An Improved Analytical Protocol for the Determination of Sub-nanogram Gold in 1–2 g Rock Samples Using GFAAS After Polyurethane Foam Pretreatment

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ABSTRACT: Gold (Au) is an important indicator in many geochemical studies, but the quantification of sub-nanogram Au in rock samples is challenging. Herein, a simple and rapid analytical protocol for the determination of sub-nanogram Au in 1–2 g rock samples is established using graphite furnace atomic absorption spectrometry (GFAAS) after polyurethane foam (PUF) pretreatment. By employing the optimized extraction conditions, Au recovery can reach up to 95% even for 0.1 ng g⁻¹ Au. Six international rock reference materials (RMs) of basalt, diabase, and gabbro were used to validate the feasibility of this protocol. The results are in agreement with previously reported values obtained using instrumental neutron activation analysis (INAA) or inductively coupled plasma mass spectrometry (ICP-MS), where less or the same amount of sample rock powders were used. Furthermore, the rock RMs of TDB-1 and JB-2 are found to be homogeneous with a precision of < 10% (2 RSD) using only 1 g of sample mass, making them suitable for method validation or quality control for inter-laboratory comparison. Owing to its simplicity, speed, reliability, and low cost, this protocol can be used for Au measurement and tracer provenance in the geochemical community.

INTRODUCTION

Gold (Au), a precious metal and highly siderophile element, is of ultra-low abundance (typically 0.5–5 ng g⁻¹) in the Earth's crustal and mantle rocks.¹ A precise quantification of the Au abundance in different types of rocks is important for many frontier fields of geoscience.^{2–13} However, there is little data on the Au content in rocks, and the metal–silicate partition coefficient of Au measured by different researchers varies dramatically, as much as 2–3 orders of magnitude.^{14,15} Therefore, the accurate determination of sub-nanogram Au content in rocks is key for achieving a clear understanding of the sources of Au and its circulation in the Earth,

which can facilitate important breakthroughs in related fields of Au geochemistry.

Nevertheless, the quantification of sub-nanogram Au in rock samples is demanding. On the one hand, the nugget effect of Au and the platinum group elements (PGEs) necessitates relatively large amounts of rocks to obtain precise data, which still exhibits large deviations. On the other hand, since Au has only one isotope (¹⁹⁷Au), it cannot be quantified by the precise isotope dilution method, like PGEs; therefore, various methods have been established that are associated not only with instrumentation development but also chemical pretreatment for ultra-low Au

quantification of geological samples.^{16,17}

As for instrumental development, inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) have become the main tools for ultra-low Au measurement because of their simplicity, economics, and ready availability in various institutions.^{18,19} Compared with GFAAS, ICP-MS has a lower detection limit,^{20,21} but oxide interference by $^{181}\text{Ta}^{16}\text{O}$ can occur when it is employed for ^{197}Au detection. Owing to the high Ta abundance in rock samples, the high intensity of Ta can cause the Au content to be overestimated by 5–15%, even after interference correction.^{22,23} GFAAS, which has a completely independent measurement principle from that of ICP-MS, has been used for Au determination, and its sensitivity improves with an increase in the testing sample volume.

With regard to chemical pretreatment methods, nickel sulfide fire assay (NiS-FA) with tellurium coprecipitation is widely used to preconcentrate PGEs as well as Au from rocks.^{24–27} However, in addition to the high blank and complicated procedure, this method is not reliable for Au or Re analysis because they are partially volatilized during processing.²⁴ Wet acid digestion is considered as a suitable alternative to FA for extracting Au from geological samples. In this approach, the commonly used enrichment methods such as precipitation, ion exchange resins, solvent extraction, polyurethane foam (PUF), extraction chromatography, and novel solid adsorbents are used in combination.²⁸ As described by Schiller,²⁹ PUF is a more effective adsorbent for Au than PbS , $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and anion exchange resin (Dowex 1-X8). Moreover, in contrast to the multi-stage chemical pretreatment associated with Au loss, the PUF preconcentration procedure is easy, simple, rapid, and low cost in comparison to the above-mentioned approaches.

