

Microwave Preparation of Geological Samples in UltraWAVE System for the Determination of Platinum Group Elements and Rhenium by Mass-Spectrometric Isotope Dilution

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Abstract—We report the first results of the application of UltraWAVE reactor-type microwave system for geological sample preparation ($T = 250^{\circ}\text{C}$ and P up to 80 bar) with a mixture of concentrated nitric and hydrochloric acids (3 : 1). Determination of the platinum group elements — Ru, Pd, Ir, Pt (PGE) and Re after acid digestion was carried out by isotope dilution using the high-resolution mass-spectrometer ELEMENT after chromatographic separation of analytes on an AG50Wx8 cation exchange resin. The monoisotopic rhodium was determined with ^{195}Pt as an internal standard. The achieved detection limits were from 0.003 ng/g (Ir) to 0.09 ng/g (Pt). The correctness of the new procedure was confirmed by the analysis of geological reference samples—GP-13, UB-N, BHVO-2. The proposed procedure significantly accelerates and simplifies the preparation of geological samples for PGE and Re determination compared to the Carius tube technique.

Keywords: inductively coupled mass-spectrometry (ICP-MS), isotope dilution (ID), platinum-group elements (PGE), UltraWAVE microwave system

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INTRODUCTION

The determination of platinum group elements (PGE) and rhenium in geological samples is very difficult analytical task both due to their low abundance and heterogeneous distribution in rocks and problems with sample decomposition (Kubrakova et al., 2020; Grebneva-Balyuk and Kubrakova, 2020; Meisel and Horan, 2016; Qi et al., 2011). The nanogram concentrations of PGE and rhenium are usually determined by isotope dilution (ID) using acid digestion in Carius tube (CT) (Qi et al., 2011; Ishikawa et al., 2014; Chu et al., 2013, 2015; Li et al., 2014, 2015; Puchtel et al., 2014; Zou et al., 2020; Sato et al., 2021; Nicklas et al., 2021; Paquet et al., 2022; Sun et al., 2021) and high-pressure asher—HPA-S, Anton Paar, Graz (Wang, Becker, 2006; Meisel and Moser, 2007; Aulbach et al., 2019; van Acken et al., 2016, 2018; Feignon et al., 2022). Following these techniques, samples are treated with a mixture of HCl and HNO₃ in variable proportions (“aqua regia” and reverse “aqua regia”) at high temperatures (240–270°C and up to 300°C in CT, 250–300°C in HPA-S). These conditions provide the attainment of equilibrium between added isotope spikes and dissolved PGE and rhenium in the highest oxidation state, which is necessary to determine their concentrations by ID. The process takes from a few hours in HPA-S to several days in CT. The advantage

of these methods is the achievement of the lowest values of procedural blanks compared to the fire assay or combination of acid decomposition with additional melting of insoluble residue using diverse reagents (Meisel and Horan, 2016; Qi et al., 2011; Men’shikov et al., 2016; Todand et al., 1995).

Acid digestion in microwave systems is used much less frequently for PGE and rhenium determination (Kubrakova et al., 2020; Qi et al., 2011; Todand et al., 1995; Kubrakova and Toropchenova, 2013; Paleskiy et al., 2009; Boch et al., 2002), although they provide an increase of the rate of physicochemical processes during sample preparation and a decrease of introduced contaminations due to the application of closed vessels and decrease of the reagent amount (Kubrakova and Toropchenova, 2013). We have demonstrated that the temperature and pressure used in the MARS-5 microwave system are insufficient to reach isotope equilibrium for iridium, which results in a systematic underestimation of iridium concentrations in the analyzed reference materials GP-13 and UB-N (Paleskiy et al., 2009). However, the input of inert gas in reactor-type UltraWAVE microwave system prior to heating provides higher pressure in leaching vessels, which is comparable to those of CT and HPA-S (Table 1). The UltraWave microwave system could serve not only as efficient tool for sample preparation, but also significantly reduces its duration. An import-

Table 1. The comparison of operation principles and *P-T* parameters used for sample preparation in different systems

| Parameter | MARS-5 | UltraWAVE | HPA-S | CT |
|--|---|---|--|--|
| Principle of operation | Microwave heating of sealed autoclaves | Microwave heating of vessels using technology Single Reaction Chamber (SRC) | Thermal exchange heating of quartz or glass-carbon vessels in a sealed reactor | Heating of sealed glass tubes in reactor |
| Maximum permissible operation conditions | $T = 200^{\circ}\text{C}$ $P = 24 \text{ bar}$ | $T = 280^{\circ}\text{C}$ $P = 190 \text{ bar}$ | $T = 250\text{--}320^{\circ}\text{C}$ $P > 100 \text{ bar}$ | $T = 250\text{--}300^{\circ}\text{C}$ $P > 100 \text{ bar}$ |

ant argument in choosing this automated system is that this procedure makes it possible to avoid difficulties and risks related to the use of CT (Kozmenko et al., 2011).

