====== **ANALYSIS OF SUBSTANCES** ======

Combined Methods of Analysis of Metal-Containing Raw Material (Review)

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Abstract—Methods of analysis of reusable metal-containing material (RMR) are considered in the review: X-ray fluorescence, atomic absorption spectrophotometry, and atomic emission and mass spectrometry with inductively coupled plasma. Peculiarities of the applied methods are shown, and a method of analysis with consideration of the specificity of RMR should be developed for every object. In the most cases, the methods of sample processing harmonized with the applied method of analysis and sample content.

The reusable metal-containing material (RMR) is the collective concept including all types of recyclables, different metal-containing wastes, and also technogenic metal-containing raw material accompanying all steel production stages. RMR is a big class of metal-containing products which may be considered from the different viewpoints—both as valuable "rich" metallurgical raw material and as a pollutant of the environment by toxic elements, especially on the territories close to mining and smelting enterprise. There are many such territories in Russia, and solution of the RMR recycling problem is a federal issue. In any case, the first step to solve the global problem is the fullest RMR chemical analysis with determination of the valued and associated components, as well as the impurity elements. In this case, it is required to take into account the properties of RMR as the object of analysis—complex and variable composition, wide range of analytes, and inhomogeneity.

Thus, the analysis of reusable metal-containing raw material for the content of valuable components is a challenge; in order to solve this problem, it is required to develop a scientific methodological approach and modern universal multicomponent and high-precision methods of analysis.

At the stage of examining, analyzing, and sorting scrap and wastes, express methods of radiation control and nondestructive testing (X-ray fluorescence with energy dispersion, nuclear-physical methods with penetrating radiation—neutrons and gamma rays) are usually used for the evaluation of the radiation safety of the raw material. Test methods (methods of indication, identification, or qualitative analysis) are considered promising.

Chemical, physicochemical, combined, and physical methods of elemental, phase, substance, molecular, isotopic, and other types of analysis are used for the analysis of the raw material test sample after the sample preprocessing. Selection of the applied procedures depends on the list of the analytes, their composition, and the required precision of analysis. As a rule, general X-ray fluorescence and atomic emission analysis giving a general idea about the complete chemical composition of the recyclables precedes the determination of the given components. Elements for further determination are selected on the basis of this identification experiment.

Cu, Al, Fe, Ni, platinum metals (Rh, Ru, Ir), rare refractory metals (Nb, Ta, Zr), rare dispersed elements (Ga, In, Ge, Re), and many others are determined in reusable metal-containing raw material apart from noble metals (Ag, Au, Pt, and Pd).

Methods of atomic absorption spectrophotometry and atomic emission spectrophotometry, spectrophotometry, and X-ray fluorescence and classical methods of gravimetric and potentiometric analysis are applied for the analysis of resuable metal-containing raw material.

Application of these methods are dictated by the aforementioned peculiarities of the objects of analysis; in this case, the direct determination without special sample processing, separation, and concentration is carried out in very rare cases. That is why the method of analysis with the transformation of the sample into

an optimum form for the selected method providing the most precise results is developed in any single case. This review considers the above-mentioned combined methods with regard to the different RMR types.

The *X-ray fluorescence* (XRF), characterized by high expressiveness, relatively simple sample processing, and little restrictions on physical properties and chemical composition for the object of analysis [1, 2], is often used in analysis of reusable metal-containing raw material: for determination of precious metals in catalysts [3], technological products and wastes [4], scraps and platinum concentrates [5], and reusable raw materials containing precious metals [6, 7]. The integrated approach including titrimetric determination of the main mass of noble metals and further X-ray fluorescence of the catalyst granules after leaching [8] was also applied for the determination of noble metals in catalysts.

Sorption X-ray fluorescence methods with application of polymeric thioester and urethane foam sorbents [9, 10] are used for the determination of the associated and toxic elements As, Se, Te, Bi, Co, Cd, Sn, Pb, Sb, Fe, Au, In, Cu, Ni, Ag, Zn, Hg, and Mn.