Since 1970, the classical PUF technique has mainly been used

for the treatment of ore samples.^{30–32} However, the determination of sub-nanogram Au by GFAAS in 1–2 g of rock samples after polyurethane foam pretreatment has never been attempted and reported because of the following reasons. First, less than 2 g of sample powder may or may not be sufficient for sub-nanogram Au preconcentration, although it is ideal for normal acid digestion. Second, ultra-low amounts of Au are typically unstable and can be lost due to glass adsorption.³³ Third, the suitability of PUF for the precise quantification of low Au content in rocks has not been validated in prior literature. Fourth, the matrix effect between low Au and other elements in the final elution solution should be carefully evaluated during GFAAS measurements.

In this study, PUF pretreatment is employed for the determination of sub-nanogram Au in 1–2 g of rock powder samples prior to GFAAS. To obtain high Au recovery, the experimental conditions for adsorption and elution are optimized during the chemical procedure. Moreover, the matrix effects are evaluated to enhance the data quality during GFAAS measurements. Six international rock reference materials (RMs) of basalt, diabase, and gabbro are used to evaluate the robustness of the current protocol. The main goal is to develop a simple and low-cost analytical protocol for the determination of sub-nanogram Au in 1–2 g of rock samples using GFAAS after polyurethane foam pretreatment, which can be used for Au measurement and tracer provenance in the geochemical community.

EXPERIMENTAL

All chemical pretreatments and GFAAS measurements were performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing. The experimental procedure is illustrated in Fig. 1.

Fig. 1 Schematic of the analytical procedure for the determination of sub-nanogram Au in unmineralized rock samples.

Reagents, materials, and labware. HCl and HNO₃ (BV-III grade, Beijing Institute of Chemical Reagents, P.R. China) were purified by sub-boiling distillation using a Savillex™ DST-1000 Teflon® apparatus. Ultrapure water with a resistivity of 18.2 MΩ-cm was obtained using an Elix Milli-Q™ water purification system (Merck Millipore Corporation, USA). A commercial PUF (an open-cell type polyurethane, JX-1) was purchased from Jixiang Sponge Co., Ltd. (P. R. China).

An eluent consisting of 1% m/m thiourea (analytical grade, Sinopharm Chemical Reagent Co. Ltd., Shanghai, P. R. China) in 0.1 mol L⁻¹ HCl was used to remove Au from PUF. An Au(III) stock solution (1000 µg mL⁻¹) was prepared by placing an appropriate amount of HAuCl₄·4H₂O (Merck & Co., Inc., USA) into a 100-mL volumetric flask and diluting to the mark with ultrapure water. Working standard solutions of Au(III) were freshly prepared by gravimetrically diluting the Au(III) stock solution with the eluents.

BIR-1a, BHVO-2, and BCR-2, obtained from the United States Geological Survey (USGS), JB-2 from the Geological Survey of Japan (GSJ), and TDB-1 and WGB-1 from the Canadian Certified Reference Material Project, Energy Mines and Resources, Canada (CCRMP) were used to evaluate and validate the proposed protocol. Inductively coupled plasma optical emission spectrometry (ICP-OES) (IRIS Advantage, Thermo Scientific, USA) was employed for the analysis of metal ions in the final solution.

A muffle furnace (SX2-4-10, Great Wall Furnace Company, P.R. China) was used for sample digestion. A model L550 centrifuge (Xiangyi Centrifugal Machine Equipment Co., Ltd., P. R. China) was employed to separate the acid-insoluble residues. A THZ-C-1 horizontal shaking bath (Taicang Instrument Factory, P.R. China) was used for the static-mode PUF extraction.

Aqua regia digestion. Approximately 1 or 2 g of rock powder (200 mesh) was weighed into a 10-mL ceramic crucible and roasted at 650 °C for 1 h in a muffle furnace to eliminate sulfur, carbon, and organics. After cooling, the sample powder was transferred into a 60-mL Savillex PFA vessel, and 2.5 mL of Milli-Q water was used to rinse the crucible and wet the sample powder. After addition of 2.4 mL of aqua regia (HCl: HNO₃ = 3:1), the lid was tightened and the vial heated on a hot plate at 150 °C for 24 h. The amount of acid used was calculated relative to that used for a 10-g sample powder.³¹ After cooling, the digested sample was transferred into a 25-mL centrifuge tube, and 6 mL of Milli-Q water was used to rinse the PFA vessel, which was then combined with the sample solution. After centrifugation (3500 rpm, 15 min), the supernatant was transferred to a pre-weighed centrifuge tube, and 3 mL of Milli-Q water was used to rinse the tube and residue. After centrifugation, the supernatant was also combined with the

sample solution. Finally, the medium of the final sample solution was approximately 17% aqua regia, which was in the appropriate range (10-30%) for PUF preconcentration without requiring a drying or media transfer step.