In this work, we attempted to estimate the efficiency of the UltraWAVE microwave system for geological sample preparation with subsequent determination of PGE and rhenium by mass-spectrometric ID.

EXPERIMENTAL

Analyzed Objects

To control and verify the developed technique of PGE and rhenium determination, we used international reference materials: basalt BHVO-2 (US Geological Survey, USA), serpentinite UB-N (Association Nationale de la Recherche Technique, France), and spinel lherzolite—GP-13. The contents of some PGE (Ru, Pt, Ir) and rhenium were certified only in BHVO-2 (Jochum et al., 2016), while numerous data on their contents in UB-N and GP-13 obtained using diverse instrumental methods and ways of decomposition are given on GeoReM (URL: http://georem.mpch-mainz.gwdg.de/sample_query.asp.31).

Equipment and Reagents

All studies were carried out using only specially purified reagents: deionized water MilliQ ($R > 18.2 \text{ M}\Omega/\text{cm}$), HCl and HNO_3 of high-purity grade doubly distilled by sub-boiling technique (DuoPure Milestone). Aliquots were weighted on a Sartorius BP211D balance (Germany) with accuracy corresponding to four digits. Mixtures obtained after decomposition in an UltraWAVE microwave system were centrifuged on a SIGMA 3-16L centrifuge. Chromatographic separation of analytes was carried out on an ion-exchange columns using AG50Wx8 cationite (Palesskiy et al., 2009).

Preparation of Geological Samples

During weighing, the aliquots of analyzed reference materials (0.2–0.3 g) placed in quartz vessels were spiked with tracers enriched in stable isotopes (^{99}Ru , ^{106}Pd , ^{191}Ir , ^{194}Pt , ^{185}Re), the content of which was calculated based on the contents of analytes in analyzed samples. They were added with 1.5 mL concentrated acids ($\text{HCl} : \text{HNO}_3 = 1 : 3$). Vessels with

loose caps were mounted in holder and placed in a sealed reactor of the UltraWAVE microwave system (Fig. 1). The reactor represents a stainless vessel that contains polytetrafluorethylene glass filled with base solution (150 mL water and 5 mL concentrated HNO_3). Then, the reactor was tightly closed with a lid and fixed with clamp, and the inert gas, argon, was pumped into it, with initial pressure of 40 bar for the UltraWAVE microwave system. Subsequent microwave radiation (power—1500 W) is absorbed first of all by base solution, which provides homogenous heating of all samples without vessel rotation. The microwave system was controlled by special terminal with sensor monitor, which provided the maximum automatization of the sample preparation (Michel, 2010).

The microwave treatment proceeded in one stage: sample was heated for 30 min and then held for one hour at 250°C and pressure up to 82 bar. Then, the system was cooled to a room temperature, and the pressure was dropped according to set program.

During treatment of samples in the UltraWAVE microwave system, the isotope equilibrium in solution with spikes was attained by acid digestion of PGE and Re. Obtained solutions were evaporated to wet salts, transformed into chlorocomplex, centrifuged, and separated by ion exchange chromatography from matrix on an AG-50Wx8 cationite. For analysis, the second and third milliliter of eluent with the maximum PGE and Re contents were collected. 0.6 M HCl was used as eluent (Palesskiy et al., 2009). The acidity level and total salt content of final solutions corresponded to those required for ICP-MS solution analysis and are suitable for measurements without dilution.

ICP-MS Measurements

Obtained solutions were analyzed on a high-resolution ELEMENT Finnigan MAT inductively coupled plasma mass spectrometer (Germany) at the Institute of Geology and Mineralogy of SB RAS. The contents of analyzed elements were calculated using ID formula based on the measured ratios of chosen isotopes $\text{Ru}^{99}/\text{Ru}^{101}$, $\text{Pd}^{106}/\text{Pd}^{105}$, $\text{Re}^{185}/\text{Re}^{187}$, $\text{Ir}^{191}/\text{Ir}^{193}$, $\text{Pt}^{194}/\text{Pt}^{195}$. The required characteristics of spikes (isotope composition and concentration) were preliminarily determined (Table 2). The concentration of monoisotopic rhodium, to which the ID method is



Fig. 1. UltraWAVE microwave system (Milestone, Italy).

not applicable, was determined using ^{195}Pt as an internal standard (Savelyev et al., 2018).

