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Research Article

Bismuth-Remaining Cupellation Fire Assay Preconcentration Combined with Inductively Coupled Plasma Mass Spectrometry for the Simultaneous Determination of Ultratrace Au, Pt, Pd, Ru, Rh, and Ir in Geologic Samples

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In this work, a novel method of bismuth fire assay (Bi-FA) combined with inductively coupled plasma mass spectrometry (ICP-MS) simultaneous determination of ultratrace gold (Au), platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), and iridium (Ir) in geologic samples was established. Bismuth oxide (Bi_2O_3) was used as noble metal elements fire assay collector, and Bi-remaining protection cupellation was employed to generate Bi granule. After the Bi granule was microwave-digested by aqua regia (40%, v/v), ^{197}Au, ^{195}Pt, ^{106}Pd, ^{101}Ru, ^{103}Rh, and ^{193}Ir in the sample solution were determined by ICP-MS. Using Bi as cupellation protector, volatile Ru could be collected effectively and without volatilization loss during microwave digestion and decompression. Moreover, the toxicity of Bi was exceptionally low compared to toxic nickel oxide and lead oxide in nickel sulfide/lead fire assay; thus Bi-FA was a green environmental analysis method. The mineral composition and decomposition character of chromite, black shale, and polymetallic ore were investigated, and pretreatment procedures were optimized for such special samples. Besides, the influence of mass spectrum interference of coexisting elements was discussed. Under the optimal conditions, excellent curve fittings of Au, Pt, Pd, Ru, Rh, and Ir were obtained between 0.01 and 100 ng·mL^{-1}, with the correlation coefficients exceeding 0.9995. The detection limits were from 0.002 ng·g^{-1} to 0.025 ng·g^{-1}. The developed method was applied to analyze the Chinese Certified Reference Materials (CRMs) and the determined values were in good agreement with the certified values.

1. Introduction

Au, Pt, Pd, Ru, Rh, and Ir are noble metal elements, due to their high melting point, good conductivity, corrosion resistance, thermal stability, and catalytic activity, known as the “industrial vitamin,” which are widely applied in industrial catalysis [1, 2], military industry [3], energy, and biomedical fields [4, 5]. Mineral resource reserves of Au, Pt, Pd, Ru, Rh, and Ir are limited, and their abundances in the crust are extremely low (mass fraction is between 10^{-8} and 10^{-9}) and their distributions are uneven [6–8]; thus the accurate determination of noble metal elements has always been a challenge to geoanalysts.

The ordinary chemical analysis methods with small amount of sample weight (<3 g) and low sensitivity could not meet the demands of ultratrace analysis; thus methods with large amount of sample weight were developed to preconcentrate and detect noble metal elements. Fire assay was the application of metallurgical principles and techniques to analytical chemistry, which was an important method for precious metal elements enrichment. The target precious metals in rock, soil, metallurgy, and other samples were concentrated by Pb/Ni/Sb/Sn/Cu/Bi-containing collectors and successfully separated from the sample matrix. Fire assay methods by weighing 10~40 g samples with good sampling representative and high enrichment factor combined with high sensitivity graphite furnace atomic absorption spectrometry (GFAAS) and ICP-MS were used to determine noble elements [9–13]. The commonly used methods include lead fire assay (Pb-FA) [13, 14], nickel sulfide fire assay (NiS-FA) [9, 10, 12, 15–17], antimony fire assay (Sb-FA) [18], and tin fire assay (Sn-FA) [19, 20]. Pb-FA was the earliest classical method, and it could quantitatively preconcentrate noble metal elements. However, due to the high blank and high toxicity of collector reagent, as well as the volatilization loss of Ru and osmium (Os) during cupellation, the application in determination of ultratrace noble metal elements in geological samples was seriously restricted. The high blank problem was also existing for NiS-FA; then the collector should be purified tediously, or highly toxic nickel carbonyl was employed [15, 16]. Moreover, the capture efficiency of NiS-FA for Au was not ideal. For simple matrix samples, Sb-FA could replace Pb-FA to quantitatively enrich noble metal elements. However, impurity elements such as Cu, Pb, Bi, Ni, and Co could also be collected into Sb granule, which was prone to disturb the determination of noble metal elements. Sn-FA was effective for black shale, but the volatilization loss of Ru and Os during HCl digestion was inescapable [21].