Static-mode PUF extraction. Approximately 5 g of the sample solution (equivalent to 1/3 sample) was weighed into a 25-mL centrifuge tube for the spike recovery tests. Then, a 12.5-mg cube of PUF was added to the residual sample solution (approximately 10 g, equivalent to 2/3 sample) and shaken vigorously (300 rpm) for 4 h using a mechanical reciprocating shaker to attain equilibrium. The PUF cube was then retrieved using a plastic rod, squeezed, and rinsed several times with Milli-Q water, and the residual liquid was passed through dust-free paper. Approximately 2 g of the elution solution was weighed into a 5-mL centrifuge tube, and the Au-adsorbed PUF cube was added into this centrifuge tube and boiled in a water bath for 20 min. Finally, the PUF cube was removed and squeezed with a plastic rod several times and the eluent measured directly by GFAAS.

GFAAS. GFAAS measurements were performed using a PerkinElmer® PinAAcle™ 900T atomic absorption spectrometer, equipped with a transversely heated graphite atomizer (THGA) and an autosampler (PerkinElmer, Inc., USA). A hollow cathode lamp and end cap graphite tubes (PerkinElmer part no. N9307832) were used. Longitudinal AC Zeeman-effect background correction was employed to correct for non-specific absorbance. The sample injection volume was 40 µL and the output signals were collected and processed in continuous peak area mode. The optimum instrumental parameters for the determination of Au are listed in Table 1. During Au analysis, an aliquot of 2 ng g⁻¹ Au standard solution was used regularly for evaluating the reproducibility and accuracy of the instrument.

Table 1. Instrumentation Parameters, Thermal Program, and Action Sequence for the Analysis of Au by GFAAS

Spectrometer	PerkinElmer PinAAcle 900T			
Wavelength (nm)	242.8			
Spectral bandwidth (nm)	0.7			
Lamp current (mA)	11			
Signal measurement	Peak area			
Matrix modifier	5 µg Pd + 3 µg Mg (NO ₃) ₂			
THGA				
Steps	Temperature (°C)	Ramp time (s)	Hold time (s)	Internal flow (mL / min)
Drying	110	1	60	250
Drying	130	15	30	250
Ashing	800	10	30	250
Atomization	1800	0	5	0
Cleaning up	2450	1	3	250
Inject 40 µL sample solution and 5 µL matrix modifier				
Run steps 1 - 5				

RESULTS AND DISCUSSION

Optimization of graphite furnace heating program. The pyrolysis and atomization temperatures for Au analysis were optimized using certified reference material (CRM) TDB-1. Although a high pyrolysis temperature can reduce the background absorption, it should be as low as possible to ensure that there is no loss of target element. A low atomization temperature can increase the service life of the graphite tube; however, it should be sufficient to achieve sensitivity and reproducibility. The optimal pyrolysis and atomization temperatures are shown in Fig. 2 and Table 1. Under these optimal conditions, the absorption signal can return to the baseline within a 5 s atomization time.

Detection limit and total procedural blank (TPB). The detection limit and TPB are the key factors for the determination of Au concentrations. The characteristic mass, instrumental detection limit (IDL), TPB over a period of two years, and method detection limit (MDL) are listed in Table 2. The blank values are subtracted from all the results obtained in this study. The detection limit of this method (0.19 ng g^{-1} , TPB + 10SD) meets the requirements for the analysis of Au content in rocks, where the Au concentration is typically $0.5\text{--}5 \text{ ng g}^{-1}$.

