EDXRF AND INAA ANALYSIS OF SOILS IN THE VICINITY OF A METALLURGICAL PLANT*

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In this work *Energy-Dispersive X-ray Fluorescence* (EDXRF) and Instrumental *Neutron Activation Analysis* (INAA) techniques were used to determine the soil composition and its pollution with heavy metals and trace elements in the vicinity of Iron and Steel Works at Galati, Romania, which is one of the most important metallurgical complexes in the South-East of Europe. EDXRF analyses were carried out using portable Thermo Scientific XLTj NITON analyzers from 700 series at Dunarea de Jos University of Galati and Iron and Steel Works of Galati. For INAA determinations of long-lived nuclides the neutron irradiation was carried out at the TRIGA research reactor at Institute of Nuclear Researches-ICN Pitesti, Romania and the gamma-ray spectrometric measurements were performed at "Horia Hulubei" National Institute of Physics and Nuclear Engineering (IFIN-HH). k_0-INAA technique based on short-lived activity was applied at Portuguese Research Reactor of the Technological and Nuclear Institute (ITN) in Sacavem, Portugal. The following elements were determined: Ag, As, Au, Ba, Br, Ca, Cd, Co, Cr, Cs, Fe, Hf, Hg, K, Mo, Na, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, U, W, Zn, Zr, and rare-earth elements (Ce, Eu, Gd, La, Lu, Nd, Sm, Tb, and Yb) by long-lived activity INAA; Al, K, Mg, Mn, Na, Sr, Ti, and V by short-lived activity INAA; Ag, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V, and Zn by EDXRF. The results obtained by using the two analytical techniques were compared with the permitted concentration values for heavy metals and trace elements published in Romanian legislation and with other values found in the literature for European and world median elemental concentrations.

Key words: EDXRF, INAA, soil, heavy metals, metallurgical plant.

1. INTRODUCTION

Soil pollution is one of the most serious problems in the world, with long term consequences on human life. In recent years, with the rapid development of

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industry, various dangerous pollutants such as heavy metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, V, and Zn) have been released due to production, smelting and tailings, and got deposited in soils around industrial areas causing serious pollution and soil quality degradation. Iron and steel manufacturing produces important quantities of solid wastes containing heavy metals [1,2]. Heavy metals and some trace elements are biologically toxic and can affect and threaten the health of human being owing to their accumulation and persistence in the compartments of the food chain. Hence, it is very important to investigate and monitor soil contamination for economic sustainable development and people's health.

Several analytical techniques have been extensively employed for environmental pollution monitoring, such as: Instrumental Neutron Activation Analysis (INAA) [3-9], X-Ray Fluorescence Analysis (XRF) [5,10-13], Particle-Induced X-ray Emission (PIXE) [14,15], Atomic Absorption Spectrometry (AAS) [6,9,13,16,17] and Inductively Coupled Plasma Spectrometry-Atomic Emission Spectroscopy (ICP-AES) [17]. INAA, without chemical preparation of sample before or after the neutron irradiation, has shown to be a powerful technique for multi-elemental analysis of a variety of environmental matrices, including soil. INAA is one of the preferred methods for the assessment of the elemental composition of soils and sediments [5,7,8] because it is suitable for the analysis of solid samples requiring minimum preparation, and information on a large number of elements can be obtained simultaneously. It has a high sensitivity and good accuracy and it is non-destructive. For the analysis of environmental samples EDXRF has the advantage of being a rapid and inexpensive method with a simple sample preparation [5,10,18]. Quantitative and qualitative analyses by XRF techniques are performed without chemical digestion and a great number of elements can be determined simultaneously in a short time [13].

The main goal of the present research was to use EDXRF and INAA techniques in order to determine the soil composition and pollution with heavy metals and trace elements, in the vicinity of Iron and Steel Integrated Works (ISIW) at Galati, Romania and to compare the elemental concentrations with the maximum values admitted by the Romanian legislation and with other values found in the literature for the European and world median concentrations in topsoil. This work is an extension of the previous XRF studies of soil pollution in the Galati region related to industrial activity [10,12], and is part of the Project PNCDI2 No. 72-172/2008 funded by National Plan of Research, Developing and Innovation, of implementation of high precision and sensibility methods for the bio-monitoring of the environmental pollution in South, South-East and Central regions of Romania. INAA of a soil sample collected at Galati was carried out at "Horia Hulubei" National Institute of Physics and Nuclear Engineering (IFIN-HH) in Magurele, Romania (long half-life radionuclides) and Technological and Nuclear Institute (ITN) at Sacavem, Portugal (short half-life radionuclides), in connection with a previous investigation of air pollution in some industrial areas in Romania, in the frame of EU FP5 research project IDRANAP, based on elemental contents in transplant lichens, bulk deposition and airborne particulate matter [19].

