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OPTIMIZATION OF X-RAY FLUORESCENCE TECHNIQUE FOR THE ANALYSIS OF HEAVY METALS CONTAINED IN WASTES FROM THE ELECTRICAL AND ELECTRONIC EQUIPMENT INDUSTRY

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Abstract
The present paper presents the results obtained by the application of energy-dispersive X-ray fluorescence spectrometry (ED-XRF) for the determination of the elemental composition of various waste industrial materials. The technique was optimized for the analysis of several industrial hazardous wastes with a high content of heavy metals and sludge samples resulted from galvanizing processes, produced by a company which manufactures electrical and home appliances.

Keywords*: industry, industrial sludges, hazardous wastes, ED-XRF technique.*

1. INTRODUCTION

The main objective of this paper is to determine the heavy metal content in the sludge from the galvanizing processes in order to choose the appropriate modality for collection, neutralization and disposal of the hazardous industrial wastes and for the safety of environmental factors. The galvanizing processes are applied by a private company from Timis county, Romania, for the manufacturing of household appliances.

Determination of the heavy metal concentrations in the sludge from the galvanizing processes was performed by applying the energy-dispersive X-ray fluorescence spectrometry technique (ED-XRF) at the company S.C. SetCar S.A. Braila, Romania, specialized in neutralization of various industrial hazardous wastes [1].

The energy-dispersive spectrometers measure the magnitude of the voltage pulse coming from a semiconductor detector, this magnitude being proportional to the energy of the detected X photons. The resolution of the energy-dispersive spectrometer gets better with the wavelength decreasing, which makes it very useful for detecting shorter wavelengths [2].

2. EXPERIMENTAL

An application of the ED-XRF method was performed in the RENAR accredited laboratory of SetCar S.A. Braila, using a portable Genius XRF spectrometer manufactured by Skyray Instruments

Inc., equipped with a large area Si detector with Be window and an excitation source of 40 kV / 100μA miniature tube X-ray with an Ag-target (Fig. 1) [3].

The spectrometric system has an energy resolution up to 139 eV, and the detection limits of the part per million (ppm) order. The calibration method was automatic, using an internal standard of Ag.

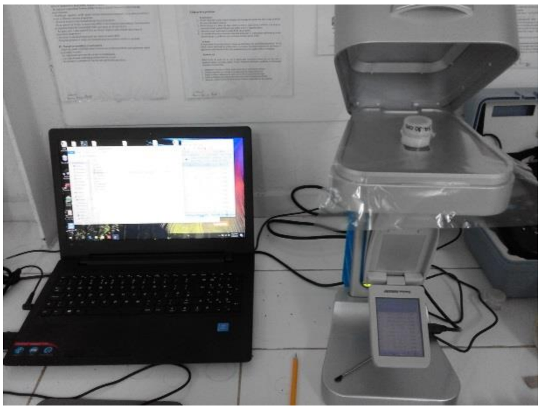

Fig. 1. Portable Genius XRF spectrometer used for the investigation of industrial sludge samples

A total of 10 samples of galvanic sludge were collected, dried at 105 degrees Celsius for 24 hours, crushed and sieved to a 0.01 mm grain, then added to specific capsules covered with a Myler foil (Fig. 2). The prepared samples were duplicate excited, for 60 seconds and 120 seconds, respectively.

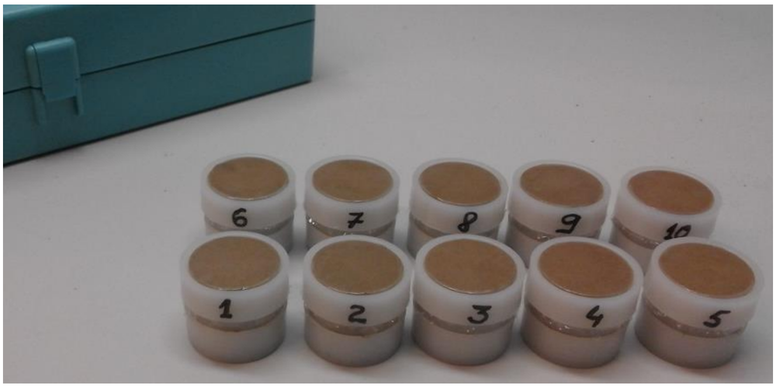

Fig. 2. Capsules of industrial sludge samples prepared for XRF analysis

3. RESULTS AND DISCUSSION

Concentrations of the heavy metals obtained in the waste sludges are of most interest and have to be compared with the heavy metal concentration values indicated by the Romanian legislation on the management and storage of hazardous wastes. According to Romanian law, adapted according to European laws and directives, dangerous waste can only be accepted in a final deposit if the content of heavy metals in the leachate falls within the limits imposed presented in the Table 1 [4].