Extraction conditions for Au recovery during PUF pretreatment

Effect of shaking time and initial concentration. According to the results of Li³⁴ and Wu *et al.*³⁵, 10–30% aqua regia is a suitable acid medium for Au adsorption by PUF. Furthermore, a low temperature is better than a high temperature.³⁰ Therefore, to simplify the analytical process and optimize the efficiency; an acid medium of 20% aqua regia and an adsorption temperature of 25°C were used to study the effect of shaking time on Au adsorption. The extraction efficiency of Au by PUF using 10 ng of Au standard solution was first investigated for various shaking times ranging from 15–120 min. More than 90% Au is adsorbed during the first 15 min. Since the Au content of most rocks is at the sub-nanogram levels ($\sim 0.5 \text{ ng g}^{-1}$), for 2 g of rock sample the initial concentration is as low as 0.1 ng g^{-1} . Therefore, standard solutions of 0.5 , 1.0 , and 2.0 ng g^{-1} were used to establish the relationship between initial Au concentration and recovery. As shown in Fig. 3, with a decrease in Au concentration, the recovery rate decreases, and at 0.5 ng g^{-1} , the recovery is less than 90%. Since the adsorption was far from equilibrium at low concentrations, to reach adsorption equilibrium and achieve high Au recovery, the shaking time, PUF mass, and initial concentration (concentration in the initial solution) were increased.

Effect of PUF mass and elution method. Fig. 4 shows that doubling the shaking time from 120 to 240 min is effective. For 0.5 ng g^{-1} of standard solution, doubling the shaking time increases the recovery of Au from 88% to 97%. Furthermore, the Au

Fig. 2 Pyrolysis and atomization curve of GFAAS measurement (AA: atomic absorbance; BG: background absorbance).

Fig. 3 Effect of initial concentration and elution method on Au recovery. Method 1: PUF is squeezed several times and discarded; Method 2: PUF is washed with hot eluent several times. Conditions: 12.5 mg PUF, 25°C , 20% aqua regia, 10 g standard solution, and 120 min ($n = 3$). Error bars represent the standard deviation (SD).

recovery for a concentration as low as 0.1 ng g^{-1} can also be up to 95%. However, using a shaking time of 240 min, increasing the PUF mass or increasing the initial concentration does not significantly improve the recovery rate. This observation is also supported by previous studies.³⁶ Therefore, the shaking time was only increased to 240 min. Based on this intensive investigation, for a rock sample with a low Au content, more shaking time is required to achieve quantitative Au recovery.

The most common elution method (method 1) involves squeezing the PUF several times and, after boiling in acidic thiourea solution for 20 min, discarding it. Although the Au recovery achieved using this method is sufficient for the ore samples, the solution remaining in PUF can affect the Au recovery

Table 2. Analytical Performance, Detection Limit, and Total Procedural Blank (TPB) in this Study

Element	Characteristic mass, pg	Slope, abs g ng ⁻¹	R ²	IDL, ^a ng g ⁻¹	TPB, ng g ⁻¹	SD, ng g ⁻¹	MDL, ^b ng g ⁻¹
Au	14.2	0.0124	0.9999	0.024	0.026	0.016	0.19

^a The IDL was calculated as three times the standard deviation over slope of 10 replicate measurements by taking an eluent solution;

^b The MDL in the sample was based on TPB plus 10 times the standard deviation of 10 individual total procedural blanks according to Gold Book of IUPAC assuming a dilution factor of 1.

Fig. 4 Effects of shaking time, PUF mass, and initial concentration on Au recovery for solutions with low concentrations of Au ($n = 3$). Error bars represent the SD and shaded area represents 95–105% recovery.

Table 3. Recovery of Au in Various RM Solutions During GFAAS Analysis ($\pm$ standard deviation)

Sample (ng g ⁻¹)	Expected concentration increase	Measured concentration	Recovery (%)
BHVO-2	-	0.61	-
	1.0	1.63	102
	-	0.73	-
	1.0	1.68	95.0
	-	0.80	-
	1.0	1.76	96.0
Mean $\pm$ SD			97.7 $\pm$ 3.8
TDB-1	-	0.94	-
	1.5	2.40	97.3
BCR-2	-	0.87	-
	1.5	2.32	96.7

for rock samples, which has significantly lower Au concentrations. Therefore, a hot eluent was used to wash PUF several times (method 2). As shown in Fig. 3, method 2 results in lower Au recovery compared to that achieved by method 1. This can be due to the fact that there is insufficient time for the hot eluent to leach Au from PUF. However, based on these results, the dissolution equilibrium of Au can be achieved in 20 min, *i.e.*, the Au concentration in the recovered eluent may be the same as that remaining in PUF. Thus, based on the total weight of the eluent before adding PUF, the amount of Au adsorbed on PUF can be quantitatively calculated.

