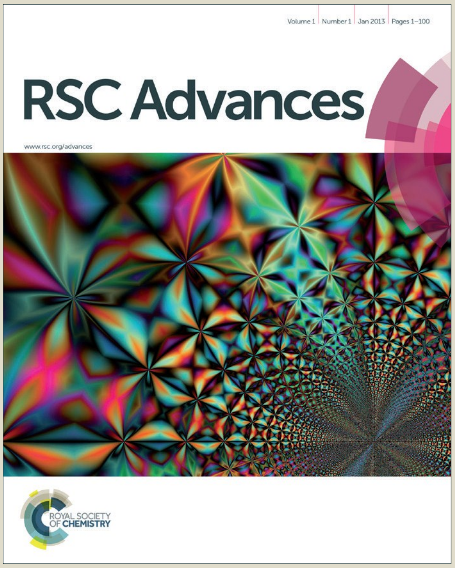
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Determination of sub-ng g^{-1} Au in geological samples by ion molecule reaction ICP-MS and CH_4 plasma modifier

Wei Guo*, Wenke Xie, Lanlan Jin, Qinghai Guo, and Shenghong Hu*

State Key Laboratory of Biogeology and Environmental Geology, School of Environmental Studies, China University of Geosciences, Wuhan, 430074, PR China

---

*Corresponding author. Fax: (+86) 27-67883456; Tel: (+86) 27-67848602.

E-mail address: guowei012345@163.com (Wei Guo); shhu@cug.edu.cn (Shenghong Hu)

Abstract

Direct determination of sub-ng g^{-1} levels of gold by inductively coupled plasma mass spectrometry (ICP-MS) is complicated because of the presence of serious mass interferences, and the high first ionisation energy of Au (9.225 eV) also results in poor analytical sensitivity. A reliable method based on the combination of ion molecule reaction (IMR) ICP-MS and addition of a CH_4 plasma modifier technique was evaluated for the direct determination of Au in geological samples. The interfering $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$ (the sample matrix source) on the mono-isotope ^{197}Au were successfully eliminated by oxidation using O_2 as the reaction gas. The deduced IMR mechanism in the reaction cell involved the oxidation of $^{197}TaO^+$ and $^{197}HfOH^+$ to the higher oxides $^{213}TaO_2{}^+$ and $^{213}HfO_2H^+$, $^{229}TaO_3{}^+$ and $^{229}HfO_3H^+$, and $^{245}TaO_4{}^+$ and $^{245}HfO_4H^+$, while the target Au does not react with O_2. In addition, to further improve the method's signal to background ratio (SBR), a CH_4 modifier was introduced to the ICP plasma at 2 mL min^{-1}; the poor sensitivity of Au^+ was increased by a factor of four and the background signal (at m/z 197) was decreased to 50%. The improvement of the SBR (eight fold) was due to both the carbon enhancement effect (for Au) and the carbon competition effect (with the interfering oxide ions) in the CH_4 modified plasma. The proposed method was applied to the direct determination of Au in ten different types of geological standard reference materials (SRMs). The results of all SRMs were found to agree well with the certified values. This method has great potential for the direct determination of trace levels of Au in various geological samples.

Introduction

Quantifying Au abundance in geological samples is critical for exploring areas such as planetary differentiation, core-mantle interaction manifesting as plume volcanism, meteorite impacts and the effects thereof [1-3]. However, gold is typically present in common terrestrial rocks at low to sub-ng g^{-1} (parts-per-billion) levels [1] and very difficult to quantify accurately. Thus, highly sensitive analytical techniques are required for Au determination in geological samples.

Inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for the determination of trace levels of Au and other metals [4-6], because it offers exceptional sensitivity and/or higher throughput than other elemental analysis techniques, such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), instrumental neutron activation analysis (INAA), and total reflection X-ray fluorescence spectrometry (TXRFS). Unfortunately, the direct analysis of geological samples via ICP-MS is a challenging task because of (i) the presence of significant oxides and hydroxides of matrix metals (*i.e.* $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$) which interfere with the monoisotope ^{197}Au (Table 1); (ii) the poor analytical sensitivity for Au due to its low ionisation efficiency (<50%) in Ar plasma [7]; and (iii) the low concentration of 0.1−10 ng g^{-1} in most samples [8]. Although the mass interferences can be corrected using mathematical equations that include $^{181}Ta^{16}O^+/^{181}Ta^+$ and $^{180}Hf^{16}OH^+/^{180}Hf^+$ ratios, the results for $^{197}Au^+$

determination have large errors because both the Ta and Hf contents are thousands of times higher than the Au content in geological samples (*i.e.* rock and sediment).