The metals determined in this work in the samples subjected to two-steps X-ray exposure, using different irradiation times, were the following: Cr, Ni, Mo (Table 2), Sb, Cu, Zn (Table 3), Fe, As, Pb (Table 4), Ag, Sn, V (Table 5), as well as Ca, Mn, Co, Rb, Sr, Zr and Nb. In Tables 2-5 we present the heavy metal concentrations (c) and the analysis errors (E), expressed in ppm, for each experimental time used for irradiation. Typical ED-XRF spectra for the sample no. 1 irradiated at 60 s and 120 s are illustrated in Figs. 3 and 4, respectively.

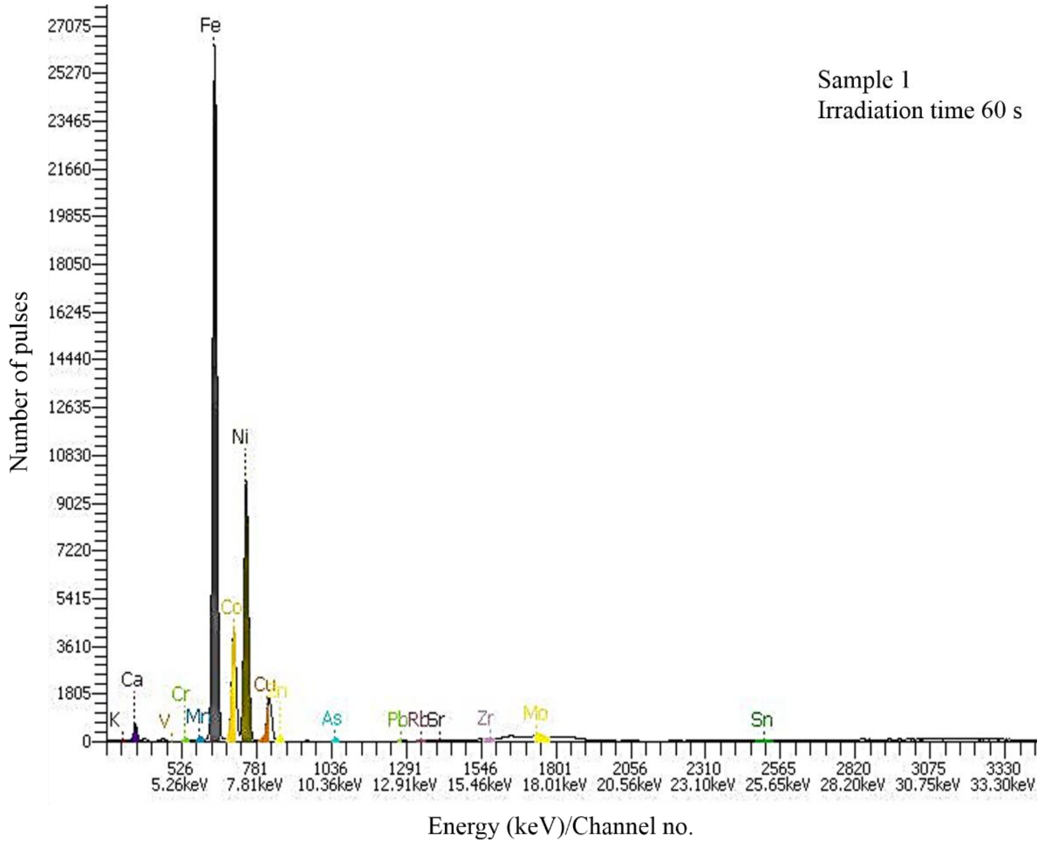

Fig. 3. The XRF spectrum for sample 1 irradiated for 60 s

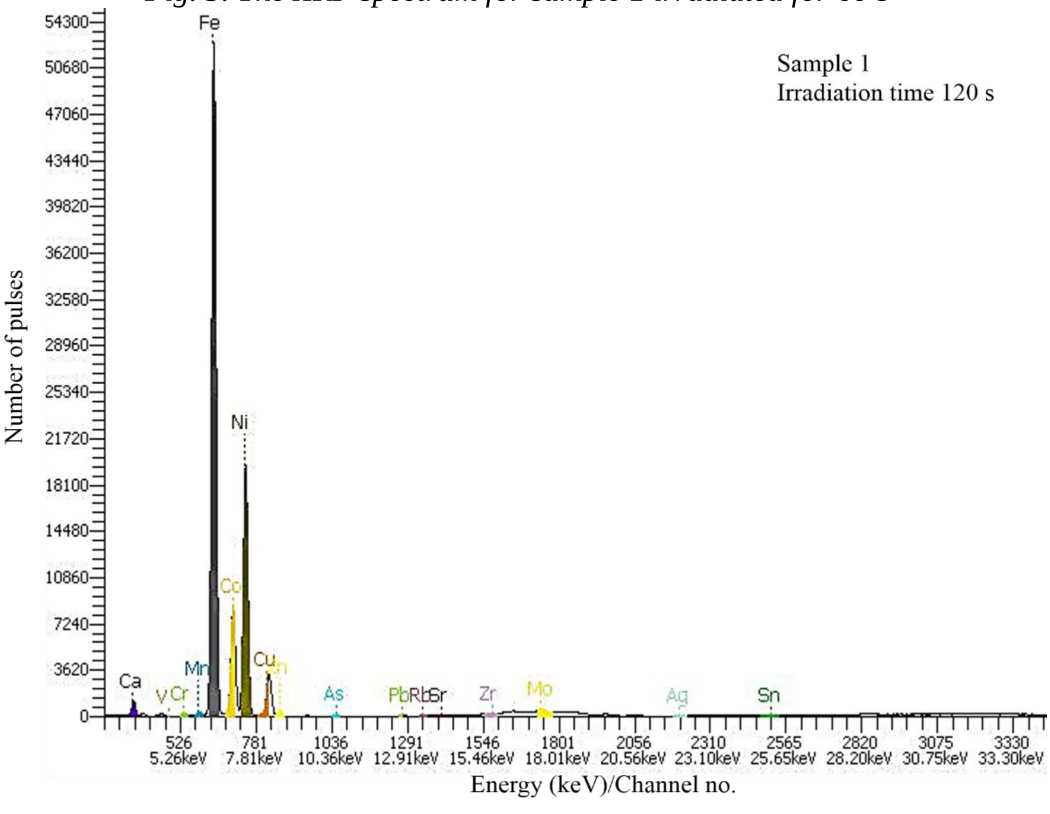

Fig. 4. The XRF spectrum for sample 1 irradiated for 120 s

Table 1. Criteria for acceptance of hazardous waste on landfill sites and limit values for leachates.

Chemical element	L/S = 2 l/kg	L/S = 10 l/kg	C_0
	ppm dry substance	ppm dry substance	ppm
Cr (total)	25	70	15
Ni	20	40	12
Cu	50	100	60
Zn	90	200	60
As	6	25	3
Pb	25	50	15
Mo	20	30	10
Sb	2	5	1

L/S - Liquid/Solid; C_0 - Leaching test

Table 2 shows very high values of heavy metals, for example Cr has values ranging from 2983.5±65.9 to 3300.2±70.4 ppm after irradiation at 60 s and values between 3017.0±46.9 and 3317.2±49.7 ppm after irradiation at 120 s, limit values for leachate being 15 ppm. The Ni concentration is between 53199.7±146.4 and 71807.3±174.2 ppm (60 s) and from 53187.2±103.3 to 70310.9±121.2 ppm (120 s), limit values for leachate being 12 ppm.

The Mo concentration is between 5.2±0.2 and 10.0±0.3 ppm (60 s) and between 4.9±0.2 and 7.8±0.2 ppm (120 s), the limit values for leachate being 10 ppm. It can be seen that Mo concentrations fall within the legal limits.

Table 2. Heavy metal (Cr, Ni, Mo) content in the investigated galvanic sludge samples

