Mendeleev Commun., 2003, 13(6), 249–250

A new approach to the determination of noble metals in natural and technological samples

Irina V. Kubrakova,* Galina V. Myasoedova, Tatyana V. Shumskaya, Elena A. Zakhartchenko and Tamara F. Kudinova

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 938 2054; e-mail: i_kubrakova@geokhi.ru

10.1070/MC2003v013n06ABEH001766

A new approach to the analysis of platinum-containing materials is proposed; it includes microwave-assisted high-temperature decomposition of samples with acids, sorption preconcentration of platinum metals and gold on fibrous complexing sorbents in a dynamic regime and instrumental determination.

One of the most actual problems of present-day geology is the search, study, development and use of new potential sources of platinum-containing raw materials. The latter are characterised by low content of platinum metals (PM) and their varied speciation. In addition, they contain a high quantity of organic matter. This makes special difficulties in the determination of PM,[1] and sample preparation techniques for such materials are insufficiently reliable. Preparation techniques for samples containing trace PM usually include matrix decomposition and analyte preconcentration. A combination of decomposition and preconcentration, fire assay (mostly on a nickel sulfide button[2]) is most widely used for geological sample preparation. However, this method is sensitive to sample composition and unsuitable for organic matrices. Alternative analytical procedures are based on dissolution (chemical digestion) followed by the separation of PM from macrocomponents. The drawbacks of this approach are mainly related to digestion and are caused by losses of PM resulted from incomplete dissolution of a mineral matrix, formation and losses of volatile compounds on heating in open vessels, and difficulties of oxidation and separation of metamorphised organic matter. Thus, the use of microwave sample preparation, which provides rapid and complete decomposition (in particular, of organic matrices) without losses of PM at this stage is promising.

The second step of sample preparation consists in the separation of PM from matrix components by preconcentration followed by instrumental analysis [inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) or electrothermal atomization atomic absorption spectrometry (ETAAS)]. Preconcentration should be fast and selective and ensure a completeness of extraction of PM, and a concentrate should be free of impurities. Sorption methods are most often used for these purposes. Complex-forming sorbents are very effective for the preconcentration of PM. They provide the necessary selectivity of extraction of PM and their separation from accompanying elements. Highly effective complex-forming sorbents as fibrous ‘filled’ materials can be used in a dynamic preconcentration regime.

The preparation of the concentrate for the following determination of PM is also essentially important. The desorption of PM, the ashing of a sorbent or its acid decomposition are time-consuming operations accompanied by losses of PM. The use of fibrous ‘filled’ sorbents and the determination of PM can be carried out either in the sorbent phase or in solution after microwave digestion with nitric acid.

The aim of this work was to optimise sample preparation operations and to develop an effective method for the analysis of PM-containing raw materials, in particular, with a high content of organic carbon.

High-temperature sample decomposition under microwave irradiation was used for the dissolution of samples. It is well known that ashing for eliminating elemental sulfur and organic substances, as well as samples decomposition in the presence of hydrochloric acid, can lead to the losses of PM.[3] This is due to the formation of volatile chloride compounds and, in the presence of organics, the carbonyl and carbonyl chloride compounds of PM[4] even at a rather low-temperature (> 70 °C). The losses can be excluded using closed vessels at high temperature and pressure and aggressive media (concentrated nitric and hydrofluoric acid, aqua regia, *etc.*). In addition, for the effective decomposition of natural carbon-containing objects, the most severe conditions coupled with the simultaneous effect of a few factors (electromagnetic radiation, temperature, and pressure) are necessary.[5] The nitric acid digestion of the samples was carried out in this work. As an example, Figure 1 illustrates the dependence of the temperature of a reaction mixture and the pressure in the vessel during the decomposition of carbonaceous matter. The decomposition time does not exceed 20 min.[†]

Table 1 Concentrations of macrocomponents (μg cm^{-3}) in a solution after the decomposition of sulfide ore before and after sorption preconcentration of PM (determined by ICP-AES).

Element	Concentration in the sample solution	Concentration in the solution after preconcentration and dissolution of the sorbent
Mg	168	—
Al	210	0.03
Fe	4170	1.1
Cu	410	0.2
Ni	256	—
Ti	18	—
Co	12.5	—

The most effective method for the preconcentration of trace amounts of PM and the simultaneous separation of interfering elements is sorption by complexing sorbents.[1] The selectivity and completeness of the extraction of PM are provided by the introduction of a complex-forming sorbent such as of POLYORGS[6] into a fibre. In this work a POLYORGS-17n fibrous ‘filled’ sorbent was used. Along with the group extrac-

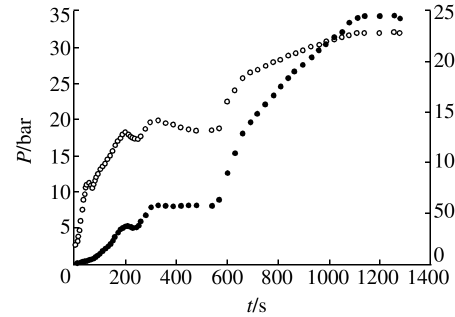

Figure 1 Time dependence of temperature of a reaction mixture (○) and pressure in a vessel (●) upon microwave decomposition of a coal sample.