It is almost impossible to directly determine Au quantitatively through an ICP-MS method and a separation and pre-concentration stage to account for the removal of the matrix interferences and low abundances is required. The predominant separation and pre-concentration method is nickel sulfide (NiS) fire assay [9-11], which has been modified into a good geochemical exploration tool in many geological analytical laboratories. Although fire assay is used extensively, it is highly labour intensive, the large amounts of reagents required often elevate blank levels to low ng g^{-1} levels, and one of its most serious limitations is a dependence of the quality of results on the experience of the analyst [8]. Anion-exchange procedure was attempted to separate the Au and platinum group metals (PGEs) from matrix elements, and 0.3 mol L^{-1} thiourea was used to elute Au. Their results indicated that the acceptable recovery was acquired for some of the selected geological samples containing high concentrations (*i.e.* > 1,000 ng g^{-1}) of Au; however, poor recovery (<50%) and precision were obtained for most geological samples (< 200 ng g^{-1}). Although the decomposition of eluates (theiourea) with HNO_3 prior to analysis was attempted to reduce the total dissolved solids (TDS), this led to poorer and more erratic results, and increased contamination [8, 12].

Recently, Yim et al. [13] reported a method based on collision cell technique (CCT) to remove the polyatomic ions ($^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$) and for the direct determination of Au in rocks. However, the capability for the elimination of oxide interferences is limited (*i.e.* 5−50 fold for TaO^+ and $HfOH^+$) because the hexapole rods CCT cannot effectively filter out the generation of new TaO^+ and $HfOH^+$ from Ta and Hf. Fortunately, an alternative strategy based on selective ion-molecule reactions in a quadrupole dynamic reaction cell (DRC) has proved to be effective for the alleviation of mass spectral interferences [14-16]. Some studies [17, 18] on reducing the interferences using O_2 as the reaction gas in a DRC have been published since the first systematic study carried out by Simpson et al. [19]. In our previous works, the methods of ion molecule reaction ICP-MS with O_2 as the reaction gas has been successfully used to eliminate the complicated oxide interferences for the direct determination of Cd, Ag, Hg, and As in environmental and biological samples [20-27].

Additionally, like other particular elements (*i.e.* As, Se, and Hg), Au sensitivity in ICP-MS is only 30–50% that of most metal elements (*i.e.* Li, In, and Bi), which is due to its high ionisation potential (9.225 eV) [28]. As reported in our recent papers, the addition of small amounts of carbon-containing compounds (*i.e.* methanol, glycerol) to the ICP plasma can improve the signal intensities of As and Se up to 3–5 times [20, 24, 27, 29]. The signal enhancement of elements with high ionisation potential (9–11 eV) is mainly due to the increased degree of ionisation in carbon-modified plasma, which due to the charges transfers from C^+-species to analyte atoms in the central channel of the plasma discharge.[30-36].

The aim of this work was to develop a reliable method for direct determination of sub-ng g^{-1} Au in geological samples using ion molecule reaction ICP-MS with a CH_4 plasma modifier. The elimination of the interfering $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$ on

^{197}Au was evaluated through the reaction with CH_4 gas in a DRC in combination with the addition of CH_4 gas to the ICP plasma to improve SBR by increasing the poor sensitivity of Au^+ and decreasing the background signal. Optimisation of this technique, the ion molecule reaction mechanism, the performance of the analytical method, and its application to the direct determination of trace Au in a series of geological standard reference materials (SRMs) are described.

Experimental

Instrumentation

A PerkinElmer® NexION® 300D ICP-MS instrument with DRC (PerkinElmer, Inc., Shelton, CT, USA) has been described in detail elsewhere [27]. The diagram of the experimental setup is shown in Fig. S1 (Seen ESI†). CH_4 (99.999%) gas was added through an additional port in the cyclonic spray chamber (PC^3, Elemental Scientific, USA) *via* a calibrated mass-flow controller (32907, Cole-Parmer, USA), capable of regulating minute (measuring range of 0−10 mL min^{-1}, precision of 0.01 mL min^{-1}) flows of the gas. O_2 (99.999%) was selected as the reaction gas in a DRC owing to its high reaction efficiency for Au determination. The instrumental operating parameters used in this work are summarised in Table 2.