Irradiation time [s]	Sample No.	Chemical element					
		Cr		**Ni**		**Mo**	
		c (ppm)	**± E (ppm)**	**c (ppm)**	**± E (ppm)**	**c (ppm)**	**± E (ppm)**
60	**1**	3260.5	70.3	71807.3	174.2	6.0	0.2
	2	3068.5	67.0	62593.6	160.2	8.1	0.3
	3	3189.1	68.7	63496.6	162.1	7.9	0.3
	4	3169.6	68.2	69803.2	169.1	7.6	0.3
	5	3123.9	67.9	59601.8	157.0	8.0	0.3
	6	3174.4	68.9	57799.4	155.5	5.2	0.2
	7	2983.5	65.9	57409.3	153.2	10.0	0.3
	8	3099.8	66.9	53880.1	147.7	9.1	0.3
	9	3239.5	68.3	53199.7	146.4	7.0	0.3
	10	3300.2	70.4	67328.2	167.9	7.2	0.3
120	**1**	3273.0	49.5	70310.9	121.2	7.4	0.2
	2	3017.0	46.9	62897.9	113.5	6.2	0.2
	3	3186.9	48.7	68233.5	119.1	6.9	0.2
	4	3248.0	48.9	62582.7	113.5	7.7	0.2
	5	3054.0	46.8	57187.4	107.3	6.7	0.2
	6	3189.6	48.7	58761.8	110.4	6.8	0.2
	7	3169.9	48.4	60138.1	111.5	4.9	0.2
	8	3165.7	47.8	53504.5	104.0	6.0	0.2
	9	3227.2	48.1	53187.2	103.3	7.3	0.2
	10	3317.2	49.7	67337.9	118.3	7.8	0.2

In Table 3 it could be observed extremely high concentrations of heavy metals, e.g. Sb values ranging from 24.3±5.1 to 118.2±13.5 ppm (irradiation at 60 s), and between 14.4±2.5 - 56.8±6.2 (irradiation at 120 s), the limit values for leachate being 1 ppm. The Cu concentration has values ranging from 891.7±17.9 to 1147.9±21.0 ppm (irradiation at 60 s) and from 937.5±13.0 to

1138.6±14.7 (irradiation at 120 s), which exceed the limit values for leachate of 60 ppm.. The Zn concentration is ranging between 974.3±16.4 - 1517.3±21.2 (60 s) and between 1038.8±12.0 and 1520.4±14.9 (120 s), being much higher than the limit values for leachate of 60 ppm.

Table 3. Heavy metal (Sb, Cu, Zn) content in the investigated galvanic sludge samples

Irradiation time [s]	Sample No.	Chemical element					
		Sb		**Cu**		**Zn**	
		c (ppm)	**± E (ppm)**	**c (ppm)**	**± E (ppm)**	**c (ppm)**	**± E (ppm)**
60	**1**	-	-	1147.9	21.0	1219.8	18.9
	2	65.2	9.5	1087.7	20.1	1345.5	19.6
	3	50.4	8.2	1015.3	19.5	1371.3	19.9
	4	-	-	1038.7	19.6	1194.2	18.4
	5	24.3	5.1	1035.6	19.7	1265.8	19.1
	6	56.0	8.8	1001.6	19.4	1319.4	19.6
	7	-	-	973.2	18.9	1326.1	19.5
	8	24.5	5.1	929.8	18.4	1380.3	19.8
	9	-	-	891.7	17.9	974.3	16.4
	10	118.2	13.5	1110.0	20.5	1517.3	21.2
120	**1**	-	-	1100.8	14.4	1215.1	13.3
	2	-	-	1104.2	14.3	1336.3	13.8
	3	-	-	1138.6	14.7	1353.7	14.0
	4	56.8	6.2	1040.1	13.9	1291.1	13.6
	5	32.0	4.3	976.5	13.3	1219.5	13.1
	6	16.5	2.8	1055.0	14.1	1337.2	13.9
	7	-	-	1061.2	14.1	1324.6	13.8
	8	-	-	951.6	13.1	1477.5	14.5
	9	30.4	4.1	937.5	13.0	1038.8	12.0
	10	14.4	2.5	1085.0	14.3	1520.4	14.9

Table 4. Heavy metal (Fe, As, Pb) content in the investigated galvanic sludge samples

