emission of a photon of characteristic energy. This photon emission is recorded by an optical spectrometer. The intensity of radiation is proportional to the concentration of each element of the sample and, by the help of several calibration curves, the concentration is measured directly.

The linearity range of the method extends over 5 to 6 orders of magnitude, so that it allows determination of both major components and impurities, without making any dilution of the sample. Generally, the detection limits are very low for most of the elements, ranging from 1 $\mu\text{g/mL}$ to 100 $\mu\text{g/mL}$, taking into consideration that only classical methods have been used for sampling procedure.

The two methods show high compatibility, the correlation between measured experimental data being previously reported [5].

The present study concerns the analysis of composition and history of several soil samples taken from different country locations (two sets of samples are coming from the south part, and one set from the east part of Romania). All three sets are taken from industrial areas, at a 5cm depth, and the sampling interval – totalling 3 series of determination – was every 4 months throughout the year 2006. The two sets sampled from the south part are identified as set A, and set B, respectively, and the set sampled from the east part is labelled as set C.

Experimental Part

Materials. EDXRF analysis does not require major processing of the samples; only small mechanical processing may be required in order to adjust the size of the sample to the dimensions of the spectrometer's cuvette.

For the ICP-AES analysis, all standards have been prepared from Merck standard solutions, according to USEPA standard specifications. Bulk solutions have been preserved in double cap sealed polyethylene vials, at 1000-5000 ppm concentration.

Apparatus: PW4025 – MiniPal – Panalytical type EDXRF Spectrometer (Fig. 1);
Liberty 110 – Varian type ICP-AES Spectrometer (Fig. 2).

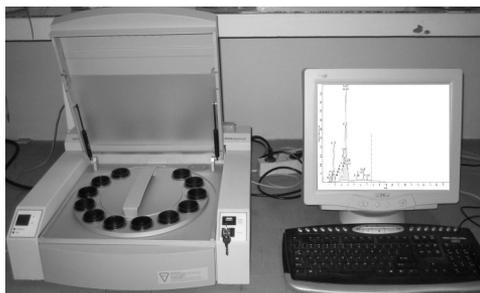


Fig. 1 EDXRF Spectrometer

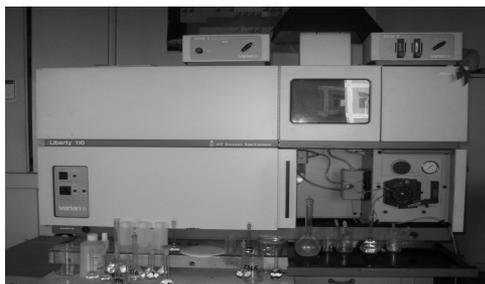


Fig. 2 ICP-AES Spectrometer

Sample mineralization has been performed on a Berghoff microwave type digester, following a custom method, by the use of concentrated nitric acid, concentrated fluoric acid and boric acid as neutralizer for the excess fluoric one; the content of the digester's glass has been transferred in a 100 mL calibrated flask and diluted to the sign with bidistilled water.

Results and Discussion

EDXRF is a nondestructive and rapid method for analytical measurements of multielement liquid or solid samples. Being generally used as basic analytical method, EDXRF is one of the few atomic spectrometry techniques readily available for portable instruments.

The determinations have been carried out in Helium atmosphere, for a period of 300 seconds, without any filter, at 16 kV voltage and automatically adjusted current intensity, and for the construction of the cuvette a 3.6 μm Mylar film was used. The results are presented in Table 1.

Table 1. Experimental data obtained by EDXRF, as milligrams of element per kilogram of dried soil, determined from samples A, B, and C, respectively.

Sample	A1	A2	A3	B1	B2	B3	C1	C2	C3
Element									
Ni	11	10.5	10	38	35	30	100	97	
Cr	37	32	25	84	79	75	9.2	8.0	90
Cd	5	4.2	3.8	32	31	27	8	5	6.2
Cu	232	220	200	450	430	400	130	115	3.5
Pb	41	38	30	25	20	17	120	110	102.5

The program used with the ICP-AES analysis, Rapid Quant, allows semi-quantitative determination of 36 metallic elements, both as monoelement, for calibration purposes, and as multielement, the matrix constitution of the sample, by solving spectral interference of the matrix. The results are shown in Table 2.

Table 2. Experimental data obtained with ICP-AES, for the three sets of samples.