Reagents and standards

High purity water (≥18.2 MΩ-cm^{1}) used for preparation of the blank, standards, and samples was obtained from a Millipore water purification system (Millipore, France). Nitric acid (99.9999%), hydrofluoric acid (99.999%), and hydrochloric acid (99.999%) were purchased from Alfa Aesar Ltd (Tianjing, P.R. China). Single element stock solutions (Au, Ta, Hf, and Tl) were purchased from the National Center for Analysis and Testing of Steel Materials, China. Ten geological SRMs were used to evaluate the accuracy of the established method, which included two sediments, four rocks, and four trace gold ores. Two of these SRMs (AGV-1 andesite and BCR-2 basalt) were purchased from the United States Geological Survey (USGS) and the remainder (GBW07107 shale, GBW07108 argillaceous limestone, stream sediments GBW07309 and GBW07311, and trace gold ores GBW07805, GBW07806, GBW07242, and GBW07243a) from the Institute of Geophysical and Geochemical Exploration of China (IGGE).

Sample preparation

0.5000 g of the homogenised sample was weighed into a 25 mL comparison tube, and then 6 mL of aqua regia, and 2 mL of HF were added. After the samples were decomposed entirely by heating on a hot plate at 150 °C overnight, each solution was evaporated. Then, 2 mL of 2:1 aqua regia : HF mixed acid was added and heated at 150 °C overnight. After this solution was evaporated, residues were dissolved in 5% aqua regia and diluted to 100g using 2% aqua regia. After filteration, the solution was subjected to ICP-MS.

Results and Discussion

Reduction of oxide interferences

As the two predominant sources of mass interference in ^{197}Au determination, the presence of $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$ can result in significant positive bias. In our previous study [27], a method based on an ion molecule reaction was conducted to alleviate potential interference in Se determination, and the interfering ion ($^{40}Ar^{40}Ar^+$) was successfully eliminated using CH_4 as the reaction gas in the DRC. A charge transfer reactions possible: $Ar_2^+ + CH_4 \rightarrow Ar+Ar+CH_4^+$, ΔH_r = -181 kJ/mole, or $Ar_2^+ + CH_4 \rightarrow Ar+Ar+CH_3^+ + H$, ΔH_r = -10 kJ/mole [37]. The precondition of this charge transfer is the ionization energy (IE) of reaction ions higher than that of the reaction molecule, i.e, 14.4 eV (Ar_2^+) > 12.6 eV (CH_4) [37]. However, the reductive gas CH_4 cannot react with the complicated oxide-based interferences $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$ by charge transfer, which due to the IE of TaO (8.61 eV [38, 39]) and HfOH (no available data, only IE of HfO is 7.60 eV [39, 40]) much lower than that of CH_4 (12.6eV). Another reaction scheme based on O_2-atom transfer reactions was explored to address the above interferences in Au determination. SBR was used as a criterion for the optimisation of DRC conditions. Fig. 1 shows the effects of O_2 gas flow rate on the signals of the matrix blank and 1 ng mL^{-1} Au + matrix blank at m/z 197. A mixture of 700 ng mL^{-1} Ta, 5,300 ng mL^{-1} Hf, and 2 % aqua regia was treated as the matrix blank to simulate the interfering elements on Au according their average crustal abundances. As shown in Fig. 1, at a low O_2 flow rate, there was a sharp increase in the signals of interfering species at m/z 197. With increasing O_2 flow rate, the background signal decreased rapidly at m/z 197 (Fig. 1); the optimum O_2 flow rate was 2.0 mL min^{-1} and the signal at 197 amu, generated by interfering ions was reduced by three orders of magnitude (from 630,125 to 432 cps).

The reaction mechanism between O_2 and various ions in the DRC were explored by monitoring related mass spectra in ICP-MS. The procedure of reactions between Ta or Ta-oxides and O_2 was monitored throughout the course of an optimisation procedure with increasing O_2 gas flow rates. As shown in Fig. 2, the $^{181}Ta^{16}O^+$ signal intensity increased initially and reached a maximum, followed by $^{213}TaO_2^+$, $^{229}TaO_3^+$, and $^{245}TaO_4^+$. Finally, at the optimised gas flow rate of 2.0 mL min^{-1}, the signal intensity was 11,708 cps for $^{213}TaO_2^+$, but only 427 cps for $^{197}TaO^+$ (Fig. 2). Similar types of multiple oxide generation profiles can also be seen for Hf-hydroxides. Therefore, the interference from $^{181}Ta^{16}O^+$ and/or $^{180}Hf^{16}OH^+$ in $^{197}Au^+$ determination was significantly reduced by the reactions with molecular oxygen, and the proposed ion molecule reaction mechanisms are given as follows:

$$M^+ \rightarrow MO^+/MOH^+ \rightarrow MO_2^+/MO_2H^+ \rightarrow MO_3^+/MO_3H^+ \rightarrow MO_4^+/MO_4H^+$$

M represents Ta or Hf. In addition, a high rejection parameter q (Rpq) value of 0.80 was selected to filter out large Ta^+ and Hf^+, which effectively prevent the generation of fresh TaO^+ or $HfOH^+$ from Ta^+ and Hf^+. Similar dioxides and higher oxide formation from mono-oxides (i.e. MO^+) have been reported by Bohme's group [41], who used an inductively coupled plasma/selected ion flow tube (ICP/SIFT) tandem mass spectrometer.