Irradiation time [s]	Sample No.	Chemical element					
		Fe		**As**		**Pb**	
		c (ppm)	**± E (ppm)**	**c (ppm)**	**± E (ppm)**	**c (ppm)**	**± E (ppm)**
60	**1**	414309.3	622.1	110.4	2.8	102.5	3.6
	2	418677.9	616.0	107.8	2.7	92.3	3.3
	3	427289.5	625.3	170.6	3.8	109.6	3.7
	4	401206.2	602.8	86.4	2.4	76.5	2.8
	5	425748.2	623.7	108.8	2.8	106.2	3.6
	6	433522.9	633.0	112.1	2.8	114.5	3.8
	7	427564.9	621.7	128.6	3.1	108.8	3.7
	8	452875.6	636.8	166.3	3.7	86.6	3.0
	9	459377.0	639.5	99.2	2.6	111.6	3.7
	10	430762.9	631.5	91.7	2.5	97.8	3.4
120	**1**	410169.6	435.1	101.6	1.9	104.4	2.5
	2	412671.1	432.2	113.0	2.0	101.8	2.5
	3	418092.8	438.4	176.0	2.7	106.8	2.6
	4	422513.4	438.5	104.7	1.9	102.0	2.5
	5	425470.1	435.1	110.3	1.9	109.1	2.6
	6	429380.3	443.8	102.4	1.9	110.1	2.6
	7	426420.8	441.3	117.0	2.0	98.3	2.4
	8	446105.9	446.4	167.9	2.6	105.0	2.5
	9	456994.5	450.1	94.4	1.8	113.0	2.6
	10	426611.6	442.5	93.4	1.8	101.1	2.5

In Table 4 high values of heavy metal concentrations can be observed, for example Fe has values ranging from 401206.2±602.8 to 459377.0±639.5 ppm (irradiation at 60 s), and from 410169.6±435.1 to 456994.5±450.1 ppm (irradiation at 120 s). Concentrations of As range from 86.4±2.4 to 170.6±3.8 ppm (irradiation at 60 s) and from 93.4±1.8 to 167.9±2.6 ppm (irradiation at 120 s), the limit value for leachate being 3 ppm. The concentration of Pb has values between 76.5±2.8 and114.5±3.8 ppm (60 s) and from 98.3±2.4 to 113.0±2.6 ppm (120 s), exceeding the limit value for leachate of 15 ppm.

Table 5. Heavy metal (Ag, Sn, V) content in the investigated galvanic sludge samples

Irradiation time [s]	Sample No.	Chemical element					
		Ag		**Sn**		**V**	
		c (ppm)	**± E (ppm)**	**c (ppm)**	**± E (ppm)**	**c (ppm)**	**± E (ppm)**
60	**1**	-	-	91.2	3.4	262.0	16.3
	2	4.7	0.2	82.9	3.2	256.7	15.9
	3	-	-	100.9	3.5	206.7	13.8
	4	-	-	87.5	3.3	227.3	14.6
	5	-	-	91.1	3.3	275.9	16.7
	6	7.9	0.3	81.8	3.2	295.4	17.4
	7	-	-	84.5	3.2	186.5	12.8
	8	12.7	0.5	106.5	3.6	210.5	13.8
	9	13.7	0.5	110.5	3.7	298.5	17.2
	10	-	-	82.8	3.2	200.4	13.6
120	**1**	3.1	0.1	123.2	2.8	255.5	11.3
	2	-	-	67.9	2.0	244.3	10.8
	3	17.2	0.4	73.9	2.1	233.0	10.6
	4	-	-	94.1	2.4	259.9	11.3
	5	-	-	84.9	2.3	204.0	9.5
	6	-	-	84.4	2.3	230.8	10.5
	7	1.8	0.1	106.5	2.6	244.2	10.9
	8	-	-	102.5	2.5	234.5	10.5
	9	-	-	72.3	2.1	237.5	10.5
	10	-	-	55.8	1.8	236.5	10.7

Table 5 shows that Ag has values are ranging from 4.7±0.2 to 13.7±0.5 ppm (irradiation at 60 s), and from 1.8 ±0.1 to 17.2±0.4 ppm (irradiation at 120 s). The concentration of Sn ranges from 82.8±3.2 to 110.5±3.7 ppm (irradiation at 60 s) and from 55.8±1.8 to 123.2±2.8 ppm (irradiation at 120 s). The concentration of V has values between 186.5±12.8 and 298.5±17.2 ppm (60 s) and from 204.0±9.5 to 259.9±11.3 ppm (120 s).

The relative errors of the technique are very low for the majority of the elements (several percents), but in the case of the irradiation time of 120 seconds the XRF technique is optimized, in the way that the signal-to-background ratio in the spectra is increased, the relative errors being improved by a factor of 1.16-1.68 (calculations not shown).

4. CONCLUSIONS

The galvanic technique brings significant damage to environmental factors due to the resulting sludge that is super-concentrated in heavy metals.

It has been shown that energy-dispersive X-ray fluorescence (ED-XRF) spectrometry analysis is very useful for the determination of heavy metal concentrations in hazardous industrial sludge at part-per-million level and with a good sensitivity, which can be improved by appropriate choosing the exposure time.

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