Sample Element	A1	A2	A3	B1	B2	B3	C1	C2	C3
As	–	–	0.001	–	–	–	0.001	–	–
Ag	–	–	–	–	–	–	–	–	–
Ti	0.04	0.039	0.04	0.02	0.009	0.03	0.08	0.08	–
Pd	–	–	–	–	–	–	–	–	–
Zr	0.01	–	–	0.03	–	0.02	–	–	0.01
Tl	–	–	–	–	–	–	–	–	–
Se	–	–	–	–	–	–	–	–	–
Al	1.14	0.99	1.07	0.56	0.70	–	2.45	3.01	2.99
Mo	0.22	0.19	–	–	–	–	–	0.10	–
Sr	0.05	0.02	0.02	0.56	0.54	0.54	–	0.06	0.08
Ca	231	196	297	7.20	6.99	6.78	65.9	78.6	69.7
Ba	0.14	0.29	0.21	1.89	1.56	0.99	0.89	1.25	0.88
Co	18.7	23.2	19.9	16.5	15.9	15.8	7.99	7.54	6.99
Ni	12.8	9.23	5.99	39.2	35.1	29.9	107	99.9	81.2
Si	70.26	71.9	71.0	104	99.9	99.8	78.9	83.7	106
Hg	–	–	–	–	–	–	12.1	10.9	–
Mn	2021	1999.8	2010	847	906	899	1045	1067	1099
Fe	989.1	881.5	979.8	1021	1029	989	920	780	890
Pt	–	–	–	–	–	–	–	–	–
Au	–	–	–	–	–	–	–	–	–
Cr	34.0	31.2	30.8	84.5	80.2	79.6	9.70	8.56	7.99
Mg	0.94	0.79	0.88	67.2	65.1	69.0	123	156	179
V	12.5	13.1	12.9	–	–	–	0.05	–	–
Na	1023	999.8	1001	567	345	378	123	157	182
Bi	–	–	–	–	–	–	–	–	–
Sb	–	–	–	–	–	–	–	–	–
W	–	–	–	–	–	–	–	–	–
B	0.045	0.039	0.05	–	–	0.01	–	–	–
Sn	0.14	0.19	0.20	–	–	0.05	0.09	–	0.06

Table 2. continued

Sample Element	A1	A2	A3	B1	B2	B3	C1	C2	C3
Zn	12.3	13.4	12.9	4.56	3.99	3.23	–	0.98	1.23
Cd	5.34	4.73	3.21	32.7	30.8	27.1	8.9	8.56	7.99
P	0.421	0.399	0.23	24.9	31.2	29.9	12.7	10.1	5.2
Cu	235	221	196	456	423	389	132	126	99.5
Pb	41.5	39.8	35.2	27.4	23.7	19.1	121	109	99.78
Li	0.23	0.79	0.99	10.2	12.1	9.23	5.21	2.32	2.19
K	23.9	29.7	31.2	10.2	9.34	7.99	15.89	12.1	10.2

The general analysis procedure is adapted to the sample to be analysed, based on the pre-determination of the order of magnitude of the concentration of metallic components. In order to eliminate the spectral interferences, the following wavelengths are established for the elements of interest in the present study:

Element	Wavelength (nm)
Ni	231.604
Cr	267.716
Cd	214.438
Cu	324.438
Pb	214.914

The sample concentration is derived through the expression corresponding to each adapted procedure. The results, expressed as mg/kg of dried soil, are presented in Table 3.

Table 3. Experimental data obtained by ICP-AES, as milligrams of element per kilogram of dried soil, determined from samples A, B, and C, respectively.

Sample Element	A1	A2	A3	B1	B2	B3	C1	C2	C3
Ni	13.1	9.45	6.01	39.5	34.9	29.3	110	98.7	80.1
Cr	34.5	29.9	27.9	85.5	79.2	78.6	8.99	7.96	7.00
Cd	5.10	4.33	2.99	31.1	30.0	27.2	9.9	8.16	7.47
Cu	212	209	191	423	398	361	129	119	99.9
Pb	39.5	37.8	35.1	26.1	23.2	19.9	111	107.2	92.88

Conclusions

Many analytical techniques based of physical phenomena, like the energy dispersive X-ray fluorescence, X-ray diffraction, various types of electronic microscopy, mass spectrometry based on molecular or atomic emission or absorption, have been proven their utility in several application for environment monitoring. The present study proposes and advanced and more efficient technique, through the combination of EDXRF and ICP-AES, whose only purpose is to significantly improve the results and to diminish the associated cost per analysis ratio.

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