XRF ANALYSIS OF ARSENIC AND SELECTED METALS IN CONTAMINATED SAND FROM THE DISMANTLING OF INDUSTRIAL DISTILLATION PLANTS

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Abstract. *This paper refers to the application of XRF method for the simultaneous determination of arsenic and selected metals from waste samples resulted from the dismanlting of distilleries in the perimeter of Azomures S.A., Mures County, Romania. The dismantling operation was carried out by a specialized Romanian company, and from this operation resulted several refractory construction wastes, such as sands with a very high content of arsenic and its chemical compounds. In order to determine the arsenic and other metals concentration, the energy-dispersive X-ray fluorescence (ED-XRF) spectrometric technique was employed. Application of the ED-XRF method was performed in an accredited laboratory for the determination of toxic substances from various samples, using a Genius portable XRF (p-XRF) spectrometer manufactured by Skyray Instruments Inc.*

Keywords: portable ED-XRF; arsenic; industrial solid wastes; sands; distillation plants.

1. INTRODUCTION

Arsenic (As) is an extremely toxic chemical that is widely distributed in all environmental factors from both natural and anthropogenic sources. Studies show that more than 60% of the amount of As present in the environment is of anthropogenic origin. Several anthropogenic activities such as the use of copper arsenate treated wood, arsenic pesticides used in agriculture, burning fossil fuels and non-conforming storage of semi-processed industrial waste contribute to the increase of arsenic in environmental factors [1].

The migration of arsenic and its chemical compounds into soils depends on the absorption-desorption reaction in the solid phase (e.g., oxides and hydroxides of Fe, Al, Mn, in the clay composition) have an increased affinity for arsenic [2]. The average concentration of As in soil and sediment across Europe is less than 100 ppm [3] and between 11.6 and 12.2 ppm [4]. European laws for the regulation of the total As concentration in soils indicate between 10 and 500 ppm [5]. At global level, the average arsenic concentration in soils is lower and ranges between 5.0 and 7.2 ppm [6].

Waste sand samples resulting from the dismanlting of distilleries might pose a danger to the environment due to very high content of arsenic and other chemical compounds. In this respect, the hazardous waste treatment programs should be designed for the management of

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wastes and control the waste composition in order to select the appropriate way for its treatment, storage or disposal.

X-ray fluorescence spectroscopy with energy dispersion (ED-XRF) is a rapid and non-destructive analytical method for the simultaneous determination of a number of chemical elements in various complex matrices for interdisciplinary studies [7-9]. The spectrometers have been optimized to become mobile and portable instruments [10-14] in order to be deployed for different types of analyses in industrial sectors, pollution control and waste management [15, 16]. Nevertheless, in dependence on the analytical tasks, the technique could be used in complementarity with other multielemental nuclear techniques such as INAA [17], PIXE [18, 19] and PIGE [19]. With the evolution of the detection techniques and the X-ray tube shrinking, portable X-ray fluorescence (p-XRF) spectrometers have become more accessible [20, 21], displaying detection limits that are good enough for environmental monitoring and faster in operation than destructive methods such as AAS, ICP-MS and ICP-OES [22, 23].

p-XRF analysis is very sensitive to matrix effects, spectral interferences, and analysis conditions [21] which might affect the accuracy and precision of this technique. The aim of this work was to apply X-ray tube-based p-XRF with specific analysis modes for the determination of arsenic and other chemical elements in waste sands resulted from the dismantling of distilleries and to optimize the experimental conditions in order to diminish the analysis errors by improving the spectral peak-to background ratio for selected elements.

2. MATERIALS AND METHODS

2.1. SAMPLING AND SAMPLE PREPARATION

The sampling of sand contaminated with As was not performed *in-situ*. This operation was carried out after the dismantling of the industrial distillation columns, the decommisioning of the working area within the Azomures plant, the Mures County, Romania, and the taking over of all the hazardous wastes resulting from the decontamination work, as mentioned in Table 1.

Table 1. Quantities of hazardous waste containing As taken from the decontamination work

Type of the hazardous waste	The amount [tonnes]
metallic wastes contaminated with dangerous substances	81
waste with arsenic content	59
refractory materials waste	29
insulating materials waste	9
liquid waste	10

From the samples presented in Table 1, only the refractory wastes (29 tonnes) resulted from the decontamination of the Azomures industrial area of 800 m^2 were analyzed, namely an arsenic contaminated sand waste that was extracted from the interior of the dismantled distillation plant. Sampling of the contaminated sand was carried out on the industrial decontamination and neutralization platform of hazardous substances held by the authorized company in this field.

