[4] Bartoňová l., Unburned carbon from coal combustion ash: An overview, Fuel Processing Technology vol. 134, pp. 136–158, 2015

[5] Predeanu G. et al., Coal ash characteristics to assess its possible uses, International Multidisciplinary Scientific GeoConference : SGEM : Surveying Geology & mining Ecology Management; Sofia, pp. 309-316, 2013.

[6] Popescu L.G. et al., Analysis of heavy metal content to evaluate leaching characteristics of coal ash wastes, International Multidisciplinary Scientific GeoConference : SGEM : Surveying Geology & mining Ecology Management; Sofia Vol. 1, pp. 33-39, 2013

[7] Popescu L.G. et al, Environmental impact of ash and slag deposit Ceplea Valey of Energetic Complex Turceni, International Multidisciplinary Scientific GeoConference : SGEM : Surveying Geology & mining Ecology Management; Sofia, Vol. 5, pp. 345-352. 2012

[8] Bruno V. et al, Undifferentiated Inorganics in Coal Fly Ash and Bottom Ash: Calcispheres, Magnesiacalcispheres, and Magnesiaspheres, Minerals, vol. 8, issue 4, no. 140, pp. 1-27, 2018

RECENT APPROACHES REGARDING THE SELECTION OF APPROPRIATE METHODS FOR THE CHARACTERIZATION AND ANALYSIS OF USED OILS IN ORDER TO ASSESSMENT OF THE METALS CONTENT

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ABSTRACT

This paper presents a recent study regarding choosing and optimizing of the appropriate test methods to characterization and analysis of used oils from different sectors of activity, in order to evaluate the heavy metal content. In the first step, the samples preparation stage for metal analysis, a number of preparation methods have been tested and finally chosen as optimal, a microwave digestion method. For comparison the metals were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS). The results obtained by the two methods are comparative and indicate in all analyzed samples the presence of heavy metals such as Fe, Ni, Zn, Cr and Mn. The methods used have been demonstrated to be appropriate by use of the certified reference material for metals in lubricating oils. From the results obtained it is found that the methods of characterization and analysis can be used as optimal and good methods for evaluation of the content of metals in used oils

Keywords: used oil, heavy metals, ICP-MS, AAS, characterization

INTRODUCTION

The waste oils are mineral oils which during use have lost their characteristic properties, becoming unsuitables for subsequent use for the same purpose. Due their persistence and their ability to spread on soil and water surfaces, waste oils are considered environmentally hazardous, forming a film that do not allow the oxygen to penetrate, resulting in a significant environmental degradation.

The presence of metals in waste oils, on the one hand, induces a major impact on environmental pollution through their emission into the atmosphere during combustion processes or uncontrolled co-incineration in boilers and thermal power plants. On the other hand, control of the presence of metals in petroleum derived products is an important aspect in the petrochemical industry. It is well known that the presence of metals in liquid fuels, even at trace levels, can lead to the formation of solid particles that are usually called gum. These gum is deposited on the internal surface of the engines, reducing their durability and efficiency [1, 2].

Considering these aspects and taking into account that most metal analysis techniques allow their determination in aqueous solution, a number of methods for the preparation and processing of used oils compatible with metal analysis techniques in the solution have been proposed in the literature. For this purpose, for the determination of metals from the waste oils or petroleum oils, either direct methods without prior pre-treatment, such as NAA (neutron activation analysis), X-ray spectroscopy, DS-GFAAS (atomic absorption spectrometry with furnace graphite) or coupled techniques such as LA-ICP-MS (laser ablation coupled with an inductively coupled plasma mass spectrometer) or indirect

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methods by which the samples can be processed by wet or dry digestion, emulsification, dilution or extraction [3-7].

Mainly, for the digestion of the organic matter, liquid oxidants such as HNO_3 and H_2O_2 or gases (air or oxygen) are used. These methods based on the use of reagents in the liquid or gaseous phase are classified as wet digestion or combustion methods. In wet digestion, the purity of the reagents is an important aspect due to the risk of the contamination and, for this reason, it is generally necessary to purify them by distillation. In the case of the burning gases, they are expected to be marketed in a pure state and a lower risk of contamination [4].