Matrix effect on GFAAS determination and PUF adsorption

Matrix effect on GFAAS determination. Although PUF has a

high affinity towards Au, many other elements may be present in the final solution and affect Au analysis. Therefore, the final solution was analyzed using ICP-OES to determine the contents of elements that easily adsorb on PUF (Table 1S). It was found that almost all of the elements are separated from Au. However, the concentrations of these residual elements are four orders of magnitude higher than that of Au. To ensure that there was no matrix effect on Au determination, the standard recovery and standard addition (SA) methods were employed.

Standard recovery of Au from various RMs. To examine the effect of the matrix on the analysis step, the sample solutions were spiked and the recovery of Au was calculated (Table 3). As shown, the BHVO-2 recovery is 97.7% $\pm$ 3.8% with the addition of a matrix modifier (Pd + Mg (NO₃)₂). Similar results are obtained for BCR-2 and TDB-1. The matrix modifier may already eliminate the matrix effect during GFAAS analysis.

Comparison of SA and external standard (ES) method. To further confirm this conclusion, the SA technique, which can overcome a specific type of matrix effect that would otherwise afford a biased result, was utilized. Notably, several assumptions and considerations must be evaluated before using this technique. First, the slopes obtained using the SA and ES methods should be compared to ensure that the SA method provides a high accuracy of analysis. Second, good linear correlation is required to ensure that the degree of matrix interference does not depend on the target/interference element ratio. Finally, all measurements, before and after addition of the analyte, must be performed at concentrations below the upper limit of analysis.^{37,38} As shown in

Fig. 5 (A) Linearities and slopes obtained for BHVO-2 using the SA (blue line) and for standard solutions using ES (orange line) methods. (B) Comparison of the results obtained using SA and ES methods for the same RM solutions. Most of the values are consistently within a few percent uncertainties.

Table 4. Recovery of Au from Various RMs in the Entire Procedure ($\pm$ standard deviation)

Sample /Au	Added (ng)	Measured (ng)	Recovery (%)
BCR-2	2.10	2.06	98.1
	2.10	2.22	106
	2.10	2.26	108
		Mean $\pm$ SD	104 $\pm$ 5
BIR-1a	2.10	2.07	98.6
	2.10	1.99	94.8
	2.10	2.04	97.1
		Mean $\pm$ SD	96.8 $\pm$ 1.9
JB-2	2.10	2.29	109
	2.10	2.25	107
	2.10	2.20	105
		Mean $\pm$ SD	107 $\pm$ 2

Fig. 5a, the linearity and slope obtained for BHVO-2 using the SA method are sufficient to afford accurate results.

In this study, the results obtained using the SA and ES methods for the same purified sample solution are compared. Although the RMs have different Au contents, a good linear relationship ($R^2 = 0.996$) is observed. Furthermore, the results of the ES method agree well with those of the SA method (relative error is mostly within 5%, Fig. 5b). This further indicates that the matrix effect is negligible during GFAAS analysis and a simple ES method can be used for routine analysis.

Matrix effect on PUF adsorption. Since the GFAAS analysis step provided accurate results, it was further examined if a large number of coexisting elements in the sample solution could affect the adsorption of Au by PUF. The digested sample solution (the 1/3 part in Fig. 1) was spiked with the Au standard solution, and the Au recovery was thereafter determined for the entire process. As shown in Table 4, standard recovery rates of 96.8–107% are obtained for the three RMs, showing that the coexisting elements in the digested rock sample solution have no effect on the Au enrichment and, therefore, PUF has very high affinity for Au. It

can, therefore, be stated that all of the analysis steps of this improved protocol are reliable (Table 4).

Method validation. To further validate this proposed protocol, six international rock RMs were analyzed, and the results compared with certified^{39,40} and published values.^{22,24,27,41–52} As shown in Fig. 6 and Table 5, CRM TDB-1 yields a mean value of 6.29 ± 0.54 ng g⁻¹ (2SD, $n = 5$), which is consistent with the certified value of 6.3 ± 1.0 ng g⁻¹. This result indicates that TDB-1 is homogeneous in the 1-g sample and that this method is precise and reliable, and has a 2SD value (0.54) smaller than the certified uncertainty (1.0), which is typically obtained using a sample mass of ≥ 10 g.^{39,53} Compared with other reported values, the results of NiS-FA in combination with ICP-MS are typically lower, which indicates that this process may involve Au loss because of volatility issues, as is also reported in prior literature (Table 6).²⁴