Au, Pt, Pd, Ru, Rh, and Ir could form a series of alloys or metal intercompounds with Bi at high temperatures; thus Bi could quantitatively collect the noble metal elements in geological samples [22]. In this work, a novel method of Bi-remaining cupellation fire assay preconcentration combined with ICP-MS simultaneous determination of ultratrace Au, Pt, Pd, Ru, Rh, and Ir in geologic samples was established. Minimal toxic Bi_2O_3 was used as fire assay collector, and Bi-remaining protection cupellation was employed to enrich the noble metal elements into Bi granule. After the Bi granule was microwave-digested by aqua regia, the target analytes in the sample solution were determined by ICP-MS. It was worth mentioning that volatile Ru could be accurately determined by the proposed Bi-FA method. Compared with Pb-FA and NiS-FA, the reagent blank of Bi_2O_3 was relatively low and could be directly employed to collect noble metal elements without purifying. Moreover, the harm of toxic collector to the analyst and environment was avoided by using the nontoxic Bi_2O_3. The developed method was applied to analyze the Chinese Certified Reference Materials and the determined values were in good agreement with the certified values.

2. Materials and Methods

2.1. Instrumentation. A quadrupole (Q) ICP-MS (Model iCAP RQ, Thermo Scientific, USA) with a polyfluoroalkoxy (PFA) concentric nebulizer was used in all experiments for the determination of Au, Pt, Pd, Ru, Rh, and Ir. The operating parameters are summarized in Table 1. The MWS-3^+ microwave digestion system (BERGHOF, Germany) was employed for sample digestion.

The scanning electron microscopy and energy spectrum graph of chromite slag was characterized by scanning electron microscope (FEI Quanta 650F, Australia) and electron energy disperse spectroscopy (Bruker QUANTAX, Germany). X-ray powder polycrystal diffractometer (SmartLab SE, Rigaku Corporation, Japan) was used for component analysis of chromite slag.

2.2. Standard Solutions and Reagents. The multielement calibration standard solutions (Au, Pt, Pd, Ru, Rh, and Ir $10\,\mu g{\cdot}mL^{-1}$, respectively) in 10% aqua regia were bought from SPEX CertiPrep Group (USA). 8% (v/v) aqua regia was used as diluent and mixed standard solution of Au, Pt, Pd, Ru, Rh, and Ir ($100\,ng{\cdot}mL^{-1}$) was employed as stock solution. Rhenium (Re) standard solution ($50\,ng{\cdot}mL^{-1}$) was used as internal standard.

Bi_2O_3, glass powder, sodium carbonate anhydrous (Na_2CO_3), sodium borate ($Na_2B_4O_7{\cdot}10H_2O$), and flour were of analytical reagent (AR) grade and purchased from Tianjin Commie Company. HCl and nitric acid (HNO_3) were of excellent reagent grade. Deionized water was used throughout the whole experiments.

For covering agent, Na_2CO_3, $Na_2B_4O_7{\cdot}10H_2O$, glass powder, Bi_2O_3, and flour were mixed well at 55 g: 15 g: 20 g: 40 g: 4 g.

2.3. Sample Pretreatment

2.3.1. Fire Assay Recipes and Melting Process for Geochemical Samples. Regarding refractory chromite, chromite was difficult to melt and therefore presintering was required. 10 g chromite sample was mixed well with 30 g CaO and 40 g Na_2O_2, and then it was put on the porcelain dish padded with quartz sand, which was sintered at about 700°C for 1.5 hours. Once cooled, the sample was smashed and transferred into a 500 mL ingredient bottle. The following fusing and cupellation procedure were the same for the common geological samples.