From a total of 29 tonnes of sand, 10 samples were collected, which were further processed in the laboratory for spectroscopic analysis by energy dispersion X-ray

fluorescence. Sample processing consisted in drying sand samples under conditions controlled by temperature (23°C) and humidity (40%) for 7 days, crushed and sieved to a 0.01 mm grain, then added to specific capsules covered with a Myler foil. The processed samples were subjected to X-ray exposure in two steps, namely for 60 and 120 seconds, respectively.

2.2. INSTRUMENTATION

Application of the p-XRF method was performed in an accredited laboratory, specialized for the quantitative and qualitative determination of hazardous chemicals in various samples, using a portable Genius XRF spectrometer (Skyray Instruments Inc., Dallas, USA) equipped with a large area Si detector with Be window and an excitation source of 40 kV/100 µA miniature X-ray tube with Ag-target [24]. The spectrometric system had an energy resolution up to 139 eV, and the detection limit of part-per-million (ppm) order. The calibration method was automatic, using an internal standard of Ag [16]. Data and ED-XRF spectra processing was achieved at the INPOLDE research center at Dunarea de Jos University of Galati, Romania.

3. RESULTS AND DISCUSSION

Concentrations of the As and the other heavy metals obtained were compared with the heavy metal concentration values of 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 by the legislation [25], given in the Table 2.

Table 2. Criteria for acceptance of hazardous waste on landfill sites. Limit values for leachate [25]

Element	L/S = 2 L/kg (Liquid/Solid)	L/S = 10 L/kg (Liquid/Solid)	C_0 (Leaching test)
	[ppm d.w.]	[ppm d.w.]	[ppm]
As	6	25	3
Ni	20	40	12
Cu	50	100	60
Cr (total)	25	70	15
Zn	90	200	60
Mo	20	30	10
Sb	2	5	1
Pb	25	50	15

Taking into account that a high peak-to background ratio in nuclear and atomic spectra leads to a more precise analysis [26], in this work we applied p-XRF for the determination of As and the other chemical elements (heavy metals or non-hazardous metals) in two steps, using different irradiation times (60 and 120 seconds). The approach was also used in a previous paper [16], demonstrating that longer irradiation times in XRF investigation of materials led to an optimized analysis of complex samples, in the way that the signal-to-background (S/B) ratio in the spectra is increased, the relative errors being improved.