The authors of [9] developed a simple and universal sorption X-ray fluorescence method for determination of a number of elements, including As, Au, Se, and Te, incorporating concentration on polymeric thioester. The method is characterized by a high recovery rate: the relative standard deviation in determination of $300-1000$ μg of metal per 1.2 g of sorbent is $0.02-0.03$. The thresholds of detection of elements in terms of 400 mL of sample solution are $5.2 \times 10^{-3}-4.7 \times 10^{-2}$ μg/mL. The method may be used for the analysis of technological solutions, products of metallurgical plants, and objects in the environment.

The sorption X-ray fluorescence (SRF) method for the determination of heavy metals on urethane foam (UF) sorbents after concentration in aqueous solutions in the form of acid complexes, chelates, or ion associates was improved in [10]. Experimental approaches to increase the signal/noise ratio in the XRF spectrum was proposed; this allows additional improvement of the sensitive hybrid SRF UF methods for determination of a number of metals (Mn, Fe, Co, Ni, Hg, and Pg) to units of ng/mg units and enlargement of the range of linearity of the calibration curves up to two orders of magnitude.

The following unique experience of the integrated determination of the elements in derivative products was gained by Norilsk Nickel: a method of X-ray spectral analysis of products of metallurgical plants as concerns both noble metals and nonferrous, rare, and toxic metals was developed. The range of the determined compositions is from 0.001 to 100 wt %.

Atomic absorption spectrophotometry (AAS) allows analyzing liquid, solid, and gas samples; however, most of the methods refer to the analysis of solutions, which is connected with the dosing convenience and concentration of samples and calibration simplicity [11−15].

Significant interferences are possible because RMR contains a high number of associated elements. A number of methods were developed in the AAS; these methods allow, if not complete suppression of interferences, then at least a sharp decrease in them (for example, increase in the atomization temperature in the flame). Comparison test samples comparable in composition to the analyzed test samples are used as well. The most widely used method for the elimination of influences is matrix modification by addition of buffering solutions which are selected experimentally [16].

The AAS method is widely used for determination of platinum metals in reusable metal-containing raw material [16−25]. Different ways of the preliminary concentration with S- and N-containing sorbents [26, 27] and co-deposition on hydroxides [28−30] are used for the determination of toxic elements by this method.

The feasibility of mercury determination by atomic absorption spectrometry with electrothermal atomization (ETAAS) in acid solutions containing an oxidizer was investigated in [6], as well as the feasibility of selenium and arsenic determination after their sorption concentration on the S- and N-containing sorbents with the use as the Pd, Pt, Ir, Rh, and Au modifiers.

The elements As, Sb, and Bi were determined in copper electrical cable by the ETAAS method in a graphite furnace [7]. The difference in evaporation of the sample base element (copper) and analyte and also the methods of eliminating interferences from copper were studied in order to increase the analyte signal/unspecific absorption signal ratio.

The ETAAS method used in [8] for determination of arsenic in copper sulfuric acid electrolytes and electrolytic copper after arsenic co-deposition on the collector, lanthanum or iron hydroxide, provides high precision of results and low detection threshold.

The main disadvantage of the AAS method is the sequential but not simultaneous identification the elements. Certain advantages of AAS connected with the absorption registration in the center of the atomic line and with high sensitivity disappear during manufacturing of the equipment for multielement AAS with the use of continuous radiation sources. The narrow range of the working concentrations [13] complicates the multielement implementation of AAS.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) in recent decades has been the most popular method of RMR analysis owing to the combination of such parameters as flexibility, wide range of determined compositions, multielement nature, accessibility of modern equipment, high productivity, and, in many cases, efficiency. Limitations of the method are the necessity to transfer the test sample into solution and application of different methods of selection and concentration. But even with

consideration of these limitations, the ICP-AES method is preferable in most cases.

Most of the works referring to RMR analysis by the ICP-AES method concern the determination of noble metals. This method is used after sample processing for the analysis of dead catalysts: high-temperature fusion [31–34]; dilution in an acid mixture [32, 35, 36]; and autoclave breakdown [37]. Description of the analysis of recyclables containing noble metals is given in [38–41]; sludge of nitric acid production, in [42]; fire clay waste, in [43].