Improvement of signal to background ratio by CH_4 plasma modifier

It is well known that addition of a small amount of carbon to the plasma can improve the SBR by increasing the analyte signal and/or decreasing the background signal [28, 33, 42-44]. Our recent studies showed that the signal of As or Se can be improved three- to four-fold by addition of 4% methanol or ethanol to the analytical solution [20, 24, 27, 29]; meanwhile, the signal of double-charged ions (Ce^{2+}) and oxide ions (ZnO^+, NiO^+, and CuOH) are reduced by a factor of two to six [27, 29]. In this experiment, to improve the poor signal of Au and further reduce the background interferences, CH_4 gas was used as the carbon source by directly introducing it to the spray chamber. Signal intensities of $^{197}Au^+$ after blank corrections as a function of CH_4 gas flow rate are illustrated in Fig. 3a. The results show that 2 mL min^{-1} CH_4 can lead to a five-fold improvement in the maximum sensitivity for $^{197}Au^+$ over that of without CH_4. This signal enhancement phenomenon can be explained by a charge transfer reaction occurring between the positively charged carbon species (i.e. C, 11.26eV, C_2, 12.00eV, CO, 14.00eV, and CO_2 13.70eV) and the high ionisation energy element (*i.e.* Au, 9.225eV) in the central channel of the plasma [7, 30, 31, 36]. On the other hand, addition of carbon to the plasma can alleviate the interference (oxide or hydroxide ions) on Au at m/z 197, which due to the conversion of MO^+ species into M^+ by reaction with C [27, 30, 45]. Fig. 3b illustrates the signals of oxide and hydroxide ions (TaO^+ and $HfOH^+$) in CH_4-Ar mixed gas (2 mL min^{-1} CH_4) plasma DRC-ICP-MS (normalised to the pure Ar-plasma

DRC-ICP-MS) as a function of nebulizer gas flow rates. When the nebulizer gas flow rate was higher than 0.77 L min^{-1}, the interference signals of TaO^+ and $HfOH^+$ were effectively suppressed with the addition of CH_4 gas in the plasma (Fig. 3b), and the signals of oxide or hydroxide ions at m/z 197 decreased up to 50% at a nebulizer gas flow rate of 0.80 L min^{-1}. The reduction in mono-oxide ions (MO^+) may have originated from the competitive formation of M^+ over MO^+ in the presence of carbon, which through the reactions between C with MO^+ ($MO^+ + C \rightarrow M^+ + CO$) [27, 30, 45]. It was also found that the interference reduction and Au signal enhancement highly depend upon the nebulizer gas flow rate in the CH_4-Ar mixed plasma. A relatively high nebulizer gas flow rate facilitates the suppression of interfering ions, whereas improvement of the Au signal requires a relatively low nebulizer gas flow rate (Fig. 3). Therefore, a protocol involving a compromise of using a nebulizer gas flow rate of 0.80 mL min^{-1} was selected to obtain the best SBR. Compared to the method without addition of a CH_4 plasma modifier, the SBR of this method was improved by eight times with contributions from two fold reduction of the background (TaO^+ and $HfOH^+$) signal and the four fold improvement of the analyte (Au^+) signal.

Analytical performances

Standard solutions with Au concentrations from 0.05 to 50 ng mL^{-1} were analyzed to construct a calibration curve (Y = 205,250X + 126) with a correlation coefficient of 0.999. Compared to the conventional ICP-quadrupole mass spectrometry (QMS) method, the SBR of Au was increased from 0.16 to 1,200 (the certified Au concentration is 1 μg L^{-1}) by the proposed method involving ion molecule reaction ICP-MS with a CH_4 plasma modifier (Table 3). The SBR was calculated by the ratio of the signal intensity (at 197 amu) of 1 μg L^{-1} Au and the simulated background matrix (a mixture of 700 ng mL^{-1} Ta, 5,300 ng mL^{-1} Hf, and 2 % aqua regia). The limit of quantification (LOQ, ten times the standard deviation of produce blank) was 0.008 ng g^{-1} for Au, which was better than these reported in the literatures[9, 12] using the conventional separation and/or pre-concentration procedures (0.05−2.0 ng g^{-1}). The LOQ is expressed as the concentration in the samples, thereby taking into account the dilution factor (200). This sensitivity is sufficient for trace or ultra-trace Au determination in various geological samples, which Au is often found at 0.1−10 ng g^{-1}. Reproducibility was calculated based on triplicate sample digestions and analyses, and was generally less than 10% (relative standard deviation, RSD).