The elements that could be analysed by p-XRF in the waste sands are: K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Rb, Sr, Y, Zr, Nb, Mo, Sn, and Sb. The concentrations of arsenic and selected chemical elements and the analysis errors, expressed in ppm, are presented in Tables 3 and 4 for each experimental time used for irradiation, as following: As, Ni, Cu, Cr (Table 3) and Zn, Mo, Sb, Pb (Table 4). Typical ED-XRF spectra are illustrated in Figs. 1 and 2, respectively, for a waste sand sample exhibiting the highest As concentration (sample no. 8) irradiated at 60 s and 120 s, respectively.
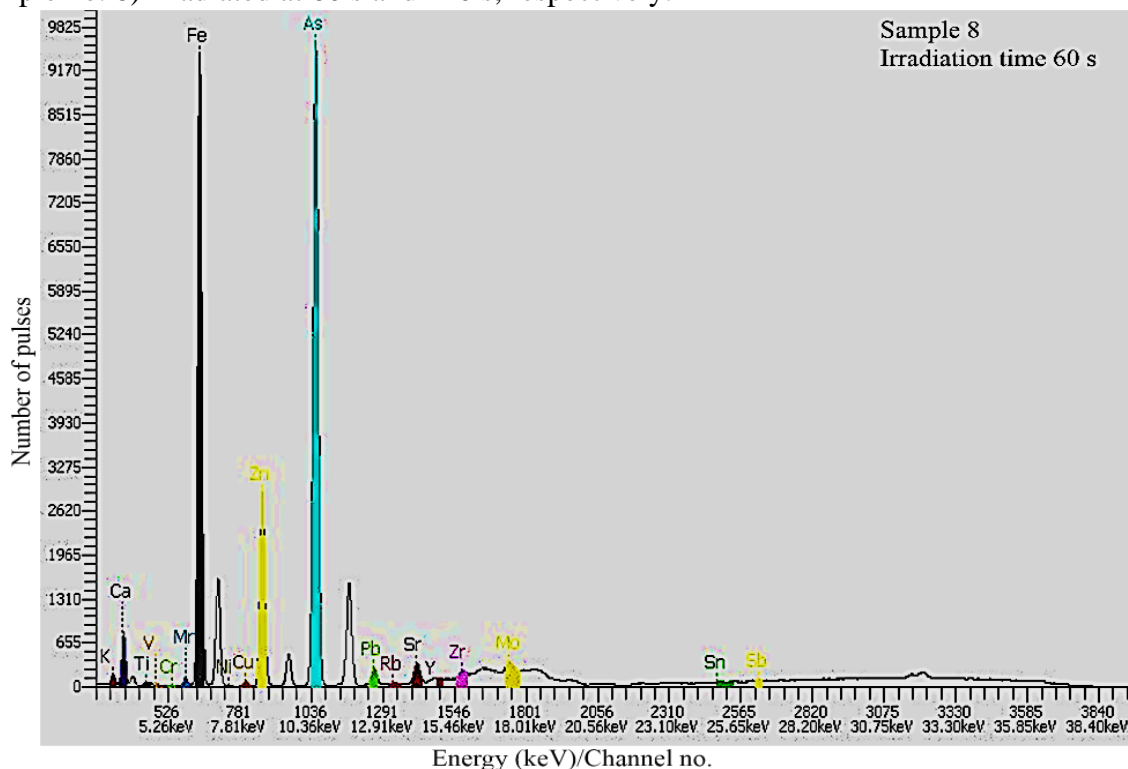

Figure 1. The XRF spectrum for the waste sand sample no. 8 irradiated for 60 s.
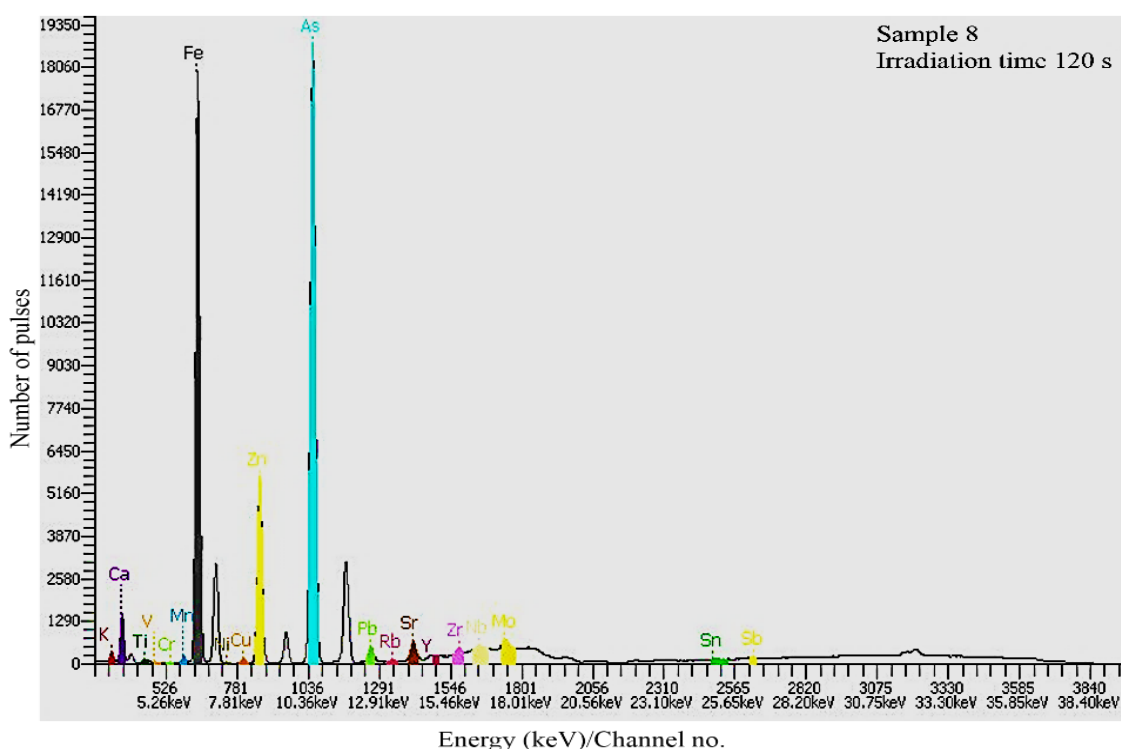

Figure 2. The XRF spectrum for the waste sand sample no. 8 irradiated for 120 s.