2. EXPERIMENTAL

Surface soil (0–5 cm depth) was collected in open areas from fields located on different cardinal directions and distances from the ISIW factory at Galati, Romania. The soils investigated in this experiment were sampled from the following urban zones: a district situated in the Southern area of the town, near the Danube River (site no. 4); two districts situated in the vicinity of the South and North gates of ISIW (sites nos. 2 and 3, respectively); inside the meteorological station, at the Eastern side of the city (site no. 1). The soil samples were air dried, homogenized and sieved at particle size of 250 µm (sites 2-4), and 400 µm (site 1).

EDXRF analyzes of three soil samples (sites no. 2-4) were carried out at the Environmental Protection Laboratory of ISIW and at Dunarea de Jos University of Galati (UDJG), using handheld Thermo Scientific XLTj-700 series NITON energy-dispersive XRF analyzers having as excitation source a miniaturized 30 kV X-ray tube. By automatically adjusting for matrix effects, NITON XRF analyzers are able to determine the content of soil samples typically in seconds, without any requirement for instrument users to input empirical, sample specific calibrations [18]. The sample name, spectrum and elemental composition are stored in a dedicated library. The XRF instrument has a sample holder attachment that allows the analysis of bulk samples of soil and dust. Each soil sample was analyzed five times for 240 s using two X-ray filters, one for elements from K to Cu and the second for elements from Zn to Sb. The analyzer features a Peltier-cooled Si-PiN X-ray detector. The standard software is programmed to analyze and automatically report 22 elements (UDJG analyzer) and 8 elements (ISIW analyzer), respectively. All major interferences by overlapping X-ray alpha emission lines (such as those between As and Pb) are known and accounted for by the program algorithm that then separates close peaks based on the element's characteristic X-ray beta lines.

INAA based on long-lived radionuclides was applied at IFIN-HH in Magurele (near Bucharest), for the determination of Ag, As, Au, Ba, Br, Ca, Cd, Co, Cr, Cs, Fe, Hf, Hg, K, Mo, Na, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, U, W, Zn, Zr, and rare-earth elements (Ce, Eu, Gd, La, Lu, Nd, Sm, Tb, and Yb) in a soil sample (site no. 1), the neutron irradiation being carried out at the TRIGA reactor of the Institute of Nuclear Researches of ICN Pitesti [20]. k_0-INAA technique based on short-lived radionuclides was applied at the Technological and Nuclear Institute (ITN) at Sacavem, Portugal, to determine Al, K, Mg, Mn, Na, Sr, Ti, and V in eight Romanian soils (including site no. 1 at Galati), in the frame of the EU FP5 research project IDRANAP of IFIN-HH [20].

3. RESULTS AND DISCUSSION

Table 1 presents the concentrations of 20 elements (Ag, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, V, and Zn) determined by EDXRF in three soil samples from Galati (sites 2-4), as well as 42 elements (Ag, Al, As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, Hg, K, La, Lu, Mg, Mn, Mo, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, W, Yb, Zn and Zr) determined by INAA (long and short-term irradiation) in the soil sample collected from the meteorological station in Galati (site no. 1) [20]. Analytical uncertainties for EDXRF are situated in the range of 4.8-10 % [18]. Co and Sc were not analyzed in this work by EDXRF due to spectral interferences. For INAA, analytical uncertainties represent combined counting uncertainties for sample and standard, with concentration uncertainty for standard. Detection limits are corresponding to 3σ of the background. For a comparison, median values for the elemental concentrations in European topsoil [21], and world median concentration values for soil [22] are also given in Table 1.

Table 2 contains the allowable concentration values for trace elements in soil, given by the Romanian legislation (normal, alert and intervention levels) [23].

