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Influence of Mineralization and Analysis Technique on the Results of Determination of Iron and Nickel in Industrial Wastes

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Abstract

An analysis of industrial wastes is a difficult and complicated procedure because of their complex contents which depend on the nature of production and technology being used. The present paper gives selected analytical problems concerning the determination of nickel and iron in wastes coming from the metalurgical industry. It has been concluded that the methods of mineralizing wastes need to be adjusted to their complexity. For emulsion wastes the most suitable method is microwave mineralization.

Keywords: mineralization, heavy metals, industrial wastes

Introduction

Industrial wastes are one of the most prevalent sources of water pollution. In 1997 in Poland alone their output was 8542.8 Hm^3; 227.1 Hm^3 of it were washed away down drains, whereas the rest found its way to receivers and contributed to pollutions of primary and secondary character [1]. Considering data as well as protection of the evironment, it is really necessary to treat sewage on the spot; the exact determination of its content is, among others, a guarantee that the procedure has been properly carried out. It is noteworthy that wastes coming from different branches of industry differ considerably from one another and are difficult to characterize. The constituents commonly found in industrial wastes include such synthetic organic substances as oils, fats, resins, dyes, phenols, tars, detergents, heterocyclic compounds, chlorine derivatives of organic compounds, hydrocarbons and their derivatives as well as such inorganic substances as acids, bases, heavy metals in different chemical forms, phosphates, chlorides, sulphides, sulphates, ammonium compounds and nitrates [2]. The type and amount of wastes produced depend upon the nature of production, the material and the technology being used. The differentiated content of wastes makes their treatment and analysis difficult and unique.

The present paper gives selected analytical problems concerning the determination of nickel and iron in wastes coming from the metalurgical industry. The wastes under investigation included used turning and grinding coolants, wastes coming from the washing of elements involved in turning, grinding and hardening, used degreasing and neutralizing baths, acid and chromic baths, and electrotechnical coolants. The treatment worked out for such wastes takes the purification of emulsion wastes including the eduction of oils into account. The purfication scheme is shown in Fig. 1. Unfortunately, the more new coolants (whose composition is their producer's secret) introduced, the more difficult the de-emulsification. To make things worse, each workshop uses their own substances. As a consequence, the problems of total purification of wastes and their analysis arise.

An analysis of metals in the complex organic matrix entails the mineralization of wastes. A great number of methods of both dry- and wet-mineralization including

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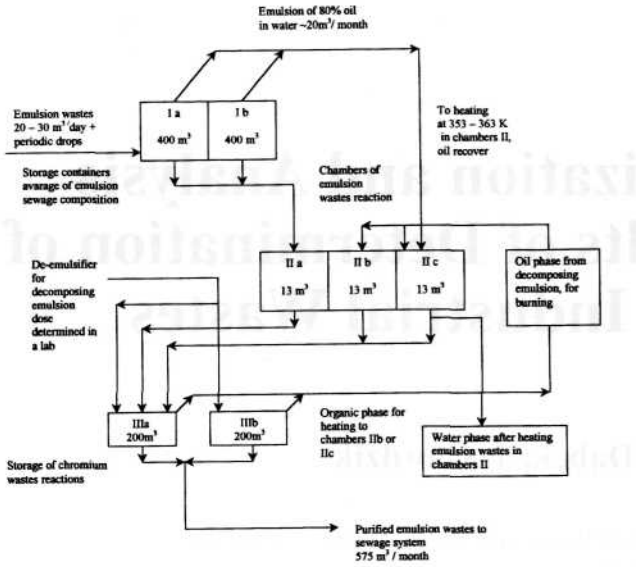

Fig. 1. Technological scheme of an emulsion sewage - treatment plant.

different oxidizers are described in literature [3-5]. Microwave mineralization is becoming more and more popular. This stage of treating a sample, crucial to transferring metals to their ionic forms, is the same for all waters and wastes, regardless of their character, in prevailing analytical procedures. The mandatory standards [6-9] affecting the determination of metals in wastes, recommend transitory heating with such oxidizers as HNO_3, H_2SO_4, H_2O_2.