For common geochemical samples, the fire assay recipes of rock, soil, river sediment, chromite, black shale, and polymetallic ore were mixed according to the mineral composition characteristics, which were shown in Table 2. Raw materials according to Table 2 were mixed well in ingredient bottle and transferred into a 500 mL fire-clay crucible and 20 g of covering agent was uniformly covered onto the recipes. Then the crucible was fused in a furnace preheated at 1000°C and gradually heated to 1060°C and kept for 40 min. The melts in the crucible were poured into a cast iron mold. Once cooled, the Bi bead was separated from the slag.

2.3.2. Bi-Remaining Cupellation and Microwave Digestion. Bi-remaining protection cupellation was employed to generate Bi granule. The Bi bead was cupellated for 30 min in magnesia cupel at 850°C until it became a small granule (~5 mg). The blank sample was also subjected to this procedure.

Table 1: ICP-MS operation conditions.

ICP-MS plasma	
Rf power	1550 W
Sampling depth	5.0 mm
Nebulizer gas flow	$1.00\ \mathrm{L{\cdot}min^{-1}}$
Auxiliary gas flow	$0.80\ \mathrm{L{\cdot}min^{-1}}$
Cool gas flow	$14.0\ \mathrm{L{\cdot}min^{-1}}$
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.5 mm
Peristaltic pump speed	40 rpm
Time-resolved data acquisition	
Survey runs	Jump
Channels	1
Number of sweeps	40
Dwell time	10 ms
Measurement mode	STD
Isotopes	^{197}Au, ^{195}Pt, ^{106}Pd, ^{101}Ru, ^{103}Rh, ^{193}Ir, and ^{185}Re

Table 2: Bismuth fire assay recipes for geochemical samples.

Sample type	Recipe (g)						
	Sample weight	$Na_2B_4O_7{\cdot}10H_2O$	Glass powder	Na_2CO_3	Bi_2O_3	Flour	KNO_3
Silicate rock	10–20	15	15	55	40	4	—
Carbonate rock	10–20	15	20	50	40	4	—
Sulfide rock*	10–20	15	20	50	40	4.5	—
Soil	10–20	15	15	55	40	4	—
Stream sediment	10–20	15	15	55	40	4	—
Black shale	10	20	20	50	80	7	5
Polymetallic ore	10	15	20	50	100	5	—
Chromite	—	25	20	30	40	6	—

*Sample was placed into the furnace maintained at 600°C for 2 hours.

The Bi granule was put into a microwave digestion tank, and 10 mL aqua regia (40%, v/v) newly prepared was added. Then the digestion tank was microwave-digested by the following microwave program: 100°C, rising 5 min, keeping 5 min; 105°C, rising 2 min, keeping 5 min; 110°C, rising 2 min, keeping 10 min; and 100°C, rising 1 min, keeping 5 min. After natural cooling, the closed tank was opened and stabilized to 50 mL volumetric bottle. Re ($50\ \mathrm{ng{\cdot}mL^{-1}}$) was online-added as the internal standard element; thence Au, Pt, Pd, Ru, Rh, and Ir in the sample solution were determined by ICP-MS.