For a 2-g sample mass of CRM WGB-1, the obtained mean value of 1.95 ± 0.93 ng g⁻¹ (2SD, $n = 3$) is lower than the certified value of 2.9 ± 1.1 ng g⁻¹ but consistent with other reported values, such as 1.79 ± 0.69 ng g⁻¹ (2SD, $n = 9$)²² and 1.7 ± 1.2 ng g⁻¹ (2SD, $n = 5$)⁵⁰ (Fig. 6 and Table 5). Although WGB-1 is not homogeneous in the 2-g sample, the 2SD (0.92) value of the present method is comparable to the certified uncertainty (*i.e.*, 1.1), which indirectly indicates the precision of this method. Because of the high background, the alkaline fusion methods afford the highest values among the published data. It is possible that this method is not suitable for Au analysis in rocks (Table 6).

For JB-2, BIR-1a, BHVO-2, and BCR-2, the results obtained in this study are compared with published values. As shown in Fig. 6 and Tables 5 and 6, the value for JB-2 (4.75 ± 0.22 ng g⁻¹, 2SD, $n = 4$) is consistent with those reported by Terashima⁴⁷ (4.56 ± 1.3 ng g⁻¹, 2SD, $n = 5$) using MIBK extraction / GFAAS, and Cheng *et al.*²² (4.76 ± 0.07 ng g⁻¹, 2SD, $n = 2$) using cation exchange resin/internal standard isotope dilution ICP-MS. For BIR-1a, the data (2.55 ± 0.35 ng g⁻¹, 2SD, $n = 3$) agree well with those reported by Constantin⁴⁹ (2.53 ± 0.42 ng g⁻¹, 2SD, $n = 5$) using instrumental

Fig. 6 Au contents of unmineralized rock RMs. Red dashed line in the middle and shaded area represent the mean value and 2SD of this study, respectively. Error bars correspond to the uncertainties (certified values) or 2SD (others); CV: certified value.

Table 5. Results of Au Content (ng g⁻¹) in RMs

Sample (Rock type)	Analysis No.	Sample mass (g)	Au (ES)	2SD	Au (SA)	2SD
TDB-1 (Diabase)	1	1.0006	6.47		6.44	
	2	1.0253	6.09			
	3	1.0299	6.68			
	4	1.0216	6.14			
	5	1.0007	6.09			
	Mean		6.29	0.54		
JB-2 (Basalt)	1	1.0070	4.84		5.01	
	2	1.0386	4.61			
	3	1.0118	4.72			
	4	1.0476	4.83			
	Mean		4.75	0.22		
BIR-1a (Basalt)	1	2.0249	2.53		2.54	
	2	2.0142	2.38		2.35	
	3	2.0388	2.73		3.01	
	Mean		2.55	0.35	2.63	0.68
WGB-1 (Gabbro)	1	2.1648	1.45			
	2	2.1858	2.37			
	3	1.9341	2.04			
	Mean		1.95	0.93		
BHVO-2 (Basalt)	1	2.0076	1.27		1.33	
	2	1.9999	1.06			
	3	2.0053	1.20			
	4	2.0046	1.33			
	5	1.9922	1.38			
	6	2.0940	1.13			
	7	2.0425	1.16			
	8	2.1230	1.05			
	Mean		1.20	0.24		
BCR-2 (Basalt)	1	2.0032	0.69		0.58	
	2	2.0035	1.02		1.08	
	3	2.0149	0.86			
	4	1.9977	0.73			
	5	1.9761	0.80			
	Mean		0.82	0.26	0.83	0.71

neutron activation analysis (INAA) for BIR-1 and the unpublished data (2.73 ± 0.10 ng g⁻¹, 2SD, n=1) of Cheng *et al.*²² Additionally, the results for BHVO-2 (1.20 ± 0.24 ng g⁻¹, 2SD, n = 8) are

consistent with the data (1.29 ± 0.24 ng g⁻¹, 2SD, n = 9) reported by Cheng *et al.*²² and for BCR-2, the data (0.82 ± 0.26 ng g⁻¹, 2SD, n = 5) are in agreement with the value (0.84 ± 0.05 ng g⁻¹, 2SD, n = 3) reported by Cheng *et al.*²² using IS-ID-ICP-MS. Based on the comparison of the published results for BHVO-2 and BCR-2, INAA is possibly not suitable for treating sample amounts of < 1 ng g⁻¹, which is close to its detection limit (Table 6).