The use of the closed cells for digestion present the advantage of being isolated from various contaminants in the laboratory compared to open systems, allowing the analysis of metals to trace. Another advantage of closed systems is that they prevent the loss of volatile species that can occur when digestion is performed in open vessels [4, 8, 9].

Ultrasonic extraction is referred to as the solubilization process of the analyte from sample matrix. This process is sometimes necessary in sample preparation process for analysis in situations where it is necessary to evaluate only the extractable analyte and not all of the sample matrix or, to maintain the integrity of the some species or compounds, especially in speciation analyzes. Extraction with diluted solution can be used in order to obtain the extraction of metals from waste oils in form of the Na or Ca salts, and also as sulfur, nitrogen, chlorine or porphyrin species [9-11].

The formation of the emulsions and micro emulsions from oils is a simple and rapid pre-treatment to overcome oil viscosity limitations and their direct introduction into analytical equipment's (AAS, ICP-EOS or ICP-MS). A micro emulsion is an emulsion in which the droplets are much smaller (between 10 and 100 nm), where the light passes through a minimally scattered dispersion and appears to be as a clear solution. For the preparation of emulsions, certain parameters must be respected, such as optimizing the amount of the oil sample, surfactant, acid water and the agitation method to produce a low viscosity and a stable emulsion. As a general rule, a hydrophilic surfactant is required to produce an oil-in-water emulsion and a hydrophobic surfactant to produce an oil-in-water emulsion [12, 13].

The paper aims to present selection and optimization steps in order to obtain an optimal method to process vary types of the used oils, from different economic sectors to determine heavy metal content.

EXPERIMENTAL PART

These study have been analyzed a series of the heavy metals from five types of waste oils from different fields of activity, using 4 methods to bring the sample into an aqueous solution.

The description of the analyzed oils and the processing and analysis methods are presented below:

U1 - motor and transmission mineral used oils;

U2 - non-chlorinated hydraulic mineral oil;

U3 - non-chlorinated unprocessed mineral oil from metalworking;

U4 - waste oil from radiators;

U5 - used oil from oil-water separators.

After bringing the samples in aqueous solution, they were analyzed by atomic flame absorption spectrometry (AAS) on the 0.1-0.5 mg / l calibration curve for Zn, Mn and Fe and inductively coupled plasma mass spectrometry (ICP-MS), calibration curve 10-50 µg/l for Ni and Cr. For each sample, three analyzes were performed, the result of the concentration obtained for each metal being the average of the three determinations.

Table 1 describes the processing methods for the waste oil samples selected from the literature and optimized according to the sample matrix.

Table 1 – Methods of processing of the waste iol samples in order to determination of the heavy metals [4, 9, 13].

Method of processing	Heavy metals	Analytical technique	Procedure
Method I (Wet digestion in open cells)	Zn, Ni, Mn, Fe, Cr	ICP-MS AAS	0.5 grams of waste oil sample was weighed accurately into a 100 ml volumetric flask. 10 ml of a mixture of HNO_3 (65%) -H_2O_2 30%) (3: 1 v / v) was added and kept for 15 minutes to the room temperature. The sample was heated on a hot plate at 80 °C until was obtains a clare solution. The solution was allowed to evaporate and the dry mass was dissolved in 5 ml of 0.2 M HNO_3. The sample was filtered through a 0.45 µm filter paper and brought to a final volume of 25 ml in a quartz with ultrapure water for analysis on AAS / ICP-MS equipment's.
Method II (Microwave digestion)	Zn, Ni, Mn, Fe, Cr	ICP-MS AAS	0.25 grams of waste oil sample was introduced into the digestion cell. 9 ml of HNO_3 (65%) and 1 ml of H_2O_2 (30%) were added. The digestion setting programs is presented below:
			Stages: 1 / 2 / 3
			Temperatures (°C): 200 / 200 / 60
			Microwave (Watts): 1500 / 1500 / 0
			Time (minutes): 20 / 20 / 20
			After the digestion was completed, solution from the digestion cell was filtered through blue band filter paper and brought to a volume of 25 ml. Subsequently was analyzed by AAS/ICP-MS equipments.
Method III (Ultrasonic extraction)	Zn, Ni, Mn, Fe, Cr	ICP-MS AAS	5 grams of waste oil sample was weighed into a 50 ml iodometric flask over which 20 ml of a 1: 1 v/v HNO_3 (5%)/HCl (0.2%) aqueous solution was added. The mixture was stirred for 30 seconds and then placed in an ultrasonic bath (20 minutes at power 170 Watts) to extract the metals from the oil in the acid solution. Subsequently, the mixture was centrifuged for 20 minutes at 4000 rpm to separate the two phases. The oily upper phase was aspirated and