3. Results and Discussion

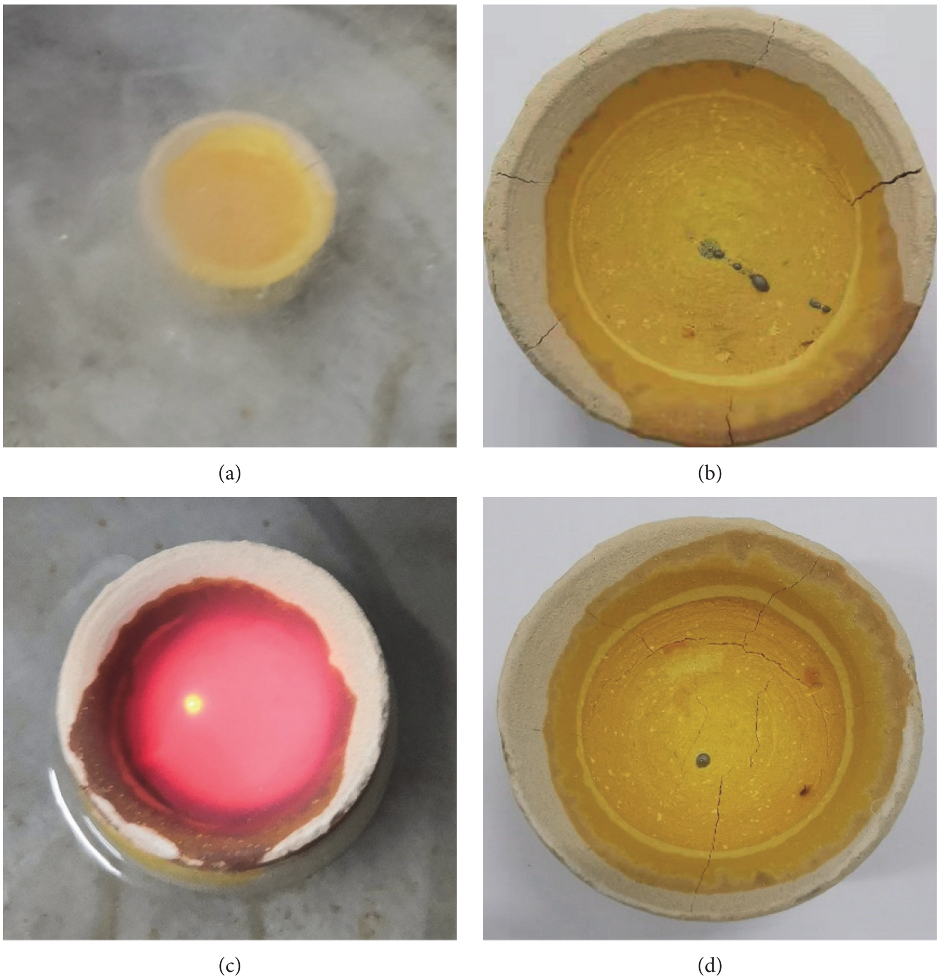
3.1. Covering Agent. The mixed reagent with almost the same formula as the fire assay recipes was used as covering agent, which could not only prevent the splash loss of the target analytes during sample melting process but also secondary collect the remaining Au, Pt, Pd, Ru, Rh, and Ir in the slag when Bi_2O_3 in the covering agent was reduced to Bi; thus the collecting rates of target analytes were improved.

3.2. Bi-Remaining Cupellation. Ag was an effective fire assay cupellation protector for Au, Pt, and Pd, but it did not work for Ru, Rh, and Ir due to the fact that it could not form alloys with Ru, Rh, and Ir. In this work, Bi was used as fire assay collector and cupellation protector, and Bi-remaining cupellation was employed to enrich Au, Pt, Pd, Ru, Rh, and Ir into ~5 mg Bi granule. It was notable that the magnesia cupel with Bi granule after cupellation could not be directly immersed into the water (Figures 1(a) and 1(b)), but it should be half-dipped to make the Bi granule gradually condense (Figures 1(c) and 1(d)), because the hot liquid Bi might be lost by splash in contact with water as shown in Figure 1(b).

3.3. Microwave Digestion. It was found that Ru had no volatilization loss under the digestion conditions of closed high temperature and high pressure [17]. Therefore, microwave digestion apparatus was used in this experiment to completely dissolve Bi granule. While ensuring the complete dissolution of Bi granule, it is necessary to reduce the dissolution temperature and time as much as possible to protect personnel safety and prolong the instrument service life. Through experiments, Bi granule could be completely dissolved by using the heating procedure.

3.4. Pretreatment of Special Samples

3.4.1. Refractory Chromite. Chromite is one of the refractory minerals with strong acid oxide and high hardness, which could not be completely melt by general fusing procedure [14]; there were still a few chromite particles entrained into slag lead to lower recoveries of noble metal elements. The significant chromite characteristic peaks before and after Bi-FA were shown in the X-ray powder polycrystal diffraction



(a) (b) (c) (d)

Figure 1: Magnesium ash dish cooling method. (a) Full immersion before cooling, (b) full immersion after cooling, (c) semi-immersion before cooling, and (d) semi-immersion after cooling.

graph (Figure 2); it could be seen that the refractory characteristic peaks still existed in the slag though the peak height decreased significantly after Bi-FA. In order to enhance the recoveries of noble metal elements, presintering of chromite samples with CaO and Na_2O_2 at 600°C was carried out to facilitate subsequent melting.