The PGE and Re mass peaks were measured using low and medium resolution to separate possible molecular interferences. In addition, the peaks of isotopes that could cause interferences in form of chlorides, argides, and oxides (Table 3) were measured to estimate the extent of analyte separation from interference elements. Over 99% separation of elements causing spectral interferences on analyzed PGE and Re was reached. The isobaric interferences of Cd^{106} on Pd^{106} and Os^{187} on Re^{187} were corrected using the recommended values of isotope abundances (Rosman and Taylor, 1998).

RESULTS AND DISCUSSION

Table 4 presents PGE and Re contents obtained in blank procedure, which involved all stages of chemical sample preparation in the absence of sample, and shows the detection limits calculated as 3σ variations of procedural blank recalculated for solid sample taking into account used sample weight (0.3 g). Achieved detection limits were sufficiently low to determine PGE and Re contents in reference materials representing mantle rocks.

Results of PGE and Re determination in reference materials GP-13, UB-N and BHVO-2 obtained after microwave UltraWAVE treatment as compared with literature data are listed in Table 5.

Table 2. Isotope ratios (IR) and concentrations (C_{av} , ng/mL) of elements in spikes

| Isotopes | $\text{Ru}^{99}/\text{Ru}^{101}$ | $\text{Pd}^{106}/\text{Pd}^{105}$ | $\text{Re}^{185}/\text{Re}^{187}$ | $\text{Ir}^{191}/\text{Ir}^{193}$ | $\text{Pt}^{194}/\text{Pt}^{195}$ |
|-------------------------|----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $\text{IR} \pm 2\sigma$ | 235 ± 1 | 134.2 ± 0.4 | 36.4 ± 0.1 | 50.8 ± 0.1 | 47.9 ± 0.1 |
| $C_{av} \pm 2\sigma$ | 42.0 ± 0.3 | 106.0 ± 0.3 | 14.5 ± 0.2 | 36.0 ± 0.2 | 116 ± 1 |

Table 3. Isotopes used for PGE and Re determination and possible interferences

| Element | Mass, a.m.u | Possible interferences | |
|---------|----------------|------------------------|---|
| | | Isobars | Molecular ions |
| Ru | 99 | — | Ni ⁶² Cl ³⁷ , Ni ⁶⁴ Cl ³⁵ , Zn ⁶⁴ Cl ³⁵ , Ni ⁶¹ Ar ³⁸ , Cu ⁶³ Ar ³⁶ , Co ⁵⁹ Ar ⁴⁰ |
| Ru | 101 | — | Rb ⁸⁵ O ¹⁶ , Ni ⁶⁴ Cl ³⁷ , Zn ⁶⁴ Cl ³⁷ , Zn ⁶⁶ Cl ³⁵ , Ni ⁶¹ Ar ⁴⁰ , Cu ⁶⁵ Ar ³⁶ |
| Pd | 105 | — | Y ⁸⁹ O ¹⁶ , Cu ⁶⁵ Ar ⁴⁰ |
| Pd | 106 | Cd ¹⁰⁶ | Zr ⁹⁰ O ¹⁶ , Mo ⁹⁰ O ¹⁶ , Zn ⁶⁶ Ar ⁴⁰ |
| Re | 185 | — | Tm ¹⁶⁹ O ¹⁶ |
| Re | 187 | Os ¹⁸⁷ | Yb ¹⁷¹ O ¹⁶ |
| Ir | 191 | — | Lu ¹⁷⁵ O ¹⁶ |
| Ir | 193 | — | Hf ¹⁷⁷ O ¹⁶ |
| Pt | 194 | — | Hf ¹⁷⁸ O ¹⁶ |
| Pt | 195 | — | Hf ¹⁷⁹ O ¹⁶ |

Table 4. Data of the blank procedure ($n = 8$) and achieved detection limits (C_{\min}) of PGE and Re in solid sample

| Element | Ru | Rh | Pd | Re | Ir | Pt |
|---------------------|-------|--------|------|-------|--------|-------|
| Blank procedure, ng | 0.009 | 0.0005 | 0.01 | 0.002 | 0.0005 | 0.017 |
| C_{\min} , ng/g | 0.06 | 0.003 | 0.07 | 0.02 | 0.003 | 0.09 |