Comparative ED-XRF spectra for a sample of similar matrix (soil) with low As content, for both times of irradiation (60 s and 120 s), are shown in Figs. 3 and 4, respectively.
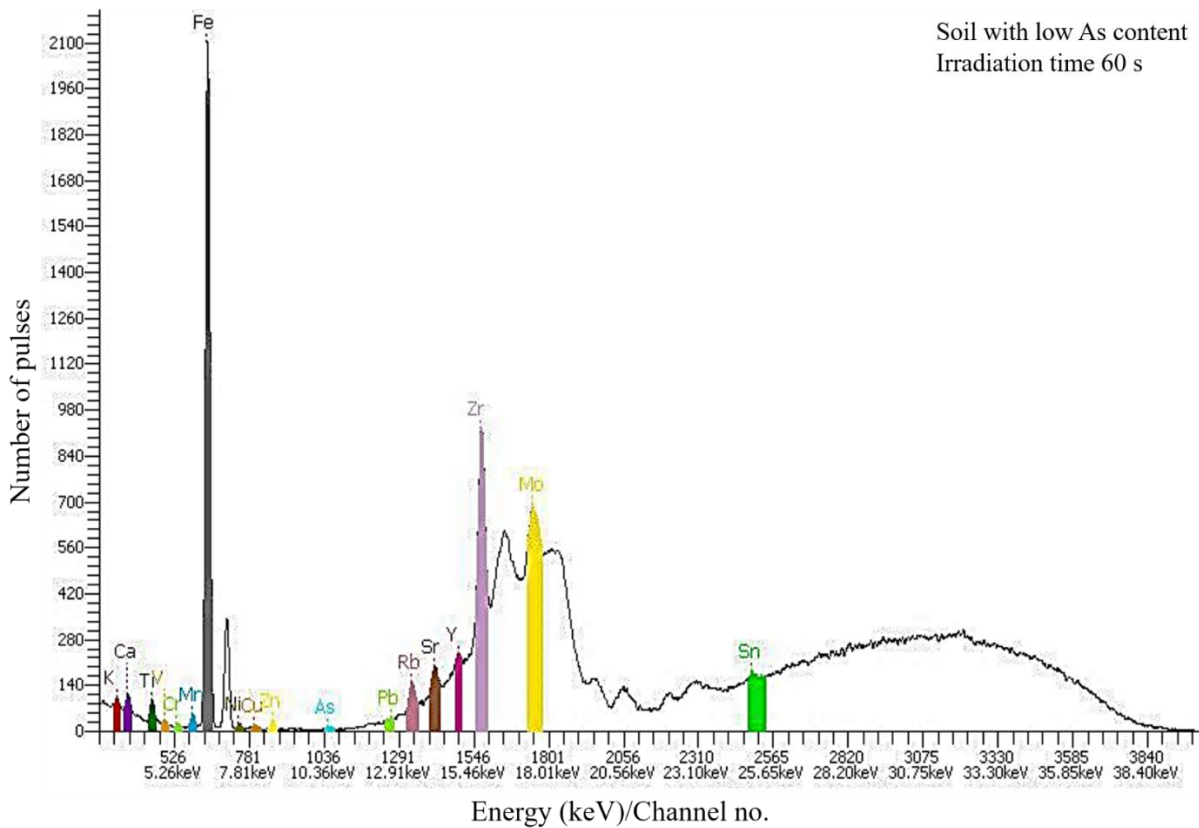

