Determination of Silver in Geological Samples by Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometry After Extraction From Boiling *aqua regia*

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INTRODUCTION

In the study of geochemical prospecting and geochemical partitioning, the concentration of silver (Ag) in such samples can be used as an important index of geochemical characteristics for the analysis of geochemical anomalies to understand element enrichment, to explore causes, and to establish the criteria of geological and geochemical ore-prospecting, etc. However, Ag is a low-abundance (to ng g⁻¹ levels) element in the earth's crust (1-2) and very difficult to quantify accurately.

Nowadays, atomic absorption spectrometry (AAS) (3-5) and inductively coupled plasma optical emission spectrometry (ICP-OES) (6-8) are the commonly used analytical techniques for the determination of trace Ag in geological samples. Compared to AAS and ICP-OES, inductively coupled plasma mass spectrometry (ICP-MS) is widely used for the determination of trace levels of Ag and other metals (9-10) owing to its high sensitivity, multi-element capability, and very wide dynamic range (11-12). However, in most geological samples, the abundance of zirconium (Zr) is several orders of magnitude higher (2300 times) than the abundance of Ag in the earth's crust (2). In addition, the oxides of Zr (⁹⁰Zr¹⁷O⁺, ⁹¹Zr¹⁶O⁺, ⁹¹Zr¹⁸O⁺), the hydroxides of Zr (⁹⁰Zr¹⁶OH⁺, ⁹⁰Zr¹⁸OH⁺, ⁹¹Zr¹⁷OH⁺) as well as the oxides

ABSTRACT

In this work, a valid method was developed for the determination of Ag in large geological samples using dynamic reaction cell (DRC) ICP-MS after extraction from boiling *aqua regia*. In the extraction procedure, over 90% of the Zr and Nb which produces oxide and hydroxide interferences was removed. The residual Nb-oxide and Zr-hydroxide interferences were eliminated by DRC technology. Under the optimized O₂ flow rate (2.7 mL min⁻¹), the background signal was reduced by two orders of magnitude at m/z 109 and the limit of quantitation (LOQ 10σ) for ¹⁰⁹Ag⁺ was 0.2 ng g⁻¹. The proposed method was applied to the direct determination of Ag in 10 different geological standard reference materials (SRMs), and the results were in good agreement with the certified values.

and hydroxides of yttrium (Y) and niobium (Nb) (⁸⁹Y¹⁸O⁺, ⁸⁹Y¹⁷OH⁺, ⁹³Nb¹⁶O⁺) interfere with the accurate determination of Ag by ICP-MS.

In order to obtain reliable results, the interferences have to be eliminated and several methods have been employed. Mathematical correction equation is a common method, but it is unable to solve the multiple atomic interference problems of Ag and could lead to significantly erroneous results (13-14). Using high-resolution sector field ICP-MS is one possible method for eliminating the interferences but the resolution required to

remove the oxide and hydroxide interferences on the isotopes of silver are 23,600 (¹⁰⁷Ag) and 31,457 (¹⁰⁹Ag) (15-16); however, both values are significantly higher than the currently available high-resolution instruments can achieve (m/Δm ≈ 10,000). The use of a matrix separation/pre-concentration procedure is inevitable and many researchers have established methods which can remove the interfering elements effectively (17-21). However, these separation methods are either time-consuming or require a special equipment setup, and pose higher risks of contamination. Fortunately, Li et al. (22) established a simple method to minimize the interferences of Zr, Nb, and Mo in the sample preparation procedure based on their extraction in boiling *aqua regia* in an open vessel, and obtained satisfactory recoveries of trace Ag. However, there are still some problems in this procedure since the residual concentrations of Zr and Nb are hundreds of times higher than that of Ag which can result in positive bias. Recently, Guo et al. (23) reported a method based on ion-molecule reactions in a dynamic reaction cell (DRC^{TM}) to eliminate oxide interferences and the direct determination of ultra-trace silver in soils. Although the interference signal can be reduced up to 100-fold, the capability of this method to eliminate interferences is limited due to the high Zr and Nb values in geological samples. This method also requires a special sample digestion device which, after repeated addition of HNO₃ to evaporate and

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remove Si and HF after the sample digestion is completed, can pose a high risk of contamination or lose target analytes. Thus, this method is not suitable for the determination of Ag in large geological samples.

In this work, a method for the direct determination of trace Ag in geological samples based on DRC-ICP-MS (in combination with sample pre-treatment by extraction in boiling aqua regia) was investigated. It was found that the oxide and hydroxide interference from Zr and Nb can be effectively eliminated. The established method was verified by determining trace Ag in 10 geological standard reference materials (SRMs) with good results.