Table 1

Elemental content of soil samples collected at Galati, compared with median concentrations reported in the literature for European [21] and World [22] topsoil.

Element	Site 1 (INAA) [20]	Site 2 (EDXRF)	Site 3 (EDXRF)	Site 4 (EDXRF)	European median [21]	World median [22]
Ag (mg/kg)	< 0.41	< 35	< 35	< 35	0.27	-
Al (g/kg)	96.9 ± 0.4				110	-
As (mg/kg)	9.04 ± 0.99	10.1	9.3	11.5	7.03	6
Au (μg/kg)	43.6 ± 4.4				-	-
Ba (mg/kg)	402 ± 32				375	500
Br (mg/kg)	8.30 ± 0.97				-	-
Ca (g/kg)	14.6 ± 2.3	47.7	14.0	22.5	9.22	15
Cd (mg/kg)	2.6 ± 1.0	< 15	< 15	< 15	0.145	0.35
Ce (mg/kg)	78.4 ± 4.9				48.2	50
Co (mg/kg)	13.1 ± 0.7	NA	NA	NA	7.78	8
Cr (mg/kg)	84.0 ± 9.2	53.0	100.3	87.5	60	70
Cs (mg/kg)	5.1 ± 0.3				3.71	4
Cu (mg/kg)	ND	30.7	23.5	24.4	13	30
Eu (mg/kg)	1.3 ± 0.1				0.77	1
Fe (g/kg)	31.5 ± 0.4	38.6	25.9	22.7	35.1	40

Table 1 (continued)

Gd (mg/kg)	5.5 ± 0.8				3.85	-
Hf (mg/kg)	9.7 ± 0.5				5.55	6
Hg (mg/kg)	< 0.25	< 3	5.74	< 3	0.037	-
K (g/kg)	14.2 ± 1.8	17.5	19.5	18.6	19.2	14
La (mg/kg)	37.1 ± 1.4				23.5	40
Lu (mg/kg)	0.46 ± 0.06				0.30	-
Mg (g/kg)	7.63 ± 0.41				7.7	-
Mn (mg/kg)	538 ± 7	771	747.5	534.7	650	1000
Mo (mg/kg)	1.4 ± 0.5				0.62	1.2
Na (g/kg)	8.29 ± 0.42				8	5
Nd (mg/kg)	50.3 ± 9.0				20.8	35
Ni (mg/kg)	67.4 ± 12.4	58.1	61.8	55.4	18	50
Pb (mg/kg)	ND	20.2	21.6	29.7	22.6	35
Rb (mg/kg)	97.3 ± 7.7	65.9	83.3	75.5	80	150
Sb (mg/kg)	1.17 ± 0.07	< 150	< 150	< 150	0.6	1
Sc (mg/kg)	10.4 ± 0.5	NA	NA	NA	8.21	7
Se (mg/kg)	1.38 ± 0.56	4.2	< 3	< 3	-	-
Sm (mg/kg)	7.12 ± 0.35				3.96	4.5
Sn (mg/kg)	ND	<125	<125	<125	3	-
Sr (mg/kg)	109 ± 20	98	75	91.4	89	250
Ta (mg/kg)	1.30 ± 0.15				0.68	2
Tb (mg/kg)	0.88 ± 0.11				0.600	0.7
Th (mg/kg)	10.9 ± 0.5				7.24	9
Ti (g/kg)	2.89 ± 0.17	4.08	4.99	4.90	5.72	5
U (mg/kg)	3.3 ± 0.5				2	2
V (mg/kg)	48.9 ± 1.7	90.8	91.4	97.4	60.4	90
W (mg/kg)	3.7 ± 1.9				< 5	-
Yb (mg/kg)	3.1 ± 0.4				1.99	-
Zn (mg/kg)	106 ± 7	126	122	119	52	90
Zr (mg/kg)	436 ± 28				231	-

NA – not analyzed by EDXRF, due to the spectral interferences.
ND – not determined by INAA.