Since the results of analysing nickel and iron in wastes coming from the metalurgical plant obtained according to the mandatory procedures in the plant laboratory differed considerably from those of the control unit, we found it necessary to account for this fact. The present study concentrated upon analysing the influence of the ways of mineralizing wastes and of the methods of analysing metals upon the result of their determination.

Experimental Procedures

The first stage of the study consisted of testing the suitability of selected methods of mineralization for the decomposition of wastes under investigation, whereas at the second stage the influence of the analytical method upon the determination of the contents of nickel and iron in a given sample was estimated. Following the process of de-emulsification (sample I) and that of total purification (sample II), the wastes were put to the test. Mineralization was carried out as follows:

1. According to the standard PN-92/C-04570/01 for determining metals by te AAS method - Method A.

50 cm^3 of the sample were placed in a test-tube of 150 cm^3 capaticy, and 2.5 cm^3 of concentrated nitric acid were added. The solution was heated to boiling and held constant for 15 minutes. After cooling, the solution was placed in a measuring flask of 50 cm^3 capacity and made up to the mark with distilled water.

2. By hot *aqua regia* - Method B.

10.5 cm^3 of concentrated hydrochloric acid and 3.5 cm^3 of concentrated nitric acid were added to 50 cm^3 of the wastes. The samples were left for 16 hours and, next, heated for 2 hours up to the appearance of white fumes. After cooling, the solution was placed in a measuring flask of 50 cm^3 capacity and made up to the mark with distilled water.

3. By the acids HNO_3 and H_2SO_4 with the addition of H_2O_2 - Method C.

2 cm^3 of concentrated sulphuric acid and 5 cm^3 of concentrated nitric acid were added to 50 cm^3 of the wastes and evaporated to the appearance of white fumes and to the discolouration of liquids. Since the solution was not colourless, another portion of nitric acid and 2 cm^3 of 30% H_2O_2 were added. The mineralized sample was boiled with small portions of distilled water so as to dispose and decompose the excess of oxidizing compounds. After cooling, the solution was placed in a measuring flask of 50 cm^3 capacity and made up to the mark with distilled water.

4. By microwave mineralization according to the MERCK procedure - Method D.

Two scoops of the Oxisolv reagent were added to 10 cm^3 of the wastes and, next, were mineralized for 60 seconds by 500 MW microwaves. Since mineralization was incomplete, three more scoops of the Oxisolv reagent were added to the sample and mineralized for another 60 seconds.

Dry-mineralization was not used here because this method is not recommended in serial analyses carried out in plant laboratories, mostly because of its time-consuming character.

The results of the mineralization of wastes carried out according to the above-mentioned procedures were as follows:

1. samples of wastes after mineralization according to Method A were turbid, yellow in colour and needed fil tration before further analysis. The extension of heating time up to 1 hour and the increase in the amount of oxidizer had no effect on the appearance of the sample. Besides, there was a greasy spot on the surface of the liquid.

2. After mineralization by aqua regia (Method B) the samples were transparent, needed no filtration, but the yellow colour made it impossible to continue the analysis by the colorimetric methods which are recommended while analysing nickel and iron, yet there was still a film of grease on the surface of the liquid. Those samples were not subject to further studies.

3. After mineralization by Method C the samples were colourless, but turbid, needed filtration, with a greasy spot on the surface.

4. After microwave mineralization (using drastic con ditions) the samples were colourless, transparent, devoid of a film of grease on the surface. With such result of mineralizations, microwave mineralization is the most ef fective method of decomposing the organic matrix for the wastes under analysis.

After mineralization by Method A the samples were analysed in relation to the contents of nickel and iron with the use of AAS, whereas after mineralization by

Methods C and D the samples were colorimetrically determined according to the procedure suggested by Hermanowicz [10].

Results

The analytical results determination of nickel and iron are given in Tables 1 and 2.

Table 1. Comparison of the content of nickel [mg/dm^3] in samples of wastes as regards the mineralization method and the chosen analytical method.