Figure 3. The XRF spectrum for a soil sample with low As content irradiated for 60 s.
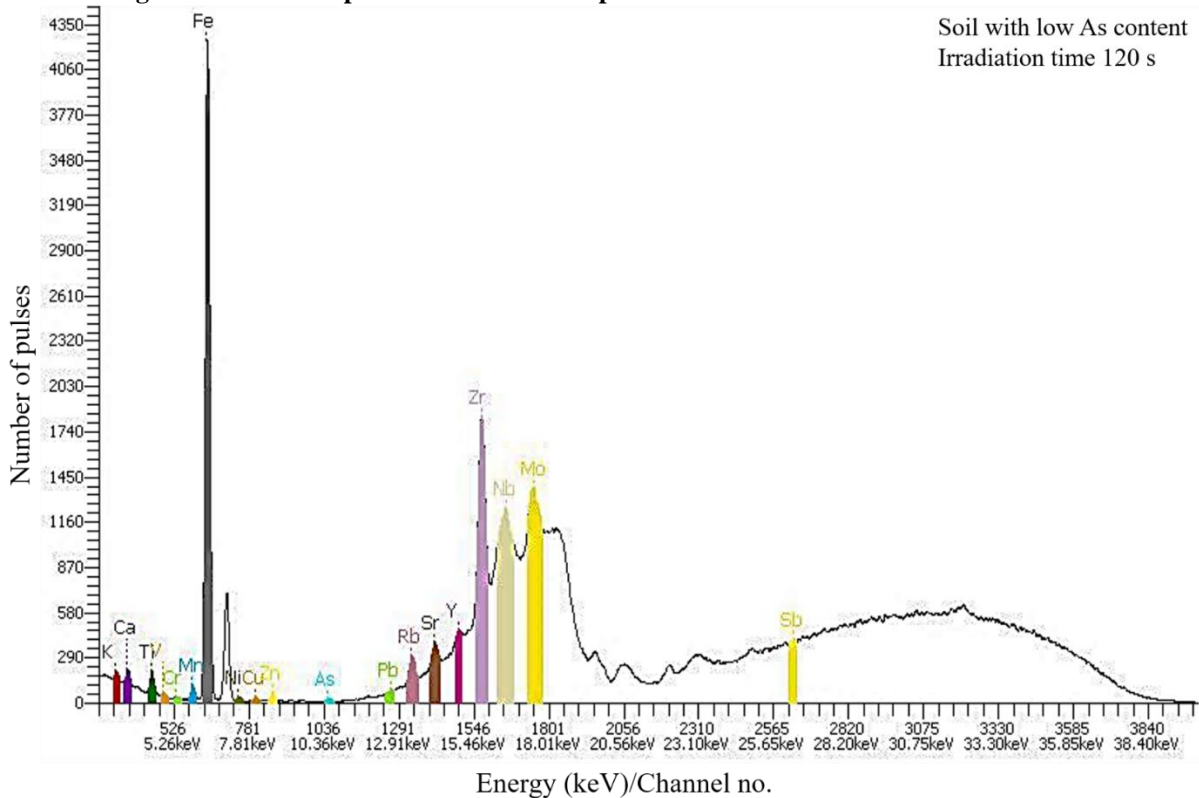

Figure 4. The XRF spectrum for a soil sample with low As content irradiated for 120 s.

Table 3. The concentration of As, Ni, Cu and Cr in the investigated sand hazardous waste.

Irradiation time [s]	Sample No.	Element concentration			
		As [ppm]	Ni [ppm]	Cu [ppm]	Cr [ppm]
60	1	13108.5±34.5	107.9 ±5.7	447.3±11.0	239.2±12.6
	2	13056.1±34.9	82.6 ±4.6	541.6±12.5	252.4±13.2
	3	12446.3±32.6	140.1±6.8	360.0±9.4	228.2±11.8
	4	12901.2±34.7	151.0±7.5	528.7±12.3	359.1±17.0
	5	11373.5±31.3	79.5±4.3	425.3±10.4	167.9±9.3
	6	13456.7±34.6	128.6±6.5	405.5±10.3	240.5±12.5
	7	11300.2±31.8	107.0±5.6	379.6±9.9	222.8±11.8
	8	13723.6±35.3	120.7±6.2	480.1±11.5	299.2±14.8
	9	11574.9±32.6	141.0±7.1	360.1±9.8	207.2±11.3
	10	12599.1±33.3	134.0± 6.7	410.3±10.3	657.7±24.6
120	1	12728.0±24.3	99.8±3.8	481.6±8.2	255.5±9.4
	2	12810.6±24.9	122.7±4.6	469.5±8.3	299.0±10.8
	3	12392.5±23.4	95.5±3.6	372.1±6.9	198.9±7.6
	4	12549.8 ±24.0	167.2±5.7	446.9±7.8	329.8±11.3
	5	11563.1±22.5	69.1±2.7	419.9±7.4	187.6±7.3
	6	13049.7±24.3	109.1±4.0	363.5±6.9	212.6±8.1
	7	11630.4±23.1	108.3±4.0	403.9±7.4	217.7±8.3
	8	13799.6±25.4	113.8±4.2	498.6±8.4	236.9±8.9
	9	11789.1±23.2	101.4±3.8	365.2±6.9	229.8±8.6
	10	12529.5±23.9	146.0±5.1	382.6±7.1	601.4±16.7