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			the lower phase transferred to a volumetric flask and analyzed by AAS / ICP-MS equipment's.
Method IV (Extraction induced by bursting of the emulsion)	Zn, Ni, Mn, Fe, Cr	ICP-MS AAS	5 ml of waste oil sample was vigorously shaken with 5 ml of a Triton X-100 and HNO_3 mixture solution of 7% w/v Triton X-100 and 10% v/v HNO_3) in a cap tube. After the emulsion was formed, the tube was transferred to the controlled temperature in a water bath and maintained at 80 ± 2 °C where it was heated until the emulsion burst. Three phases are separated by breaking the emulsion: (i) the upper phase: an organic phase containing only the oil; (ii) a surfactant-rich phase (iii): an acidic aqueous phase containing the extracted metals. The total volume of the aqueous phase was collected using a micropipette and analyzed by AAS / ICP-MS equipment's.

Table 2 presents the experimental results obtained by applying the analytical methods described above.

Table 2 - Experimental results

Methods	Parameter/ heavy metal	Measure unit	Results (average values)				
			U1	U2	U3	U4	U5
Method I	Zn	mg/kg	133.6	289.9	24.2	2.87	3.13
	Ni	mg/kg	1.78	2.03	2.93	0.77	1.20
	Mn	mg/kg	5.19	2.43	4.53	6.16	1.15
	Fe	mg/kg	8.08	7.6	5.17	2.65	1.19
	Cr	mg/kg	1.3	1.62	1.78	0.57	0.68
Method II	Zn	mg/kg	137.9	323.2	29.8	2.19	4.65
	Ni	mg/kg	2.07	2.37	3.48	0.86	1.46
	Mn	mg/kg	7.20	3.61	6.01	8.64	3.02
	Fe	mg/kg	9.94	9.82	7.28	3.97	2.92
	Cr	mg/kg	2.10	2.05	1.96	0.88	0.92
Method III	Zn	mg/kg	18.03	21.9	14.31	0.14	0.97
	Ni	mg/kg	0.12	0.93	1.09	0.17	0.43
	Mn	mg/kg	1.08	0.54	1.21	0.15	0.98
	Fe	mg/kg	1.14	1.62	1.34	0.18	0.12
	Cr	mg/kg	0.28	0.54	0.23	0.12	0.17
Method IV	Zn	mg/kg	54.03	67.8	19.5	1.83	1.98
	Ni	mg/kg	0.35	1.12	1.67	0.54	0.69
	Mn	mg/kg	2.17	1.39	2.48	1.97	1.14
	Fe	mg/kg	3.08	2.18	1.32	1.04	1.02
	Cr	mg/kg	1.01	1.18	1.28	0.26	0.23

In the following figures are graphically represented the evolution of the concentration values obtained for each method applied for Zn, Ni, Mn, Fe and Cr:

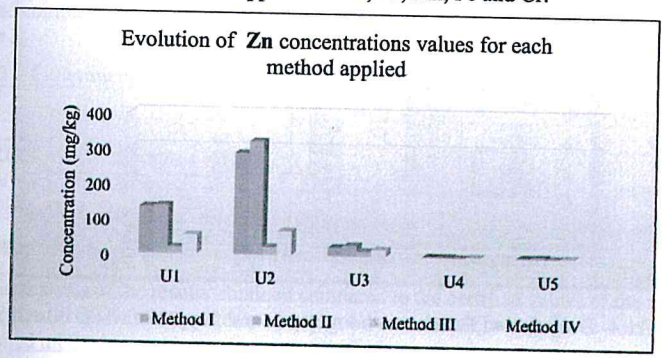

Figure 1- Evolution of Zn content – 4 methods and 5 types of waste oil samples

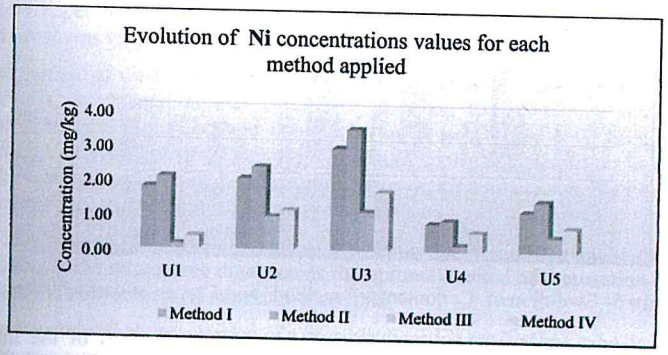

Figure 2- Evolution of Ni content – 4 methods and 5 types of waste oil samples

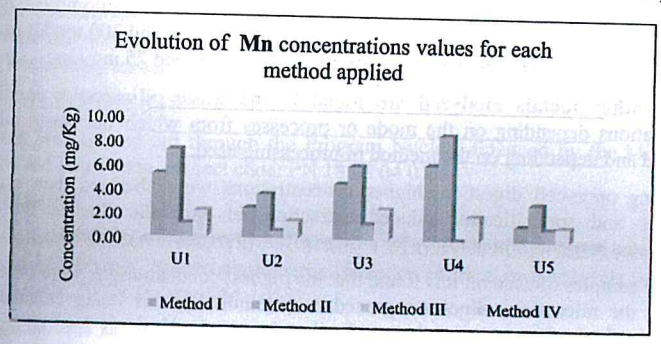

Figure 3- Evolution of Mn content – 4 methods and 5 types of waste oil samples

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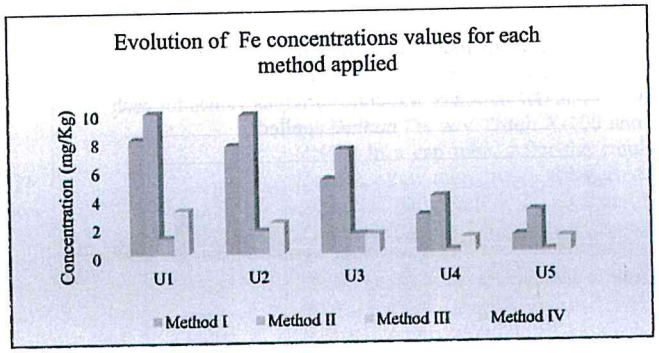

Figure 4- Evolution of Fe content – 4 methods and 5 types of waste oil samples

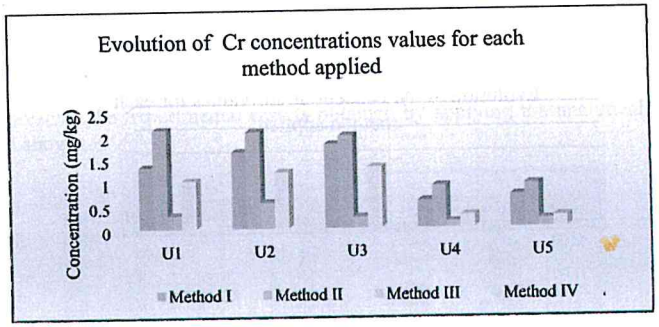

Figure 5- Evolution of Cr content – 4 methods and 5 types of waste oil samples

From the analysis of the obtained results can highlight a series of the important discussions:

- **Zinc** is predominantly found in the U1 and U2 oil samples, automotive oils, the concentration of which exceeds 100 mg / kg in the U1 sample and 300 mg/kg in the U2 sample; in other samples the zinc concentration does not exceed 25 mg / kg;

-**all the other metals analyzed** are found in the waste oil samples in different concentrations depending on the mode or processes from which the waste oils were generated and depending on the method of processing used;

- by using open-cell digestion, higher concentrations were obtained than ultrasonic extraction and emulsification-induced extraction, in particular due to the use of concentrated reagents which allow for a more efficient extraction of metals;

- for all 5 samples of used oil it is found that the highest concentrations were obtained by applying the microwave digestion procedure (Method II), this being considered the optimal method of processing the used oils when an analysis is desired total and quantitative content of metals; the other methods can be used successfully for specialty studies or when looking for a particular analyte in the sample.