3.4.2. Black Shale. Black shale is a complex mineral containing noble metal elements. The mineral composition of black shale was analyzed by electron energy disperse spectroscopy (Fig. S1) and scanning electron microscope (Fig. S2). It could be concluded that black shale was a complex mineral composed of organic carbon, molybdenite, pyrite, arsenite, nickel, apatite, quartz, gypsum, orthoclase, and barite, which also contained metallic and nonmetallic elements such as F, Cl, Br, Cu, Pb, Zn, Mn, Se, Sb, V, rare earth, U, Zr, Re, Au, Ag, Pt, Pd, Ru, Rh, Os, and Ir.

The burning of carbon and sulfur in black shale sample would cause volatile loss of Au, Pt, Pd, Ru, Rh, and Ir. Besides, the sulfur of black shale would form stable sulfide with the target noble metal elements and then further formed solid solution with sulfide of Cu, Ni, and Co and entered the slag, which would still further lower the results of Au, Pt, Pd, Ru, Rh, and Ir. Therefore, proper amount of KNO_3 was added to oxide the sulfur to sulfate into the slag, and then the formation of metal sulfides was prevented so that Au, Pt, Pd, Ru, Rh, and Ir in the sample could be completely collected by Bi bead. The recovery ratios of Au, Pt, Pd, Ru, Rh, and Ir in the black shale sample by Bi-FA with and without KNO_3 were compared, and the results were shown in Table 3. It could be seen that the sample content increased significantly with KNO_3. Therefore, KNO_3 was added for black shale sample.

3.4.3. Polymetallic Ore. Polymetallic ores are generally rich in Cu, Pb, Zn, Sb, Bi, Ni, Co, and Sn and usually accompany noble metal elements. For the pretreatment of polymetallic ores, more Bi_2O_3 was needed, some of Bi_2O_3 was reduced into Bi granule to enrich precious metals, another compound state of Bi_2O_3 was used to collect associated impurity metals into the slag, and then 100 g of Bi_2O_3 was added to minimize the interferences caused by associated impurity metals.

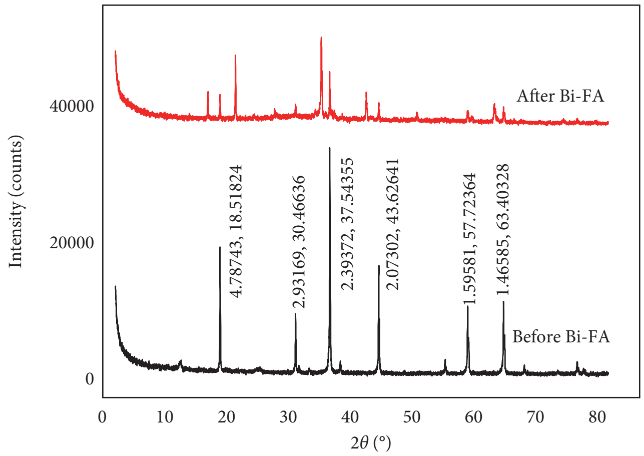


FIGURE 2: The X-ray powder polycrystal diffraction graph of the chromite slag after Bi-FA.

TABLE 3: The analytical results of different pretreatment procedures for black shale (ng·g^{-1}).