The ICP-AES method is also often used for the determination of platinum metals in catalysts. For example, the procedure of the Pt and Pd determination in dead catalysts by the ICP-AES method after breakdown of the test sample by high-temperature fusion with potassium pyrosulfate is developed in [3]. This procedure is of universal character; it allows analyzing different grades of catalysts and their mixtures with Pt and Pd content from 0.1% to several percent within a short period of time. The correctness of the results of Pt and Pd determination is proven by the comparison with the round-robin test data. Study [32] shows systematic investigations of different methods of decomposition of specimens of dead automobile catalysts (AC) on a ceramic basis by mineral acid mixtures as well as by high temperature fusion aiming at subsequent determination of platinum, palladium, and rhodium by the ICP-AES method. The behavior of the components of the sample base of dead AC and their influence on the results of determination of the platinum group metals were studied under conditions of decomposition of the test samples. The relative standard deviation of the results of analysis based on the developed procedure is 11–9% at the platinum, palladium, and rhodium content from 0.01 to 0.3%.

The current procedures [33, 44] allow determining palladium and platinum after high-temperature fusion with potassium pyrosulfate in dead palladium- and platinum containing catalysts and derivative products within the mass content of 0.001–30.0% (Pd) and 0.005–30.0% (Pt). Procedure [37] provides for the platinum, palladium, and rhodium determination in dead automobile catalysts with the use of the autoclave breakdown.

The developed procedures [38, 39] are aplied to recyclable materials of precious (noble) metals and allow determining gold, silver, platinum, palladium, and rhodium by the ICP-AES method after dilution in mineral acids.

The integrated method of atomic emission analysis with autoclave sample processing for the control of the platinum group metal content in fire clay wastes of glass manufacturing was developed in [43] with application of mathematical experimental design.

The authors of [40] developed an approach to determination of platinum, rhodium, iridium, and ruthenium in recyclable and technogenic raw material with application of sorption concentration.

Owing to the multielement nature, the ICP-AES method is widely used for the simultaneous determination of a large number of the impurity elements [45, 46], including toxic ones [47, 48].

The ICP-AES method was used in [46] for determination of eight impurities in copper (As, Bi, Fe, Ni, Pb, Sb, Sn, and Zn). The results were compared with the results of analysis of standard samples of high-purity copper material. It was found that the detection threshold with the use of a spectrometer with plasma axial observation is better as compared to radial observation.

Study [47] concerns investigation of the spectral interferences of Cd (II), Co (II), Cu (II), Fe (III), and Ni (II) with the simultaneous determination of As, Bi, Sb, Se, and Sn by the ICP-AES method with the generation of hydrides. The input of the hampering element within the concentration range from 10 to 1000 μg/mL was assessed by the intensity of the analyte signal. Different reagents (EDTA, thiocarbamide, KCN, and KI) were used for eliminating the influence; the efficiency in determination of five hydride-forming elements was compared. It was found out that application of NaOH makes it possible to eliminate the interferences of transition metals in As and Se determination. It was mentioned that considerable spectral folding on the analytical lines of the determined elements (As–Cd and Sb–Co) was observed during formation of hydrides.

The authors of [48] developed a procedure of the mercury, cadmium, and cobalt determination by the ICP-AES method within the range from 0.0005 to 0.010% in materials of the metallurgical production. The analytical error does not exceed 20%. The influence of iron on the signals of the determined elements was studied. Calibration of the spectrometer was carried out by reference solutions simulating the chemical composition of the test sample in order to eliminate the influence of the test sample basis. This approach allows leveling interferences induced by the background emission of the test sample basis. The advantages of the developed procedure are simplicity of the sample processing (direct dilution of the test sample in an acid mixture ($HCl + HNO_3$) and possibility to determine mercury, cobalt, and cadmium from the one test charge of the analyzed test sample.

Study [49] concerns the analysis of red mud and its derivative products—cast iron and slag. The feasibility of the simultaneous determination of a large number of macro-components and impurity elements within the content range from $n \times 10$ to $n \times 10^{-4}\%$ with application of the inductively coupled plasma atomic emission, infrared-absorption, and gravimetric methods of analysis is shown. The following complex of procedures for red mud analysis and its derivative products (cast iron and slag) was developed: with application of

the ICP-AES method for determination of Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, Ga, K, La and other REE, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Sc, Sn, Sr, Th, Ti, U, V, W, Y, Zn, Zr; procedure including the preliminary concentration of analytes with separation of iron hydroxide by ammonia solution, for determination of Sc, Y, La, and other REEs; a special method of dilution of the test samples was applied during determination of B and As. The error of the results of analysis is 2−3% for the macro-components and 10−30% for the impurity elements.