Table 4. The concentration of Zn, Mo, Sb and Pb in the investigated sand hazardous waste.

Irradiation time [s]	Sample No.	Element concentration			
		Zn [ppm]	Mo [ppm]	Sb [ppm]	Pb [ppm]
60	1	12300.4±55.0	10.3±0.3	107.4±11.4	912.1±11.5
	2	14887.6±61.3	9.8±0.3	0.8±0.2	867.6±11.4
	3	11967.4±52.6	10.3±0.3	21.3±4.0	875.2±10.9
	4	13097.5±57.5	7.6±0.3	197.6±16.1	871.8±11.4
	5	11278.7±51.2	10.2±0.3	2.4±0.7	738.2±10.1
	6	11969.8±53.7	10.4±0.3	-	824.5±10.8
	7	11566.2±52.9	7.1±0.2	141.3±13.2	785.2±10.6
	8	13096.0±56.7	10.3±0.3	137.4±13.1	861.0±11.2
	9	10550.4±51.2	9.9±0.3	130.3±12.8	776.0±10.2
	10	11818.1±53.1	10.0±0.3	255.0±18.0	794.9±10.6
120	1	12225.9±39.1	9.0±0.2	145.0±9.6	938.0±8.3
	2	14914.7±44.2	10.0±0.2	103.8±8.2	868.9±8.2
	3	11787.9±37.5	10.0±0.2	93.2±7.3	803.9±7.5
	4	12605.9±39.6	10.5±0.2	43.5±4.8	819.3±7.8
	5	10643.6±35.5	10.3±0.2	26.3±3.4	767.3±7.3
	6	12909.4±39.7	10.8±0.2	204.7±11.4	806.9±7.6
	7	11276.7±37.5	5.5±0.1	51.0±5.3	806.1±7.7
	8	13090.9±40.7	10.4±0.2	94.4±7.6	843.7±7.9
	9	10625.0±36.1	10.2±0.2	103.9±7.9	779.3±7.5
	10	12699.6±39.6	10.2±0.2	141.6±9.4	868.3±8.0

From the spectra displayed in Figs. 1 and 2 and Tables 3 and 4, it results that the utilization of the experimental time of 120 s is more advantageous for increasing the S/B ratio for several elements, including arsenic, thus diminishing the analysis errors (e.g., relative standard deviation). Tables 3 and 4 shows very high values of arsenic and heavy metal concentrations in the waste sand materials, in most cases exceeding the legislated values presented in Table 2.

4. CONCLUSIONS

Industrial wastes pose a major danger to environmental factors and to the health of people, and greater attention should be paid to this problem. There is a need in the future for new techniques and technologies much less polluting that would restructure the model of existing industrial processes. It can be seen that the sand resulting from the dismantling of the distillation columns and the decontamination of the working area of 800 m^2 is highly contaminated with metalloids and heavy metals such as As, Zn, Ni, Cu, Cr, Mo, Pb, Sb. The ED-XRF multielement analysis technique with portable instrumentation (p-XRF) has proven to be suitable for rapidly and efficiently determination of the concentrations of chemical elements with extremely high toxicity, ten times higher than the legislated levels. The p-XRF analyses could be optimized by increasing the irradiation time, thus increasing the number of quantifiable elements in the industrial waste samples and improving the signal-to noise ratio in the XRF energetic spectra.

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