EXPERIMENTAL

Instrumentation

A PerkinElmer® ELAN® DRC™-e (Dynamic Reaction Cell™) ICP-MS instrument (PerkinElmer, Inc., Shelton, CT, USA) was used and is described in detail elsewhere (24, 25). The typical instrument configurations and operating parameters used in this work are summarized in Table I.

Reagents, Chemicals, and Stock Solutions

The oxygen (O₂) (99.999%) was purchased from Praxair Investment Co., Ltd., P.R. China). High-purity water (18.2 MΩ·cm⁻¹) was used throughout this work and was obtained from a Millipore® Milli-Q® Direct 8 water purification system (Millipore Corporation, France). Nitric acid (HNO₃, 65–70%, w/w, 99.9999%) and hydrochloric acid (HCl, 99.999%) were purchased from Beijing Chemical Reagent Research Institute. The signal element stock solutions (Ag, Zr, Nb, and Rh) were purchased from the National Center for Analysis and Testing of Steel Materials, P.R. China. Three soils, three sediments and four rock SRMs (GBW07425, GBW07429, and GBW07451 Soil,

GBW07301a, GBW07302, and GBW07303 Sediment, GBW07103, GBW07105, GBW07110, and GBW07113 Rock) were used to assess the accuracy of this method (purchased from the Institute of Geophysical and Geochemical Exploration, Langfang, P.R. China).

Sample Preparation by Extraction in Boiling aqua regia

A homogenized sample of 0.5000 g was weighed into a 25-mL polyethylene tube to which 6.0 mL of aqua regia was added. The tube was capped and placed in a water bath at 95 °C for 2 hours. After cooling to room temperature, the solution was diluted to 25 mL with high purity water and centrifuged to remove the undissolved solid particles. A 2.0-mL amount of supernatant liquid was transferred into a 25-mL polyethylene tube and 0.25 mL of 1 mg L⁻¹ Rh internal standard solution was added. The final solution was diluted to 25 mL with high purity water.

RESULTS AND DISCUSSION

Elimination of Interferences

It is well known that the oxides and hydroxides of Zr and Nb severely interfere in the ICP-MS determination of Ag in geological samples. Fortunately, Zr and Nb can be eliminated by an incomplete digestion technique based on the extraction in boiling aqua regia (22, 26-27). Zr and Nb are lithophilic elements which are strongly bound to silicate minerals and cannot be dissolved completely in this process (26). An extraction procedure separates most of the Zr and Nb matrix (>90%) from the Ag analyte, and thus result in satisfactory recoveries (22). Although most of the interfering elements are removed by this procedure, the residual concentrations were found up to several hundredfold higher (210-fold, 259-fold, and 509-fold) than that of Ag (shown in Table II) which can result in significant positive bias.

TABLE I
Instrumental Operating Parameters

ICP-MS	PerkinElmer® ELAN® DRC™-e
Sample introduction	PFA-400 Micro Flow nebulizer
Spray chamber	Cyclonic spray chamber (PC3 Peltier Chiller), room temperature
Injector tube	1.0 mm i.d. quartz
RF power	1350 W
Plasma gas flow	16 L min ⁻¹
Auxiliary gas flow	1.0 L min ⁻¹
Nebulizer gas flow	0.78 L min ⁻¹
O2 reaction gas flow	2.7 mL min ⁻¹
Rejection parameter, q	0.8 for ¹⁰⁹ Ag ⁺ , 0.25 for ¹⁰³ Rh ⁺
Rejection parameter, a	0
Auto Lens	On
Dwell time	50 ms
Sweeps	32
Readings	1
Replicate	3
Cones	Ni
Monitored ions	¹⁰⁹ Ag ⁺ and ¹⁰³ Rh ⁺

Fortunately, the interferences from the residual concentrations of Zr and Nb can be eliminated by using the DRC technique with O₂ as the reaction gas. In this study, background equivalent concentration (BEC) was used as a criterion for the optimization of DRC conditions. Figure 1 shows the effect of the O₂ gas flow rate on the signals of the matrix blank and 1 ng mL⁻¹ Ag + matrix blank at m/z 109. A mixture of 500 ng mL⁻¹ Nb and 2000 ng mL⁻¹ Zr was used as the matrix blank to simulate the interfering elements on Ag determination. As shown in Figure 1, at a low O₂ flow rate there was a sharp increase in the signals of the interfering species at m/z 109. With increasing O₂ flow rates,

the background signal decreased rapidly at m/z 109 (Figure 1). The optimum O₂ flow rate was selected at 2.7 mL min⁻¹ and the signal at m/z 109 generated by the interfering ions was reduced by two orders of magnitude and the background equivalent concentration (BEC) was 0.03 ng mL⁻¹.