The agreement of these results confirms the accuracy of the method proposed herein, and that appropriate Au homogeneity is achieved in sample masses of 1–2 g for these RMs. In summary, all results show that this method improved the analysis of Au in rock samples and is precise and robust; in addition, these parameters are comparable to those of the IS-ID-ICP-MS method.

Advantages and limitations. The current protocol has advantages in terms of chemical preparation and spectrometric measurement in comparison to previously reported methods. On the one hand, compared with other chemical treatments, this protocol has some obvious merits (Fig. 1). First, in contrast to FA, alkali fusion and the carius tube technique, the sample digestion and preparation are easy and simple to conduct in most geochemical laboratories. Second, compared with complicated preconcentration methods (e.g., extraction resins,²¹ cation exchange resin,²² and Pb-FA⁵⁴), the PUF technique affords rapid pre-concentration at lowest cost. Third, the reagent and material consumption are approximately 1/3 of those required in other methods for the same sample powder.

On the other hand, to some extent, GFAAS also has some merits over other techniques. Compared with the less used INAA method, which is suitable for the analysis of samples with high Au content (> 10 ng g⁻¹),⁴⁹ the present method with 0.19 ng g⁻¹ MDL has an obvious advantage. Additionally, for most rock samples (0.5–5 ng g⁻¹ Au), this method is preferable to ICP-MS, since not only is the cost of GFAAS significantly lower, but the data quality of GFAAS is also almost comparable to that of ICP-MS (Table 6 and Fig. 6).

Nevertheless, the current protocol also has some limitations. For samples with Au content of < 0.5 ng g⁻¹, the high inherent sensitivity of ICP-MS affords potential advantages over GFAAS.

Table 6. Comparison of Sub-nanogram Contents of Au Obtained in this Study and Previously Published Values for the RMs

Sample (Rock type)	Sample digestion	Instrument	Sample mass (g)	n	Mean $\pm$ 2SD (ng g ⁻¹)	Reference
TDB-1 (Diabase)	-	-	-	-	6.3 $\pm$ 1.0 ^a	CCRMP, (1994) ³⁹
	Pb FA	ICP-OES	-	20	6.00 $\pm$ 1.00	Richardson <i>et al.</i> (1996) ⁴¹
	NiS FA	INAA	10-20	-	6.42 $\pm$ 0.10	Garuti <i>et al.</i> (2000) ⁴²
	NiS FA	ICP-MS	50	25	4.80 $\pm$ 2.00	Plessen <i>et al.</i> (1998) ⁴³
	Na ₂ O ₂	ICP-MS	2	-	6.70 $\pm$ 1.40	Qi <i>et al.</i> (2003) ⁴⁴
	NiS FA	ICP-MS	15	-	4.00 $\pm$ 2.30	Savard <i>et al.</i> (2010) ³⁴
	HF + AR	ICP-MS	4	21	6.30 $\pm$ 1.70	Pitcarin <i>et al.</i> (2015) ⁴⁵
	NiS FA	ICP-MS	5	4	4.35 $\pm$ 4.02	Hao <i>et al.</i> (2017) ⁴⁶
	AR	ICP-MS	2	20	6.10 $\pm$ 0.70	Cheng <i>et al.</i> (2019) ²²
JB-2 (Basalt)	AR	GFAAS	1	5	6.29 $\pm$ 0.54	This study
	AR	GFAAS	0.1-2	5	4.56 $\pm$ 1.30	Terashima (1988) ⁴⁷
	HF + AR	GFAAS	0.5-2	4-8	5.36 $\pm$ 0.54	Terashima <i>et al.</i> (1992) ⁴⁸
	AR	GFAAS	1	4	4.75 $\pm$ 0.22	This study
	-	INAA	1-3	5	6.33 $\pm$ 1.40	Constantin (2009) ⁴⁹
BIR-1a (Basalt)	AR	ICP-MS	1.5	2	4.76 $\pm$ 0.07	Cheng <i>et al.</i> (2019) ²²
	-	INAA	1-3	5	2.53 $\pm$ 0.42 ^b	Constantin (2009) ⁴⁹
	AR	ICP-MS	2	1	2.73 $\pm$ 0.10	Cheng <i>et al.</i> (2019) ²² unpublished data
WGB-1 (Gabbro)	AR	GFAAS	2	3	2.55 $\pm$ 0.35	This study
	-	-	-	-	2.9 $\pm$ 1.1 ^a	CCRMP, (1994) ⁴⁰
	NiS FA	INAA	50	5	1.70 $\pm$ 1.20	Maier <i>et al.</i> (2003) ⁵⁰
	-	INAA	-	4	1.30 $\pm$ 1.20	Maier <i>et al.</i> (2008) ⁵¹
	NiS FA	ICP-MS	50	30	2.00 $\pm$ 1.74	Plessen <i>et al.</i> (1998) ⁴³
	Na ₂ O ₂	ICP-MS	10	4	3.50 $\pm$ 0.48	Jin <i>et al.</i> (2000) ⁵²
	NiS FA	ICP-MS	5	4	1.66 $\pm$ 1.40	Juvonen <i>et al.</i> (2002) ²⁷
	Na ₂ O ₂	ICP-MS	2	-	3.40 $\pm$ 1.20	Qi <i>et al.</i> (2003) ⁴⁴
	NiS FA	ICP-MS	15	-	1.26 $\pm$ 0.50	Savard <i>et al.</i> (2010) ³⁴
BHVO-2 (Basalt)	AR	ICP-MS	2	9	1.79 $\pm$ 0.69	Cheng <i>et al.</i> (2019) ²²
	AR	GFAAS	2	3	1.95 $\pm$ 0.93	This study
	-	INAA	1-3	4	2.62 $\pm$ 1.26	Constantin (2009) ⁴⁹
BCR-2 (Basalt)	AR	ICP-MS	2	11	1.29 $\pm$ 0.24	Cheng <i>et al.</i> (2019) ²²
	AR	GFAAS	2	8	1.20 $\pm$ 0.24	This study
	-	INAA	1-3	3	1.32 $\pm$ 0.38	Constantin (2009) ⁴⁹
BCR-2 (Basalt)	AR	ICP-MS	2	3	0.84 $\pm$ 0.05	Cheng <i>et al.</i> (2019) ²²
	AR	GFAAS	2	5	0.82 $\pm$ 0.26	This study