In order to verify the performance of Method II, a Certified Reference Material (NIST 1084a) was used for the analysis of nickel, iron and chromium metals. The metals were analyzed comparatively both equipment's by ICP-MS and AAS. The results are presented in table 3.

Table 3 – Experimental results by using a Certified Reference Material (NIST 1084a)

			Heavy metal/ concentrations (mg/kg)		
			Ni	**Fe**	**Cr**
CRM (NIST 1084a)	Certified values		99,7 ± 1,6	98,9± 1,4	98,3 ± 0,8
Method II	Values obtained	ICP-MS	98,4 ± 2,4	97,6± 1,9	97,9 ± 0,9
		AAS	97,8± 1,5	98,1± 1,1	97,1± 1,2

From the analysis of the results obtained compared to the certified values of the reference material used (NIST 1084a) reveals a very good correlation, which gives confidence to this applied method.

CONCLUSIONS

In present paper we present selection and optimization steps to obtain an adequate method to process vary types of the used oils in order to determine heavy metal content.

For each sample of waste oil we apply 4 different experimental methods selected from literature by documentation and optimized according to the sample matrix. The processing methods described and applied in the present study have been selected considering that each waste oil sample is different depending mainly on how it was generated and is an ensemble of complex matrices which may contain other organic or solvent impurities that make it difficult to process them.

Of the four methods of waste oil samples processing applied in this study are clearly distinguishable the microwave digestion as the optimal method of preparation when an analysis of the total content of metals in waste oils.

It can be concluded that the selection of a possible digestion method has to be done taking into account a number of factors, among which we mention: the clear objectives of the analytical determination, the type of matrix to be analyzed, the presumed values of the elemental concentrations chemical samples in the sample to be analyzed, potential interference that may occur, potential emissions or contamination that may occur and, last but not least, safety measures to be taken.

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REFERENCES

[1] Collins GE, Morris RE, Wei J-F, Smith M, Hammond MH, Michelet V, Winkler JD, Serino PM, Guo Y. Spectrophotometric detection of trace copper levels in jet fuel. Energy & fuels, 2002; 16: pp.1054-1058.

[2] Lu Q, Wei J-F, Collins GE, Morris RE, Serino PM, Guo Y. Rapid determination of dissolved copper in jet fuels using bathocuproine. Energy & fuels, 2003; 17: pp.699-704.

https://doi.org/10.5593/sgem2018/4.2

[3] Bakircioglu D, Kurtulus YB, Yurtsever S. Comparison of extraction induced by emulsion breaking, ultrasonic extraction and wet digestion procedures for determination of metals in edible oil samples in Turkey using ICP-OES. Food chemistry, 2013; 138: pp.770-775.

[4] Mello PA, Pereira JS, Mesko MF, Barin JS, Flores EM. Sample preparation methods for subsequent determination of metals and non-metals in crude oil - A review. Analytica chimica acta, 2012; 746: pp.15-36.

[5] Pehlivan E, Arslan G, Gode F, Altun T, Musa Özcan M. Determination of some inorganic metals in edible vegetable oils by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Grasas y Aceites, 2008; 59: pp.239-244.

[6] Cassella RJ, Brum DM, Lima CF, Caldas LFS, De Paula CER. Multivariate optimization of the determination of zinc in diesel oil employing a novel extraction strategy based on emulsion breaking. Analytica chimica acta., 2011; 690: pp. 79-85.

[7] Torres S, Martínez LD, Pacheco PH. Determination of arsenic species distribution in extra virgin olive oils from arsenic-endemic areas by dimensional chromatography and atomic spectroscopy. Journal of Food Composition and Analysis, 2018; 66: pp. 121-126.