Table 2

Elemental concentrations in soil allowed by the Romanian legislation [23]

Element	Romanian norms [23]				
	NV	ALS	ALLS	ITS	ITLS
As (mg/kg)	5	15	25	25	50
Ba (mg/kg)	200	400	1000	625	2000
Br (mg/kg)	-	50	100	100	300
Cd (mg/kg)	1	3	5	5	10
Co (mg/kg)	15	30	100	50	250
Cr (mg/kg)	30	100	300	300	600
Cu (mg/kg)	20	100	250	200	500
Hg (mg/kg)	0.1	1	4	2	10
Mn (mg/kg)	900	1500	2000	2500	4000
Mo (mg/kg)	2	5	15	10	40
Ni (mg/kg)	20	75	200	150	500
Pb (mg/kg)	20	50	250	100	1000
Sb (mg/kg)	5	12.5	20	20	40
Se (mg/kg)	1	3	10	5	20
Sn (mg/kg)	20	35	100	50	300
V (mg/kg)	50	100	200	200	400
Zn (mg/kg)	100	300	700	600	1500

NV - Normal Value.
ALS - Alert level for sensitive area; ALLS - Alert level for less sensitive area.
ITS - Intervention threshold for sensitive area; ITLS - Intervention threshold for less sensitive area.

From Tables 1 and 2, it can be seen that, at all investigated sites, the concentrations of some heavy metals detected, such as Ni, Cr, and As, exceed by 3.3 - 1.8 times the normal levels allowed by the Romanian legislation, while Se, V, Cu, Pb, and Zn normal levels are exceeded only at some of the sites (4-1.2 times).

The low alert level (ALS) for Se is slightly exceeded at site 2. Cd and Ba were determined only at site 1 by INAA, while Hg at site 3 by EDXRF. At this site, Cd and Hg concentrations were found to be slightly higher than ALS and ITS allowable values, respectively.

Maximum concentration values in the investigated soils were determined for Ca, Cu, Fe, Mn, Se, and Zn at site 2 (near the South gate of ISIW); Cr, Hg, K, and Ti at site 3 (near North gate of ISIW); V and Pb at site 4 (Southern district of Galati town); Ni, Rb, and Sr at site 1 (meteorological station, Eastern side of the town).

Manganese concentrations at sites nos. 1 and 4 (rather far from ISIW factory) are very close, being lower than those found in soils collected near the factory gates (sites 2 and 3).

By a comparison with European and World median values for topsoil, in some of the soils collected from Galati higher concentration values were determined for Cd, and Hg (by one, and two orders of magnitude, respectively), and to a less extent for As, Ca, Cr, Ce, Co, Hf, Nd, Ni, Sc, Sm, U, Yb, Zn and Zr (by 1.9-1.2 times). For the other elements determined (Al, Ba, Cs, Cu, Eu, Fe, Gd, K, La, Lu, Mg, Mn, Mo, Na, Pb, Rb, Sb, Sr, Ta, Tb, Th, Ti, V) they are similar with the European and/or world median values.

4. CONCLUSIONS

EDXRF an INAA techniques, employed to investigate the soil pollution with heavy metals and trace elements in the vicinity of Iron and Steel Integrated Works at Galati, Romania, could determine a total 44 elements (42 of them by INAA, and 20 of them by EDXRF). Excepting for Pb and Cu all the elements determined by EDXRF could be measured by INAA.

Anthropogenic releases due to metallurgical industry at Galati give rise to higher concentrations of some heavy metals (Ni, Cr, and As) in all the investigated samples (3-2 times), relative to the normal levels admitted by Romanian norms. Moreover, at some of the sites elemental concentrations exceed the alert levels for Hg, Cd, and Se, as well as the intervention threshold for Hg in soil.

Compared with European and world median levels in topsoil, similar or slightly higher values were obtained for most elements in the investigated soils. Much higher Cd and Hg contents (by one, and two orders of magnitude, respectively), and, to a less extent higher As, Ca, Cr, Ce, Co, Hf, Nd, Ni, Sc, Sm, U, Yb, Zn and Zr contents (by 1.9-1.2 times) were also determined in soils from Galati.

INAA and EDXRF are complementary multielemental and nondestructive analytical techniques. INAA is matrix independent, a greater number of elements can be determined by INAA than by EDXRF, with a higher level of accuracy, and it has a special role as a reference technique for other analytical methods.

EDXRF has a short turnaround time and offers the opportunity to get data on Pb and Cu, which are important elements in many environmental studies; Pb cannot be determined by INAA and Cu is troublesome as well [8].

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