Determination of the content of rare metals in spent anion-exchange resin SIM202 by methods of neutron-activation and mass-spectrometric analysis

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Abstract. The work is devoted to the development of methods for determining the elemental and isotopic composition of spent ion-exchange resin, industrial waste and environmental objects using an inductively coupled plasma mass spectrometer and analyzing specific samples to determine the content of noble and rare metals in technological materials, industrial waste and natural objects with application of the developed techniques. This article determines the elemental composition of the spent ion-exchange resin SIM202 with the Inductively coupled plasma mass spectrometry (ICP-MS) method and also shows the comparison of the results with neutron activation analysis (NAA). The distribution coefficient of elements in a chromatographic column in ion-exchange resins TAO and SIM202 is given.

Keywords: mass spectrometry analysis, elemental analysis, waste hydrometallurgical plants, precious and rare metals, methods of concentration, extraction chromatography, Partition coefficient, separation factor, sorption, nuclear reactors, radiation, gamma spectrometry, radioactive tracers, neutron activation analysis.

1. Introduction
One of the main types of products in the Almalyk Mining and Metallurgical Combine is molybdenum, obtained from ore by a hydrometallurgical method. After dissolution, the concentrated ore is flowed through columns with anion-exchange resin SIM202, where other non-ferrous and rare metals are retained together with molybdenum. The SIM202 resin is manufactured by Pyrolite company as a trialkylamine Alamine 336, impregnated on an inert carrier (polyvinyl benzene). After saturation, the columns are washed with an eluent for selective washing out of molybdenum, then they are reused for concentrating molybdenum. At the same time, other related metals remain sorbed in the column and after repeated use, the resin is extremely saturated and its further use becomes impossible. This waste resin containing a number of rare metals in concentrated form, the main of which is expensive rhenium, is stored for storage. The problem is to determine the content of rhenium and other rare metals in the used resin SIM202. The research was aimed to develop a technique for separating sorbed metals for their subsequent analysis and regeneration of the SIM202 resin for its reuse.

Thus, there were two tasks:
1) Develop a method for the selective isolation of rhenium and other precious metals with the subsequent determination of their content in the spent resin SIM202 by mass spectrometry;
2) Develop a technique for the regeneration of used resin SIM202 for its reuse, since the price of this resin is more than $ 100 per 1 kg.
2. Equipment and reagents

For weighing the mass of the samples, a VESTA electronic balance (up to 5 kg) and a high-class MettlerToledo analytical balance (up to 200 g) were used. Dissolution of the samples was carried out in Teflon cups with heating on an electric stove. We used chemically pure nitric and hydrochloric acids. Acids and distilled water were additionally purified by the help of MilestoneSubPUR unit. Chemical procedures were carried out in special protective boxes equipped with exhaust ventilation. Elemental analysis of the prepared samples was carried out using an Agilent 7700x mass spectrometer. Agilent multi-element standard solutions were used to calibrate the mass spectrometer. The NAA samples were irradiated in a WWR-SM nuclear reactor with neutron fluxes of $10^{13}$ cm$^{-2}$/sec. The gamma spectra were measured with a HPGe spectrometer. Energy resolution of the detector 1 keV, efficiency 20%.

3. Research on the development of selective separation of elements from the spent catalyst SIM202

Due to the lack of unused extractant SIM202, we used TOA for research. Preliminary studies have shown that most of the elements interacting with TOA in various systems have the same distribution coefficients as in the case of SIM202. In this regard, in the experiments, instead of SIM202, we used TOA impregnated on Teflon powder. It should be noted that the TOA capacity is 15-20% lower than in SIM202, however, in the volumes that we used in laboratory experiments, this capacity is quite sufficient [1-3].

The method of radioactive indicators was used for the research. We studied the processes of sorption of rhenium and other elements from sulfuric and nitric acid solutions, as well as their desorption from the column.

The study of the extraction of rhenium with TOA from sulfuric acid solutions in the chromatographic version showed that the distribution coefficient of rhenium from sulfuric acid with a concentration of 0.01 to 1 M is more than 2000 and rhenium is almost completely retained in the column. Since the extraction of rhenium with TOA proceeds by an ion-exchange mechanism, as in the case of ion exchangers, a competing exchange reaction of ReO$_4^-$ and SO$_4^{2-}$ occurs. In this connection, with an increase in the concentration of H$_2$SO$_4$ in the solution, the capacity of the extractant decreases, and partly the distribution coefficient of rhenium. Despite this, even at an acid concentration of 5 M, the rhenium distribution coefficient was more than 300, which made it possible to completely sorb rhenium. However, the zone of rhenium sorption on the column was much wider than at lower ($\leq$ 1 M) acid concentrations (Figure 1).

The sorption of rhenium by the solid extractant TOA from nitric acid solutions is much weaker than from sulfuric acid solutions. Thus, at a concentration of HNO$_3$ from 1 M to 11 M, the distribution coefficient of rhenium (DRe) decreases from 9 to 0.03. Of the 4 M solution, HNO$_3$ DRe is 0.6, which allowed us to use this solution for the desorption of rhenium from TOA. In this case, the degree of extraction of rhenium during its desorption of 100 ml of 4 M HNO$_3$ from a column with a sorbent layer of 10 sm was more than 95% [4-5].
Figure 1. Dependence of the distribution profile of rhenium along the length of the chromatographic column with TOA (Teflon) on the concentration of H2SO4. A0 - activity (Bq) of rhenium in the composition of 1 ml solution. Ai - activity (Bq) of rhenium in 1 ml of eluent (i = 1,2,3,4,5).