[†] Sample decomposition was carried out using a 1200 W MARS 5 microwave oven (CEM Corp., USA) supplied with polymer vessels and a capping station. The internal pressure in the vessels can reach 100 bar, and the temperature of the reaction mixture can reach 300 °C. Samples of 0.1–1 g were decomposed with inverse aqua regia and hydrofluoric acid at 220–260 °. Vapour pressure in the vessel increased up to 60 bar. The solution after sample decomposition was filtered and evaporated; the salts were converted into chlorides.

tion of PM, it allows us to obtain a concentrate, which was practically free of impurities.[‡]

Table 1 illustrates the contents of the most important components in solution after microwave digestion with nitric acid. Low concentrations of macrocomponents in a concentrate do not interfere with the instrumental determination of PM. The concentration of carbon-containing substances in solution after digestion was lower than 1 mg cm^{-3}; this ensures a low viscosity of the solution, which can be used in the analysis by atomic spectroscopy. For the determination of PM ($< 10^{-6}$–10^{-4}%) one can use ICP-AES, ICP-MS (including isotope dilution) or ETAAS. Higher concentrations of PM can be determined directly in a solid concentrate by X-ray fluorescence (XRF). Note that the selective dynamic preconcentration of PM by POLYORGS-17n excludes a problem of reference materials and provides the versatility of analysis.

As an illustration of the efficiency of this approach the results of PM determination in natural and technological products [Russian Standard Reference Material, a product of reprocessing of sulfide ores (waste rock with a silicate matrix), nis matte with high contents of nonferrous metals and metamorphised natural coal with the concentration of organic substances of about 90%) are given in Table 2.

Thus, the microwave decomposition of various materials in combination with selective preconcentration on POLYORGS-type fibrous 'filled' sorbents provides a simpler sample preparation procedure for the trace analysis of PM, time reduction and elimination of losses at this stage. The sample preparation described above can be used for the analysis of various samples in combination with the instrumental determination of PM in a wide range of concentrations.

Table 2 Results of the determination of noble metals in rocks and related products ($\times 10^4$%).

Sample	Gold	Palladium	Platinum
Waste rock KhO-1 (Russian Standard Reference Material)			
Determined by ICP-AES	0.08±0.01	0.78±0.10	0.49±0.09
Reference data	0.07±0.01	0.84±0.17	0.43±0.09
Coal			
Determined by ICP-AES	0.40±0.03	2.24±0.11	0.43±0.08
Determined by ETAAS	0.35±0.06	2.40±0.18	0.39±0.08
Nis matte			
Determined by ICP-AES	2.08±0.10	131±12	22.4±1.8
Determined after fire assay	2.09±0.10	139±14	23.8±1.2

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32923).

References

1 *Analyticheskaya khimiya blagorodnykh metallov* (*Analytical Chemistry of Noble Metals*), eds. Yu. A. Zolotov, G. M. Varshal and V. M. Ivanov, URSS, Moscow, 2003 (in Russian).

2 M. Gros, J.-P. Lorand and A. Luguet, *Chem. Geology*, 1992, 179.

3 M. M. Totland, I. Jarvis and K. E. Jarvis, *Chem. Geology*, 1995, 21.

4 V. I. Spitsyn and I. V. Fedoseev, *Karbonil'nye kompleksy platinovykh metallov* (*Carbonyl Complexes of Platinum Metals*), Nauka, Moscow, 1982 (in Russian).

5 I. V. Kubrakova, *Usp. Khim.*, 2002, **71**, 327 (*Russ. Chem. Rev.*, 2002, **71**, 283).

6 G. V. Myasoedova and I. I. Antokol'skaya, *Zh. Anal. Khim.*, 1991, **46**, 1068 (*Russ. J. Anal. Chem.*, 1991, **46**, 767).

Received: 17th April 2003; Com. 03/2092

[‡] The preconcentration of PM was carried out by passing the solution obtained (1 M HCl, 100 ml) through the disks of POLYORGS-17n sorbent (0.15 g, ø 2.5 cm) at a rate of 1 ml min^{-1}. After rinsing the sorbent, it was decomposed with dilute nitric acid under microwave irradiation at 220–240 °C, and the solution was analysed by atomic spectroscopy.