Sample	Without KNO_3*						With KNO_3					
	Au	Pt	Pd	Ru	Rh	Ir	Au	Pt	Pd	Ru	Rh	Ir
Black shale 1	174 ± 2.5	473 ± 31	456 ± 17	1.22 ± 0.09	0.31 ± 0.02	1.51 ± 0.12	209 ± 18	505 ± 34	520 ± 28	7.42 ± 0.54	17.1 ± 1.22	3.78 ± 0.21
Black shale 2	102 ± 10	220 ± 15	227 ± 13	0.86 ± 0.04	0.24 ± 0.01	1.48 ± 0.06	149 ± 11	243 ± 14	257 ± 12	4.90 ± 0.25	9.16 ± 0.43	2.75 ± 0.13

Note: all the values were determined by Bi-FA ICP-MS. *Sample was placed into the furnace burn at 700°C.

3.5. Measured Isotopes and Interferences of Polyatomic Molecular Ion. The isotopes of the determined noble metal elements were shown in Table S1, and ^{197}Au, ^{195}Pt, ^{106}Pd, ^{101}Ru, ^{103}Rh, ^{193}Ir, and ^{185}Re were selected as measuring isotopes and internal standard isotope with the principle of high abundance and free from isobars interference.

While precious metal elements were enriched during Bi-FA, trace amounts of Cu, Pb, Sb, Ni, Co, Sn, Se, Te, and As also were collected into the Bi granule. Os, As, and Sb were oxidized into OsO_4, As_2O_3, and Sb_2O_3 and completely volatilize in the cupellation process, and trace oxides of Cu, Pb, Ni, Co, Sn, Se, and Te in Bi granule could also be absorbed into the magnesia cupel. Therefore, most of the interferences were effectively eliminated through Bi-FA, and only Bi, Au, Ag, Pt, Pd, Ru, Rh, Ir, N, H, O, and Cl were coexistent in the final sample solution after microwave digestion. The possible interferences of polyatomic molecular ion were shown in Table S2. Despite the high concentration of H in the sample solution, the contents of ^{196}Pt, ^{194}Pt, ^{105}Pd, ^{100}Ru, ^{102}Ru, ^{102}Pd, and ^{192}Pt that make up polyatomic molecular ions in the solution were at ng·mL^{-1} level, so there were no effective polyatomic molecular ion interferences to the measured isotopes of ^{197}Au, ^{195}Pt, ^{106}Pd, ^{101}Ru, ^{103}Rh, and ^{193}Ir.

3.6. Analytical Performance. The mixed standard solutions for Au, Pt, Pd, Ru, Rh, and Ir were prepared in the medium of 8% (v/v) aqua regia with the concentrations of 0.01 to 100 ng·mL^{-1}. At the optimum conditions, the intensities of Au, Pt, Pd, Rh, Ru, and Ir were detected by ICP-MS, and Re (50 ng·mL^{-1}) was online-added as internal standard element.

Then the analytical performances of the proposed Bi-FA ICP-MS method for the determination of Au, Pt, Pd, Rh, Ru, and Ir were evaluated, and the analytical results including linear ranges and limits of detection (LODs) are listed in Table 4. The dynamic linear range was covering four orders of magnitudes with the correlation coefficients (R^2) ranging from 0.9995 to 0.9999 and low background equivalent concentration (BEC) from 0.002 to 0.085 ng·mL^{-1}. According to the definition of IUPAC, the LODs (3σ) were in the range of 0.002–0.025 ng·g^{-1}. The enrichment factor, defined as the specific value of the sample weight (10 g) before Bi-FA and the weight of Bi granule after Bi-FA (5 mg), was calculated as 2000.

4. Sample Analysis

At the optimum conditions, the developed Bi-FA ICP-MS method was validated by the analysis of a series of CRMs such as soil (GBW07288, GBW07294, and GBW07340) stream sediment GBW07289, olivine GBW07290, pyroxene peridotite GBW07291, chromite GBW07292, palladium poor ore GBW07293, palladium ore (GBW07341 and GBW07342), and gold geological samples (GBW07228, GBW07229 and GBW07230), the determined values are shown in Table 5, and *t*-test was applied to the CRMs and the $t_{0.05,4}$ values for Au, Pt, Pd, Rh, Ru, and Ir in the sample are also listed in Table 5. It could be seen that the determined values were in good agreement with the certified values and *t*-test results were satisfactory, which showed that this method is suitable for trace noble metal elements analysis of soil, rock, and mineral samples.