The optimization profile (Figure 2) indicates that the interfering species decreased with increasing O₂ gas flow rates. The success of the reaction is based on the generation of multiple oxide/hydroxide species and is shown as follows:

Therefore, the oxide/hydroxide interferences (⁹⁰Zr¹⁸O⁺, ⁹⁰Zr¹⁸OH⁺, ⁹³Nb¹⁶O⁺) on the ¹⁰⁹Ag⁺ determination could be completely removed with high O₂ flow rates (2.7 mL min⁻¹).

Analytical Performance

Under the optimized experimental conditions, the limit of quantitation (LOQ, 10 times the standard deviation of the procedural blank) was 0.2 ng g⁻¹ for Ag. The LOQ is expressed as the concentration in the sample. The relative standard deviation (RSD) was calculated based on triplicate sample digestions and analyses, and was generally less than 5%.

Analysis of Geological Standard Reference Materials (SRMs)

In order to investigate the suitability, accuracy, and precision of the proposed method, 10 different types of geological SRMs, which included four rocks, three sediments, and three soils, were analyzed. As can be seen from Table III, the obtained values of the established method (DRC-ICP-MS), without any correction, are in good agreement with the certified values. However, for the low values of Zr/Ag and Nb/Ag in GBW07303, the determi-

TABLE II
Results for Zr and Nb Level in Three Geological SRMs
Using Boiling Aqua Regia

Geological SRMs	Zr (μg g ⁻¹)		Nb (μg g ⁻¹)		Ag (μg g ⁻¹)	Zr/Ag ^a Nb/Ag ^a	
	Certified	Extraction	Certified	Extraction	Certified		
GBW07425							
Soil	270±9	25.4±0.5	13.8±0.6	1.2±0.1	0.098±0.007	259	12
GBW07302							
Sediment	460±40	33.6±0.4	95±9	6.65±0.04	0.066±0.015	509	100
GBW07113,							
Rock	403±35	16.8±0.06	34.3±3.1	2.31±0.03	0.08±0.02	210	28

^a The value of Zr/Ag and Nb/Ag is that the value of extraction of Zr and Nb divided by the certified value of Ag.

Fig. 1. Effects of O₂ gas flow rate on signal intensity of ¹⁰⁹Ag⁺ + matrix, matrix blank, and background equivalent concentration (BEC). The concentration of Ag was 1 ng mL⁻¹, a solution of 500 ng mL⁻¹ Nb and 2000 ng mL⁻¹ Zr was used as matrix blank.

Fig. 2. Effects of O₂ on the ion signal intensities of ⁹³Nb⁺, ⁹³Nb¹⁶O⁺, ⁹¹Zr⁺ and ⁹²Zr¹⁶OH⁺. The concentrations of Nb and Zr were 500 ng mL⁻¹ and 2000 ng mL⁻¹, respectively.

nation values using conventional ICP-MS and DRC-ICP-MS all agreed with the certified values. For the high values of Zr/Ag and Nb/Ag in GBW07105 and GBW07301a, respectively, the results by conventional ICP-MS method are larger than the Ag certified values, which is due to the interference of Zr and Nb and, fortunately, can be solved by using the proposed method.

CONCLUSION

A method for the DRC-ICP-MS determination of trace Ag in geological samples after extraction in boiling *aqua regia* was developed. The significant oxide and hydroxide interferences from Zr and Nb were successfully eliminated by the proposed method. This method is much simpler than the conventional methods based on pre-concentration and separation, and has great potential for the direct determination of trace levels of Ag in a broad range of geological samples.

