Rhenium in Carbonaceous Rocks: ICP Mass Spectrometry of Low Concentrations

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Abstract. This study described is about problem of determining trace and low concentrations of rhenium with using of ICP-MS spectrometry in rock samples with high contain of carbonaceous and organic components. Paper describes different ways of analysis and sample decomposition that are used in a common practice. Special attention is paid for sample preparation for ICP-MS investigations as far as it requires decomposition and disposing organic and silicate components.

1. Introduction
To meet the increasing needs for rhenium in aerospace, petrochemical, electronic, electrical and other industries the search for new sources of its extraction is performed. Nowadays the only rhenium deposit in the fumarole field is known. It is located in a place with high-temperature fluids extrusion on the Kudryavy volcano (Kurile Islands). About 80% of primary rhenium reserves are collected during the extraction of non-ferrous metals from sulfide ores at certain molybdenum and copper deposits. The remaining sources of Rhenium are only secondary raw materials. This leads to an active research of non-traditional sources of significant resources of this least common metal (weight clark is 0.0007 g / ton) in the Earth’s crust. Due to the high degree of rhenium organophilicity, some types of carbon minerals – black shales, coals, shungites, natural bitumen, oil may become sources for it extraction. Despite the fact that rhenium presents there in a small quantities, these rocks are wide spread and potentially have significant reserves. Such facts are known for Paleozoic graptolitic mudstones (dictionemic shales) Baltoscandia [1]. Rhenium search efficiency and reliability depends largely on analytical methods for determining this element in complex composition of mineral raw materials. Due to the trace amounts of rhenium in similar objects and the interfering influence of a number of matrix elements its direct determination is difficult.

2. Problem review
To determine the rhenium content in analyzed mineral material optical, extraction-fluorometric, electrochemical and also radiation methods are used [2,3]. In [4], pre-treatment using Carius tubes is described. Also it is noted that when method of x-ray fluorescence analysis performed, it is necessary to separate rhenium ions from a complex matrix. In cases of expected high content of target element (ore concentrates, hydrometallurgy products, etc.), direct or reverse voltammetry is offered for use [2,
5, 6]. In [7], a review of atomic emission and flame atomic absorption methods is observed as a more complicated method of analysis. It is noted that for of the second method, experimental determination of rhenium is possible only in high flame temperatures such as acetylene-oxygen or acetylene-nitrous oxide, however detection limits of this element still remain quite high. It is worth paying attention that in all the studies above, sorption or extraction concentration of rhenium is required while preparing samples for analysis. That essentially complicates sample preparation process, increases risk of an error and does not always satisfy accuracy requirements in the analysis of low concentrations [8,3]. Many of the above methods have a sufficiently high detection limit as well as repeatability of the results of determination. Also the interfering effect is observed from some associated elements in samples. The most promising method for determining rhenium at the trace level is inductively coupled plasma mass spectrometry (ICP-MS). The purpose of this paper is to evaluate the possibility of the correct determination by ICP-MS method for the low content of rhenium in carbon-containing rocks with complex matrix. In this study it is performed for carbonaceous argillites (dictionemic shales).

ICP-MS requires transfer of analyzed samples to the solution. Due to high volatility of rhenium compounds and its low content in natural objects, it must be paid a special attention to sample decomposition procedures. Most acceptable way of chemical preparation for determining rhenium in samples with an organic matrix, is an acid decomposition in presence of an oxidizing agent, such as nitric acid. Studies [9-12] show that during evaporating nitric acid solutions containing rhenium, no its losses were observed. Therefore, for decomposition of studied samples, an analytical scheme with nitric, perchloric and hydrofluoric acids treatment was selected. With this way of decomposition, destruction of organic matrix and silicate structure of the substance observed. Also the subsequent removal of silicon in the form of a volatile SiF₄, significantly reduces salt load on the ion optics of mass spectrometer, increasing the accuracy of the analysis and providing the lowest detection limit possible.

3. Methods and materials

As the objects of study, carbonic mudstones (dictionemic shales), which are representatives of a large number of different carbonaceous silicate rocks, were chosen. After sample decomposition with a mixture of acids and transferring it to solutions ready for rhenium measurement, the dilution factor was 500. Note that using this decomposition and final dilution scheme (dilution factor 5000), quantitative determination by ICP-MS method is possible for trace elements, including rare earth ones.