The desorption of rhenium from the sorbent with TOA with a 5% NaOH solution and 2-4 M NH4OH was also investigated. The elution curves of rhenium during desorption with various solutions are shown in Figure 2. We found that when eluted with both NaOH and NH4OH, the degree of desorption of rhenium exceeds 90% and is 92.6% and 91.4%, respectively. It was also found that in the range of ammonia concentrations from 2 M up to 4 M, the degree of desorption of rhenium practically does not change.

It was not possible to study the desorption of rhenium from the SIM202 sorbent using radioactive indicators, due to the absence of a pure sorbent. The study of the desorption of rhenium from the presented sample of the spent sorbent SIM202 was carried out using neutron activation analysis. For this, 0.1 g of the spent sorbent was analyzed for rhenium content before and after desorption. The rhenium content in the original sample was 3.5 × 10^-2%. Desorption was carried out with a 4 M solution of HNO3, 5% NaOH, and 4 MNH4OH. The content of rhenium in the sorbent after desorption 4 M with HNO3 solution under static conditions was 1.1 × 10^-3%, and under dynamic conditions in the variant of column chromatography - 1.6 × 10^-5 %, which is less than 0.01% of the initial quantity. Accordingly, 99.99% of the rhenium goes into solution. However, together with rhenium, almost all elements except gold are washed out from 4 M HNO3, so their further separation is necessary.
Figure 2. Curves of rhenium elution during its desorption by various solutions from a chromatographic column with TOA. $A_0$ - activity (Bq) of rhenium in the composition of 1 ml solution. $A_i$ - activity (Bq) of rhenium in 1 ml of eluent ($i = 1, 2, 3, 4, 5$).

When eluted from the column with 5% NaOH and 4 M NH₄OH, rhenium quantitatively passes into the eluate. In this case, together with rhenium, osmium and tungsten can be partially washed out. The rest of the elements remain in the column. Then the sorbent can be washed with water and the remaining elements can be eluted with 4 M HNO₃. Gold from TOA is washed off with 70% HNO₃ only. From the eluate 4 M HNO₃, silver can be separated by precipitation in the form of AgCl by adding 10% NaCl or HCl solution to the eluate. Since the silver content in the eluate is 3 orders of magnitude greater than its solubility, more than 90% of the silver precipitates out. Then the precipitate can be filtered off and metallic silver is isolated with the help of zinc dust.

Other than rhenium, osmium sorption on anionite occurs irreversibly, by reducing it to the lowest degrees of oxidation, and therefore the subsequent desorption of osmium from ionites with the help of mineral acids and solutions of complexing agents does not exceed 25%. When the oxidizing agent K₂CrO₇, KMnO₄ or H₂O₂ is added to the sorbent and then distilled at 105 °C, up to 99% osmium is collected in a U-shaped trap with 10% NaOH or KOH [6-7].

The resin samples were washed with a 4M HNO₃ solution. In this case, all elements, except for gold, pass into the eluate. To isolate gold, the sorbent was washed with 70% HNO₃ solution. Thereafter, the volume of the eluate was brought to a certain volume by adding 0.3 M HNO₃ [8-10]. The prepared solutions were analyzed on an Agilent 7700 mass spectrometer. To control the correctness of the developed technique, the resin samples were simultaneously analyzed by neutron activation analysis. Table 1 shows the comparative results of the determination of 17 elements by methods of mass spectrometry and neutron activation analysis.

Table 1. Comparative results of analysis of samples of spent resin SIM202 by NAA and ICP-MS methods
| №  | Element  | Content of elements, ppm (g/t) |
|----|----------|-------------------------------|
|    | NAA      | ICP-MS                        |
|    | C        | ΔC, %                        | C        | ΔC, %                        |
| 1  | Ag**     | 81,4                         | 77,6     | 8,4                           |
| 2  | As*      | 14,8                         | 15,9     | 1,2                           |
| 3  | Au*      | 1,1                          | 0,9      | 11,5                          |
| 4  | Ba**     | 9,4                          | 11,1     | 8,2                           |
| 5  | Co**     | 0,20                         | 0,26     | 14,5                          |
| 6  | Cr**     | 0,75                         | 0,69     | 13,0                          |
| 7  | Fe**     | 1183,3                       | 1295,10  | 8,1                           |
| 8  | Mo*      | 4085,7                       | 3948,1   | 7,9                           |
| 9  | Na*      | 99,8                         | 131,3    | 9,8                           |
| 10 | Ni**     | 1,2                          | 0,9      | 13,3                          |
| 11 | Re*      | 353,8                        | 386,1    | 8,3                           |
| 12 | Sb*      | 1,2                          | 1,5      | 15,3                          |
| 13 | Se**     | 0,0112                       | 0,0140   | 17,2                          |
| 14 | Sr**     | 6,6                          | 7,3      | 12,5                          |
| 15 | Se**     | 274,0                        | 303,2    | 9,3                           |
| 16 | W*       | 39,5                         | 45,3     | 10,2                          |
| 17 | Zn**     | 7,5                          | 6,8      | 13,1                          |

### 4. Conclusion

Along with the indisputable advantages of the ICP-MS method in comparison with other methods of elemental analysis, there are also some problems, mainly associated with the presence of spectral interference of the determined isotopes and the effect of the matrix. When carrying out ICP-MS measurements, it is also necessary to control the possible change in sensitivity (signal drift) due to the instability of plasma parameters. In addition, during the mass analysis of solutions, even with the required salt content (0.1%), there is a gradual "salinization" of the holes of the interface cones, which significantly reduces the sensitivity. Despite all these factors, as can be seen from the results of the comparative analyzes shown in Table 1, all the results for the content of 17 elements are within the convergence range.

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