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REFERENCES

1. S. Gao, T. C. Luo, B. R. Zhang, H. F. Zhang, Z. D. Zhao and Y. K. Hu, *Geochim. Cosmochim. Acta.* 62, 1959 (1998).
2. R. L. Rudnick and S. Gao, *Treatise on Geochemistry*. Amsterdam: Elsevier (2003), pp. 1-70.
3. G. Chakrapani, P. L. Mahanta, D. S. R. Murty and B. Gomathy, *Talanta* 53, 1139 (2001).
4. I. M. Dittert, D. L. G. Borges, B. Welz, A. J. Curtius and H. Becker-Ross, *Microchim. Acta* 167, 21 (2009).
5. Y. Cao, P. Wu, W. Li, Y. L. Xuan and X. D. Hou, *Talanta* 81, 586 (2010).
6. Y. S. Chung and R. M. Barnes, *J. Anal. Atom. Spectrom.*, 3, 1079 (1988).
7. Y. C. Qing, Y. P. Hang, R. Wanjaul, Z. C. Jiang and B. Hu, *Anal. Sci.* 19, 1417 (2003).
8. A. R. Jackbson, M. B. McBride, P. Bayeye and T. S. Steenhuis, *Sci. Total Environ.* 345, 191 (2005).
9. Z. C. Wang, H. Becker and F. Wombacher, *Geostand. Geoanal. Res.* 39, 185 (2015).
10. R. M. Gaschnig, R. L. Rudnick and W. F. McDonough, *Geostand. Geoanal. Res.* 39, 371 (2015).
11. P. F. Hoekstra, B. M. Braune, B. Elkin, F. A. J. Armstrong and D. C. G. Muir, *Sci. Total Environ.* 309, 81 (2003).
12. M. Krachler and W. Shotyk, *Sci. Total Environ.* 407, 89 (2009).
13. J. Y. Hu, Z. Liu and H. Z. Wang, *Anal. Chim. Acta.*, 451, 329 (2002).
14. X. L. Liu, W. J. Sun, T. Y. Wen, T. F. Wang, W. Z. Sun, Y. X. Li and J. Guo, *Chinese J. Anal. Chem.* 43, 1371 (2015).
15. L. A. Simpson, M. Thomsen, B. J. Alloway and A. Parker, *J. Anal. At. Spectrom.* 16, 1375 (2001).
16. M. Moldovan, E. M. Krupp, A. E. Holliday and O. F. X. Donard, *J. Anal. At. Spectrom.* 19, 815 (2004).
17. J. Xu, Z. C. Hu, Y. S. Liu, S. H. Hu, H. L. Yuan and S. Gao, *Chinese J. Anal. Chem.* 36, 1493 (2008).
18. J. S. Becker, C. Pickhardt and W. Pompe, *Int. J. Mass Spectrom.* 237, 13 (2004).
19. L. Yang and R. E. Sturgeon, *J. Anal. At. Spectrom.* 17, 88 (2002).
20. C. Moor, P. Boll and S. Wiget, *Fre-*

TABLE III
Ag in Geological SRMs ($\mu\text{g g}^{-1}$) by Standard ICP-MS Mode and Proposed DRC-ICP-MS

SRMs	Zr/Ag	Nb/Ag	Ag ($\mu\text{g g}^{-1}$) (Mean $\pm$ SD)		
			ICP-MS	Proposed Method	Certified
GBW07425, soil	2755	140	0.112 $\pm$ 0.004	0.098 $\pm$ 0.005	0.098 $\pm$ 0.007
GBW07429, soil	1813	124	0.18 $\pm$ 0.03	0.14 $\pm$ 0.01	0.15 $\pm$ 0.02
GBW07451, soil	3445	208	0.108 $\pm$ 0.005	0.073 $\pm$ 0.004	0.074 $\pm$ 0.006
GBW07301a, sediment	9411	911	0.221 $\pm$ 0.008	0.035 $\pm$ 0.008	0.034 $\pm$ 0.011
GBW07302, sediment	6969	1439	0.114 $\pm$ 0.008	0.066 $\pm$ 0.012	0.066 $\pm$ 0.015
GBW07303, sediment	390	27	0.60 $\pm$ 0.02	0.59 $\pm$ 0.05	0.59 $\pm$ 0.07
GBW07103, rock	5060	1212	0.095 $\pm$ 0.007	0.032 $\pm$ 0.006	0.033 $\pm$ 0.010
GBW07105, rock	6925	1700	0.103 $\pm$ 0.008	0.038 $\pm$ 0.005	0.040 $\pm$ 0.012
GBW07110, rock	1970	122	0.20 $\pm$ 0.04	0.16 $\pm$ 0.02	0.17 $\pm$ 0.03
GBW07113, rock	5037	428	0.14 $\pm$ 0.05	0.08 $\pm$ 0.03	0.08 $\pm$ 0.02

- sen, J. Anal. Chem. 359, 404 (1997).
21. K. Ndung'u, M. A. Ranville, R. P. Franks and A. R. Flegal, Mar. Chem. 98, 109 (2006).
  22. Z. X. Li, L. P. Zhou and F. Tan, Microchim. Acta 156, 263 (2007).
  23. W. Guo, S. H. Hu, J. Y. Zhang and H. F. Zhang, Sci. Total Environ. 409, 2981 (2011).
  24. J. Y. Zhang, G. M. Li and W. Guo, At. Spectrosc. 35, 97 (2014).
  25. J. Y. Zhang, X. J. Wang, Y. H. Dong, Z. F. Xu and G. M. Li, At. Spectrosc. 37, 1 (2016).
  26. W. Guo, S. H. Hu, J. Y. Zhang, L. L. Jin, X. J. Wang, Z. L. Zhu and H. F. Zhang, J. Anal. At. Spectrom., 26, 2076 (2011).
  27. Q. Xu, W. Guo, L. L. Jin, Q. H. Guo and S. H. Hu, J. Anal. At. Spectrom., 30, 2010 (2015).