TABLE 4: Analytical performance data by the established Bi-FA ICP-MS method for Au, Pt, Pd, Ru, Rh, and Ir.

Isotopes	Linear range ($ng{\cdot}mL^{-1}$)	Linear equation	R^2	BEC ($ng{\cdot}mL^{-1}$)	LOD* ($ng{\cdot}g^{-1}$)	Enrichment factor**
^{197}Au	0.01~100	$y = 98397x + 3170$	0.9997	0.032	0.025	2000
^{195}Pt	0.01~100	$y = 70732x + 1006$	0.9999	0.014	0.008	2000
^{106}Pd	0.01~100	$y = 65527x + 12474$	0.9995	0.085	0.024	2000
^{101}Ru	0.01~100	$y = 42747x + 1066$	0.9999	0.025	0.005	2000
^{103}Rh	0.01~100	$y = 242359x + 621$	0.9999	0.003	0.002	2000
^{193}Ir	0.01~100	$y = 198777x + 456$	0.9995	0.002	0.003	2000

*LOD = 3*standard deviation of background/slope of calibration curve, for 10 g sample. **Enrichment factor was the specific value of the sample weight (10 g) before Bi-FA and the weight of Bi granule after Bi-FA (5 mg).

TABLE 5: Comparison of analytical data and recommended values for Au, Pt, Pd, Ru, Rh, and Ir in certified reference materials samples by the proposed Pb-FA LA-ICP-MS method ($n = 5$, $ng\,g^{-1}$).

Element		Au	Pt	Pd	Ru	Rh	Ir
GBW07288	Found	1.1 ± 0.2	0.23 ± 0.03	0.30 ± 0.04	0.062 ± 0.014	0.022 ± 0.005	0.038 ± 0.008
Soil	Certified	0.9 ± 0.2	0.26 ± 0.05	0.26 ± 0.05	(0.05)*	0.017 ± 0.006	0.032 ± 0.012
t-test		2.24	2.24	2.24	1.92	2.24	1.68
GBW07289	Found	12 ± 2	1.4 ± 0.2	2.5 ± 0.3	0.12 ± 0.02	0.099 ± 0.021	0.07 ± 0.02
Stream sediment	Certified	10 ± 2	1.6 ± 0.3	2.3 ± 0.2	(0.10)*	0.095 ± 0.012	0.05 ± 0.01
t-test		2.24	2.24	1.49	2.24	0.43	2.24
GBW07290	Found	1.3 ± 0.2	5.6 ± 0.4	5.1 ± 0.4	16.2 ± 2.8	1.1 ± 0.2	4.7 ± 0.3
Olivine	Certified	1.1 ± 0.1	6.4 ± 0.9	4.6 ± 0.6	14.8 ± 2.7	1.3 ± 0.3	4.3 ± 0.5
t-test		2.24	4.47	2.80	1.12	2.24	2.98
GBW07291	Found	4.7 ± 0.4	61 ± 5	67 ± 5	2.7 ± 0.3	4.9 ± 0.4	5.5 ± 0.4
Pyroxene peridotite	Certified	4.3 ± 0.3	58 ± 5	60 ± 9	2.5 ± 0.2	4.3 ± 0.8	4.7 ± 1.1
t-test		2.24	1.34	3.13	1.49	3.35	4.47
GBW07292	Found	—	23 ± 4	10.1 ± 0.7	501 ± 54	12 ± 2	144 ± 11
Chromite	Certified	—	20 ± 4	11.3 ± 1.5	527 ± 91	10 ± 2	136 ± 10
t-test			1.68	3.83	1.08	2.24	1.63
GBW07293	Found	49 ± 4	432 ± 24	597 ± 42	15 ± 2	24 ± 2	33 ± 5
Palladium poor ore	Certified	(45)*	440 ± 37	568 ± 51	13 ± 1	22 ± 3	28 ± 7
t-test		2.24	0.75	1.54	2.24	2.24	2.24
GBW07294	Found	2.1 ± 0.4	13.1 ± 2.6	17.1 ± 2.4	0.63 ± 0.15	0.92 ± 0.18	1.5 ± 0.2
Soil	Certified	(1.8)*	14.7 ± 2.5	15.2 ± 2.3	0.66 ± 0.20	1.1 ± 0.2	1.2 ± 0.3
t-test		1.68	1.38	1.77	0.30	2.24	3.35
GBW07340	Found	2.6 ± 0.3	0.61 ± 0.06	0.72 ± 0.09	0.47 ± 0.09	0.070 ± 0.007	0.18 ± 0.03
Soil	Certified	(2.3)*	0.66 ± 0.08	0.66 ± 0.08	0.43 ± 0.16	0.066 ± 0.008	0.16 ± 0.03
t-test		2.24	1.86	1.49	0.99	1.28	1.49
GBW07341	Found	—	1947 ± 122	591 ± 43	68 ± 6	5.76 ± 0.45	26 ± 4
Palladium ore	Certified	—	1900 ± 200	570 ± 50	74 ± 7	(6)*	28 ± 6
t-test			0.86	1.09	2.24	1.19	1.12
GBW07342	Found	—	5988 ± 422	1755 ± 145	1.7 ± 0.2	1.7 ± 0.3	2.6 ± 0.3
Palladium ore	Certified	—	5700 ± 500	1670 ± 130	(2)*	1.5 ± 0.5	2.1 ± 0.7
t-test			1.53	1.31	3.35	1.49	3.73
GBW07201	Found	—	11.5 ± 1.8	7.5 ± 0.8	328 ± 12	13.3 ± 2.2	95 ± 8
Chromite	Certified	—	10 ± 1	7 ± 1	305 ± 6	12 ± 1	90 ± 6
t-test			1.86	1.40	4.29	1.32	1.40
GBW07228	Found	3.5 ± 0.3	—	—	—	—	—
Gold geological sample	Certified	3.4 ± 0.2	—	—	—	—	—
t-test		0.75					
GBW07229	Found	54 ± 4	—	—	—	—	—
Gold geological sample	Certified	52 ± 3	—	—	—	—	—
t-test		1.12					
GBW07230	Found	1362 ± 28	—	—	—	—	—
Gold geological sample	Certified	1330 ± 20	—	—	—	—	—
t-test		2.56					