Table 5. Results of PGE and Re determination in reference materials (ng/g) compared to literature data

| Element | Ru | Rh | Pd | Re | Ir | Pt |
|-----------------------------|---------|---------|---------|---------|---------|--------|
| GP-13 | | | | | | |
| C_1 | — | — | — | 0.31 | 3.24 | — |
| C_2 | — | — | — | 0.33 | 3.94 | — |
| C_3 | 6.66 | 1.06 | 5.98 | 0.32 | 3.54 | 6.38 |
| C_4 | 6.65 | 1.05 | 6.08 | 0.31 | 3.31 | 7.02 |
| C_{av} | 6.66 | 1.06 | 6.03 | 0.32 | 3.5 | 6.7 |
| (S_r , %) | | | | (2.8) | (8.6) | |
| C_{av} (S_r , %) | 6.76 | 1.54 | 5.57 | 0.28 | 3.6 | 6.44 |
| (Kozmenko et al., 2011) | (6.9) | (17) | (13) | (15) | (5.2) | (16) |
| C_{av} (S_r) | 6.25 | 1.25 | 5.68 | 0.320 | 3.33 | 6.69 |
| (Meisel, Moser, 2004) | (0.063) | (0.095) | (0.047) | (0.071) | (0.028) | (0.10) |
| C_{av} (S) | 6.79 | — | 6.28 | 0.304 | 3.48 | 7.7 |
| (Liu et al., 2018) | (0.01) | | (0.7) | (0.02) | (0.54) | (1.28) |
| UB-N | | | | | | |
| C_1 | 6.2 | 1.00 | 5.27 | 0.23 | 2.97 | 6.09 |
| C_2 | 5.9 | 0.97 | 5.43 | 0.21 | 3.05 | 6.12 |
| C_{av} | 6.1 | 0.99 | 5.35 | 0.22 | 3.01 | 6.11 |
| C_{av} (S_r , %) | 6.43 | 1.1 | 5.85 | 0.19 | 3.16 | 7.31 |
| (Fisher-Godde et al., 2011) | (5.9) | (9.5) | (3.4) | (13) | (7) | (6.4) |
| C_{av} (1σ) | 6.6 | — | 5.9 | 0.184 | 3.27 | 7.37 |
| (Aulbach S. et al., 2019) | (0.37) | | (0.16) | (0.04) | (0.21) | (0.31) |
| C_{av} (2σ) | 6.6 | — | 6.11 | 0.188 | 3.35 | 7.2 |
| (Zou et al., 2020) | (0.71) | | (0.4) | (0.027) | (0.59) | (0.65) |
| BHVO-2 | | | | | | |
| C_1 | 0.12 | 0.71 | 2.6 | 0.63 | 0.04 | 6.3 |
| C_{av} (Δ) | 0.125 | 0.7 | 2.7 | 0.543 | 0.07 | 8.9 |
| (Jochum et al., 2016) | (0.018) | | (0.4) | (0.029) | (0.011) | (1.6) |

In first experiments, we analyzed reference material GP-13 with determination of Ir and Re contents. Iridium was chosen because its determination using MARS-5 microwave system yielded systematically underestimated values, and it was necessary to estimate the efficiency of the proposed sample preparation in UltraWAVE for the determination of this element. Re was chosen due to its lowest content in GP-13 among all analyzed elements. The average values of measured Re and Ir concentrations within analytical error are well consistent with literature data (Table 5), as well as with data obtained by mass-spectrometric ID in CT (Zou et al., 2020; Kozmenko et al., 2011; Liu et al., 2018) and HPA (Meisel and Moser, 2004; Aulbach S. et al., 2019; Fisher-Godde et al., 2011).

Thus, sample preparation of GP-13 in an UltraWAVE microwave system provides required conditions for correct Ir and Re determination by ID. The relative standard deviation was 2.8 and 8.6%.

Concentrations of other elements (Ru, Rh, Pd and Pt) determined in GP-13 within error fall in the range obtained in cited literature (Table 5), thus confirming that acid treatment in the UltraWAVE microwave system, as CT and HPA sample preparation, can be applied for PGE and Re determination.

The first results of analysis of reference materials UB-N and BHVO-2 (Table 5) also indicate the high promise of further experiments on the application of the described technique of microwave acid digestion.

It should be noted that the level of PGE and Re contents in GP-13 and UB-N is approximately similar, while Ru and Ir contents in BHVO-2 are much lower, which leads to higher measurement error. The analysis of BHVO-2 is frequently complicated by nugget effect (Li et al., 2014; Meisel and Moser J., 2007), and the use of HF together with an HCl and HNO₃ mixture is required for correct determination of PGE and Re contents (Li et al., 2015; Zou et al., 2020), which can be the object of further studies.

Thus, first experiments on application of the UltraWAVE microwave system (power up to 1500 W) for the acid preparation of geological samples ($T = 250^{\circ}\text{C}$, $P = 82$ bar, treated for 1.5 h) exemplified by GP-13, UB-N and BHVO-2 indicate the attainment of isotope equilibrium between spikes and dissolved PGE and Re, which allows the determination of their concentrations at the level of ng/g and lower in solid geological samples using ICP-MS ID after chromatographic separation. Sample preparation in the microwave system is express and safe method compared to CT and provides the comparable detection limits of analytes.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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