[8] Kim L, Muresan AM, Cuciureanu A, Guta D, Arama M, Cristea NI, Dediu V. Experimental models of characterization and analysis of industrial waste. 20th International Symposium - The Environment and the Industry (SIMI 2017). National Research & Development Institute Industrial Ecology Ecoind, 2017,

pp. 142-150.

[9] Soin AV, Maryutin TA, Arbuzova TV, Spivakov BYa. Sample preparation in the determination of metals in oil and petroleum products by ICP MS. Journal of Analytical Chemistry, 2010, 65: pp. 571-576.

[10] De Moraes DP, Antes FG, Pereira JS, dos Santos MdFP, Guimarães RC, Barin JS, Mesko MrF, Paniz JN, Flores ErM. Microwave-Assisted Procedure for Salinity Evaluation of Heavy Crude Oil Emulsions. Energy & Fuels, 2009; 24: pp. 2227-2232.

[11] Trindade ASN, Dantas AF, Lima DC, Ferreira SLC, Teixeira LSG. Multivariate optimization of ultrasound-assisted extraction for determination of Cu, Fe, Ni and Zn in vegetable oils by high-resolution continuum source atomic absorption spectrometry. Food Chemistry, 2015; 185: pp. 145-150.

[12] Burguera JL, Avila-Gómez RM, Burguera M, de Salager RA, Salager J-L, Bracho CL, Burguera-Pascu M, Burguera-Pascu C, Brunetto R, Gallignani M. Optimum phase-behavior formulation of surfactant/oil/water systems for the determination of chromium in heavy crude oil and in bitumen-in-water emulsion. Talanta, 2003; 61: pp. 353-361.

[13] Munirah A Z, Wan Kamaruzaman WA, Ananthy R, Catrina Ng. Concentration of heavy metals in virgin, used, recovered and waste oil: a spectroscopic study. Procedia Environmental Sciences, 2015; 30: pp. 201 – 204.

RECIRCULATION OF ASH AND SLAG WASTE AT THE CERAMIC BRICK PRODUCTION

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ABSTRACT

The flue ash and slags are accounting a significant part of thermal electric complexes waste, which operating on solid energy fuel. Most of this by-product does not find further application, accumulating in ash-disposal dump areas. Meanwhile, ash-and-slag wastes can widely use as raw materials for the production of building materials. Considering the world trend towards an increase in the share of waste secondary use, it is necessary to forecast their subsequent processing in Russia too.

The purpose of work was modeling composition of ceramic charge for Shelangovsk brick factory using Kazan CHP (Combined heat and power plant) furnace-waste as filler. For this, ash and slag wastes were mixed in various amounts with the working charge and with the initial raw clay material. After molding of ceramic small brick, samples were fired at T = 980°C and then the end products were tested for strength.

The results showed that addition 10, 15 and 20 percent of ash to working charge are consistently increasing the strength of ceramic products in compression tests. During the process of manufacturing ceramic products tested changes of their unit-weight and heat setting degree. All products withstand a load of at least 100 MPa. The maximum value of strength is achieved when introducing into the working charge 20% of the ash additive. Simultaneously with the increase in mechanical strength by 12-13%, unit-weight is decreases. At working with natural clay, the ash additive is not so effective. After carrying out physical and mechanical tests, the ceramic products were examined with an SEM and thermal X-ray analysis. The aim of the research was to establish how the ash additives affect the processes of phase transformations occurring in the batch. To determine specificity of reactions between waste and charge minerals was used X-ray analysis. Results are showed that ash and slag waste behaves as active fillers and forming new mineral phases.

The obtained results show that the use of ash wastes of Kazan CHP as mineral fillers of ceramic batch is quite acceptable. They introduce improved for physical and mechanical characteristics of wall bricks while reducing their weight. At the same time, the ash additive takes an active part in mineral formation processes, increasing the amount of crystallization contacts in ceramic products.

Keywords: Combined heat and power plant, flue ash and slag waste, recycling, ceramic production.

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