*The value in brackets is the reference value. $t_{0.05,4} = 2.77$, $t_{0.01,4} = 4.60$.

5. Conclusions

In this work, the method of Bi-remaining cupellation fire assay ICP-MS for the simultaneous determination of Au, Pt, Pd, Rh, Ru, and Ir was established. Lower toxicity Bi_2O_3 was used as fire assay collector, and Bi protection cupellation was employed. The Bi granule was microwave-digested by aqua regia and the target noble metal elements were determined by ICP-MS. Volatile Ru could be accurately determined by the proposed Bi-FA method. Compared with toxic Pb-FA and NiS-FA, Bi-FA was green and environmental protection, and it was effective for volatile Ru by using Bi as cupellation protector. The developed method was applied to analyze the multiple types of CRMs and the determined values were in good agreement with the certified values; the proposed method was suitable for the determination of trace and ultratrace Au, Pt, Pd, Rh, Ru, and Ir in geochemical samples on a large scale.

Data Availability

The tables and figures data used to support the findings of this study are included within the article.

Disclosure

Wenshan Ni and Xiangju Mao were co-first authors.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Authors' Contributions

Wenshan Ni and Xiangju Mao contributed equally to this work.

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Supplementary Materials

Fig. S1: the energy dispersive spectrum graph of the black shale. Fig. S2: the scanning micrograph of the black shale by scanning electron microscope. Table S1: isotopes of the determined Au, Pt, Pd, Ru, Rh, Os, Ir, and Re. Table S2: possible mass spectral interferences of polyatomic molecular ion in sample solutions to 197Au, 195Pt,106Pd, 101Ru, 103Rh, 193Ir, and185Re. (*Supplementary Materials*)

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