^a Certified values; ^b The result of BIR-1

ICP-MS can simultaneously provide information regarding Au and PGEs contained in the rock samples. However, ICP-MS is also associated with ultra-low blank, complex chemical procedures, and the risk of TaO interference during mass spectrometric measurements. In summary, for most rock samples, the optimized protocol presented herein is the most suitable for sub-nanogram Au analysis in the various geochemical laboratories by GFAAS.

CONCLUSIONS

In this study, an improved analytical protocol is developed for the analysis of sub-nanogram Au in 1–2 g of rock samples using GFAAS after PUF pretreatment. The current protocol is validated

by its applicability and robustness for the analysis of six common international rock RMs. The obtained results indicate that TDB-1, JB-2, BIR-1a, and BHVO-2 are homogeneous within an uncertainty of $\leq 20\%$ (2RSD) for a 2-g sample powder. In particular, TDB-1 and JB-2 afford small deviations (2RSD $< 10\%$) with rock powder samples as low as 1 g. Therefore, these rock RMs can be used to evaluate the feasibility of the method development or quality control of sub-nanogram Au analysis. The current method has the following advantages compared to the existing methods: 1) easy, simple, and fast chemical pretreatment using PUF, without complicated isolation and/or the need for special equipment, and can be easily performed in most geochemical laboratories worldwide; 2) GFAAS with low-cost and easy operation can facilitate wide application and exploration

of rock Au in various geochemical studies (*e.g.* crustal process, ore genesis, planetary differentiation, and plume volcanism); 3) only 1–2 g of rock sample is required, where pre-concentration as well as low blank levels reduce and eliminate the sample preparation time and sample or reagent consumption without compromising the precision and accuracy of the measurements. Therefore, the current protocol can be potentially applied to the analysis of limited or precious terrestrial and extra-terrestrial samples. In summary, both the protocol and the obtained data can be useful for Au measurement and tracer provenance in the geochemical community.

ASSOCIATED CONTENT

Please contact the corresponding author for Supporting Information. Table S1, Contents of various elements in the eluent for GFAAS determination.

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Notes

The authors declare no competing financial interest.

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