The analysis was performed using Agilent 7700x quadrupole mass spectrometer (Agilent Technologies, USA). A series of calibration solutions was prepared by weighting method from Standard 4 certified standard solution (No. 8500-6942 Agilent Technologies, USA) containing Re ion. Concentrations of the determining component in calibration solutions were in the range from 0.05 to 100 ppb. The use of a multi-element solution instead of a single-element standard rhenium solution during calibration makes it possible to take into account the influences on the background sensitivity from matrix effects. The value of the relative standard deviation for calibration solutions did not exceed 4.8%, which is not more than value of 5% generally accepted for ICP-MS. For measurements of rhenium concentration, isotopes $^{185}$Re and $^{187}$Re were selected. The analysis was performed in two modes: standard and with using a helium collision cell with kinetic energy discrimination. In this case, polyatomic particles having a larger physical size, collide with helium molecules more often than ions of the component being determined, thus losing energy that is not enough to overcome the energy barrier and the particle does not reach the detector. However, despite of decreasing of isobaric polyatomic interference, as well as a slight decrease in the total background noise, the sensitivity for the target element also decreases slightly. Thus, when using a helium collision cell, it is necessary to increase the signal integration time (the time that analytical data is accumulated by the detector). The sensitivity and background signal level were adjusted using a standard tuning solution containing Li, Co, Y, Ce, Tl at concentration of 1 ppb (No. 5185-5959 Agilent Technologies, USA). Relative standard deviation (RSD, %) for analytical the signal did not exceed 3.55 % and 3.32 % for the settings in the standard mode and the mode using a helium cell, respectively. The value of detection
limit was taken to be $3\sigma$, where $\sigma$ is the standard deviation of the obtained concentrations for determined component at the blank sample. To 185 weight the value was 0.002 ppb, a weight for 187 is $\sim 0.001$ ppb, due to its higher abundance.

4. Results and discussion

To control the quality of sample preparation for analysis, in particular, decomposition of the sample and measurements, the “introduced-found” method was performed. Samples with the addition of rhenium (Rhenium CGRE-1, Inorganic ventures, USA) with a concentration of 1 ppb and 5 ppb were carried through all stages of chemical sample preparation in order to assess the possible loss of the target component in this process. The calculated value of the relative standard deviation $Sr$ % did not exceed 3 % (Table 1).

| Isotope | Introduced, Re (ppb) | Found, Re (ppb) | Sr (%) |
|---------|----------------------|-----------------|--------|
| $^{185}$Re | 1.0 | 0.97 | 2.15 |
| $^{187}$Re | 1.0 | 0.97 | 1.43 |
| $^{185}$Re | 5.0 | 5.03 | 0.42 |
| $^{187}$Re | 5.0 | 4.89 | 1.57 |

The correctness of determination of rhenium was controlled by parallel analysis of standard samples JA-1 and JA-3 (Geological Survey of Japan), having passed all stages of chemical preparation, as well as the studied samples. The recommended values of rhenium content in them are 0.45 mg per ton and 0.65 mg per ton respectively. After analysis, the standard deviations of the determination results were calculated and they did not exceed 15%, which corresponds to the requirements for the accuracy of quantitative chemical analysis, adopted during geochemical studies. The reproducibility of the analysis results was estimated using data, obtained in the study of same mudstone samples by the ICP-MS method at VSEGEI named after A.P. Karpinsky in St. Petersburg (Table 2). A comparative analysis of the data shows an acceptable relative discrepancy between the results.

| Sample | Re (g/ton) VSEGEI | Re (g/ton) FEGI |
|--------|--------------------|-----------------|
| 30797  | 0.12               | 0.14            |
| 30805  | 0.12               | 0.17            |
| 24555  | 0.087              | 0.11            |
| 30793  | 0.095              | 0.11            |
| 23812  | 0.13               | 0.14            |
| 30822  | 0.091              | 0.11            |
| 24566  | 0.10               | 0.12            |
| 24573  | 0.11               | 0.13            |
| 23784  | 0.22               | 0.22            |
| 30808  | 0.23               | 0.27            |
| IDS-44/013 | -                    | 0.12          |
| IDS-46/013 | -                    | 0.12          |
The data obtained indicates that the proposed rhenium measurement technique can be effectively used to perform measurements of rhenium concentration in organic matrix samples with sufficient accuracy. A similar technique was also successfully tested in connection with a study of the geochemistry of tar limestones and low-ash coals.

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Acknowledgments

This study was supported by grant Project No. 18-2-015, “Gold-copper-porphyry mineralization of the Far East: indicators of geodynamic conditions, ore-bearing magmatism, and mineralogical-geochemical features of ore-magmatic systems in connection with the solution of the problems of forecasting, searching, evaluating and developing technologies for deposits of this type (sections 1-3)”. A comprehensive program of basic research of the Far Eastern Branch of the Russian Academy of Sciences “FAR EAST” for 2018–2020.