Data of sampling	Sample	Method of mineralization and analysis		
		Method A AAS analysis $\bar{x} \pm \Delta x$	Method C Colorimetric analysis $\bar{x} \pm \Delta x$	Method D Colorimetric analysis $\bar{x} \pm \Delta x$
04.12.98	I	1.23 ± 0.007	1.32 ± 0.018	1.66 ± 0.015
	II	0.64 ± 0.003	0.88 ± 0.007	0.98 ± 0.009
06.01.99	I	1.39 ± 0.007	1.40 ± 0.013	2.51 ± 0.022
	II	0.83 ± 0.005	0.85 ± 0.007	0.89 ± 0.008
02.02.99	I	2.01 ± 0.011	2.45 ± 0.022	2.70 ± 0.024
	II	0.81 ± 0.005	0.85 ± 0.008	0.97 ± 0.009
10.02.99	I	0.71 ± 0.004	0.75 ± 0.007	0.88 ± 0.007
	II	0.47 ± 0.003	0.47 ± 0.004	0.55 ± 0.005

Table 2. Comparison of the content of iron [mg/dm^3] in samples of wastes as regards the mineralization method and the chosen analytical method.

Data of sampling	Sample	Method of mineralization and analysis		
		Method A AAS analysis $\bar{x} \pm \Delta x$	Method C Colorimetric analysis $\bar{x} \pm \Delta x$	Method D Colorimetric analysis $\bar{x} \pm \Delta x$
04.12.98	I	32.68 ± 0.284	26.55 ± 0.305	34.80 ± 0.400
	II	10.72 ± 0.093	8.80 ± 0.101	11.90 ± 0.137
06.01.99	I	23.70 ± 0.206	22.80 ± 0.262	36.00 ± 0.414
	II	17.10 ± 0.149	14.50 ± 0.167	18.80 ± 0.216
02.02.99	I	13.04 ± 0.113	6.25 ± 0.072	14.30 ± 0.164
	II	3.31 ± 0.029	3.72 ± 0.043	5.30 ± 0.061
10.02.99	I	7.45 ± 0.065	7.40 ± 0.085	9.10 ± 0.105
	II	3.50 ± 0.030	3.70 ± 0.042	3.69 ± 0.042

Results of analyses are the arithmetic mean of the results of three values being within the limits of error of the method.

Discussion

An attempt was made to determine the content of nickel according to the standard PN-91/C-04614/03 in the samples mineralized by Methods D and C. It was impossible to determine nickel according to the mandatory standard because the solutions obtained after adding reagents were turbid and unsuitable for spectrophotometric analyses. Turbidity probably resulted from the presence of iron and chromium ions which precipitated as hydrooxides (suspensoid) under such conditions. The standard considers no disposal of interfering ions, which is included in the former trade standard based upon the method given by Hermanowicz [10] for industrial wastes. Therefore, analyses of the contents of nickel and iron for the samples mineralized by Methods C and D were carried out according to this procedure.

From the data given in Table 1 it is evident that the content of nickel in the samples mineralized by microwaves (Method D) is higher than in those mineralized by Method C. These differences are greater from emulsion wastes (sample I) than for those at the discharge out of the sewage-treatment plant (sample II). This results from the complex chemical constitution of those wastes and confirms the conclusion mentioned before that mineralization by oxidizing acids does not ensure total decomposition and a transfer of metals to their ionic forms.

The lower content of nickel in the samples tested by the AAS method can be accounted for by the fact that they needed filtration after mineralization, which might contribute to leaving part of the analyt on the filter paper and, consequently, to lowering the results. At the same time, these results approximate the values obtained for the samples mineralized by Method C and are considerably lower than those after microwave mineralization. It confirms the previous conclusion concerning the incomplete mineralization of the wastes by Methods A and C.

Iron was also determined in all the samples where nickel was analysed (Table 2). From these values it follows that, as for nickel, the determined content of iron in the samples after mineralization by microwaves is higher than after mineralization by hot acids (Methods A and C). The discrepancy between the results refers to the complex emulsion wastes (sample I) more than to those after purification. The results of analysis by the AAS method here also converge with the values of Method C and are considerably lower than for Method D.

The present studies and analytical results explicitly show that the way to mineralize wastes and the analytical method chosen considerably affect the result of determining the metals found in them. Industrial wastes must adjust the whole analytical procedure to the nature of wastes and to the level of their complexity. Replacing the trade standards with the general ones PN, no matter which branch of industry the wastes come from, does not always give reliable results.

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