The ICP-AES method, along with the infrared-absorption and gravimetric methods, was used by the authors of [50] for determination of the elemental composition of electric-furnace powder (Al, As, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Ti, V, Zn, C, S, Si).

Influence of 51 elements of the main test sample was studied in [51]. The authors claim that spectral influences of the elements of the test sample basis with low second ionization potential are more significant as compared with the elements with low first ionization potential.

An equilibrium thermodynamic model of the thermochemical processes for the ICP-AES method is proposed in [52]; the main assumptions are discussed. Nonspectral influences of the main test sample in different methods of emission observation were theoretically studied. It is shown that the model numerically describes the experimentally observed changes in the intensity of spectral lines of different analytes and plasma "hardness" parameters depending on ionization concentration and potential of different elements of the test sample basis and on the efficiency of the solution feeding and plasma power. A conclusion on the prospects of further development and testing of the model in analysis of the thermochemical processes in inductively coupled plasma was made.

As is seen, the mission tasks concerning determination of specific elements are solved in the presented works. For example, atoms of practically all the elements are excited in the ICP-AES method; this leads to different interferences which are not always easy to assess. That is why the methods of interference suppression with the help of sample processing (when basis elements are not transferred into solution) are selected in the given works.

Complex tasks of the simultaneous determination of associated, impurity, and matrix elements are hardly found in the literature, but they are essential. For the simultaneous determination of a large number of the elements at different concentration levels, it is required to take into account a lot of factors influencing the analytical results. The capabilities of the modern equipment make it possible to conduct the simultaneous measurement of intensity of any analytical lines within the range from 166 to 847 nm with high resolution within the concentration range from 10^{-7} to 100%. However, for the implementation of this capability, it is required to have the corresponding setting of the device parameters influencing the intensity of the analytical signal: generator power, height of the spectrum observation, and feeding rate of the test sample. The selected parameters should provide the best conditions for all the determined elements simultaneously.

The potential of different spectral folding arises owing to the simultaneous excitation of the spectral lines of many elements. With the simultaneous ICP-AES determination, it is required to take into account both the mutual influence of the determined elements and the influence of the main test sample.

Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most important instruments for determination of the elemental and isotopic composition of any mineral substances [53], although it is applied much less often than ICP-AES. The ICP-MS method is quite often used for the determination of platinum group metals both directly and after sorption concentration and for the determination of impurities (Ag, As, Bi, Cr, Fe, Ni, Pb, Sb, and Sn) [55]; methods of preliminary concentration are also used for the determination of trace amounts. For example, in [55], Bi, Sn, In, Tl, Cd, Cu, Co, Ni, Zn, Ti, Be, Zr, Ga, As, Sb, and V were determined by the ICP-MS method after co-deposition on $Fe(OH)_3$.

This method is used after generation of hydrides and ion exchange in [21, 56] for the determination of toxic elements As, Bi, Ge, Sb, Se, Sn, and Hg.

However, quite a strong suppression of the analytical signal—"matrix effect"—is observed in ICP-MS even with a comparatively low concentration of the test sample in the analyzed solution (at the level of 0.1−1 g/L). The influence of the elements of the test sample basis in the ICP-MS method is more significant as compared with the ICP-AES method. If analysis of solutions containing up to 1−2% of the basis elements is possible without any detectable effect on the analytical signal of the impurity element in the atomic emission method, then in ICP-MS the basis composition should be at least one order of magnitude less.

In practice, this means that, for obtaining proper quantitative results in the ICP-MS analysis of solutions with the mass fraction of the test sample basis of more than 0.02−0.05%, it is necessary to take into account the influence of the basis concentration on the change in sensitivity of the mass spectrometer.

Thus, four methods are mainly used in analysis of the wide range of reusable metal-containing raw materials: X-ray fluorescence, atomic absorption spectrophotometry, and atomic emission and mass spectrometry with inductively coupled plasma. Here, one should mention that it is necessary to develop a procedure of analysis including the sample processing methods harmonized with the applied method of analy-

sis and the test sample content for every object with consideration of the above-listed RMR peculiarities.

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