Geological standard reference material analysis

The proposed method was used to analyse ten different types of geological SRMs, which included of four rocks, two sediments, and four trace gold ores. As shown in Table 4, all of the results agreed well with the reference values. The Au concentrations in these samples (0.62−3.6 ng g^{-1}) were similar to the crustal abundance, 1.3 ng g^{-1}. For each sample, the relative standard errors were <10%. However, the results by the conventional ICP-MS method were larger (300−500%) than that of the Au values using the reference values and the proposed method (Table 4). Although the results of other two methods (ICP-DRC-MS with O_2 as DRC gas and ICP-MS with addition of

CH_4) were better than that of the conventional ICP-MS method, but they remain higher than the target reference values, which due to the interference of the Ta and Hf (Table 4). Fortunately, it can be solved by our proposed method.

Conclusion

This study demonstrated that the combination of the ion molecule reaction technique and addition of a CH_4 plasma modifier effectively eliminated the oxide interferences in Au determination via ICP-MS. The predominant interfering $^{181}Ta^{16}O^+$ and $^{180}Hf^{16}OH^+$ on ^{197}Au were reduced by three orders of magnitude using methane as the DRC reaction gas. When CH_4 gas modifier was added to ICP plasma at 2 mL min^{-1}, the background signal originating from the interfering residual oxide and/or hydroxides ions was further reduced by up to 50%; meanwhile, the poor sensitivity of $^{197}Au^+$ was improved four fold. This method has potential as a routine laboratory method for the determination of sub-ng g^{-1} levels of Au in various geological samples.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (No. 21207120) and the National Key Scientific Instrument and Equipment Development Projects of China (No. 2011YQ06010008) and the Fundamental Research Funds for the Central Universities, China University of Geosciences (Wuhan), and the Research

Program of State Key Laboratory of Biogeology and Environmental Geology of China (No. GBL11505).

References

1. J. C. Ely, C. R. Neal, J. A. O'Neill and J. C. Jain, *Chem Geol*, 1999, **157**, 219-234.
2. L. Pattou, J. P. Lorand and M. Gros, *Nature*, 1996, **379**, 712-715.
3. N. J. Evans, D. C. Gregoire, R. A. F. Grieve, W. D. Goodfellow and J. Veizer, *Geochimica Et Cosmochimica Acta*, 1993, **57**, 3737-3748.
4. P. Dolcet, A. Mambrini, M. Pedroni, A. Speghini, S. Gialanella, M. Casarin and S. Gross, *Rsc Adv*, 2015, **5**, 16302-16310.
5. I. G. Tanase, D. E. Popa, G. E. Udristioiu, A. A. Bunaciu and H. Y. Aboul-Enein, *Rsc Adv*, 2015, **5**, 11445-11457.
6. H. C. Wu, T. Y. Su, T. L. Tsai, S. B. Jong, M. H. Yang and Y. C. Tyan, *Rsc Adv*, 2014, **4**, 39226-39230.
7. G. Grindlay, J. Mora, M. de Loos-Vollebregt and F. Vanhaecke, *Spectrochim Acta B*, 2013, **86**, 42-49.
8. I. Jarvis, M. M. Totland and K. E. Jarvis, *Chem Geol*, 1997, **143**, 27-42.
9. K. Oguri, G. Shimoda and Y. Tatsumi, *Chem Geol*, 1999, **157**, 189-197.
10. R. Juvonen, T. Lakomaa and L. Soikkeli, *Talanta*, 2002, **58**, 595-603.
11. H. G. Plessen and J. Erzinger, *Geostandard Newslett*, 1998, **22**, 187-194.
12. I. Jarvis, M. M. Totland and K. E. Jarvis, *Analyst*, 1997, **122**, 19-26.
13. S. A. Yim, M. S. Choi and J. S. Chae, *J Am Soc Mass Spectr*, 2012, **23**, 171-178.
14. V. I. Baranov and S. D. Tanner, *Journal Of Analytical Atomic Spectrometry*, 1999, **14**, 1133-1142.
15. S. D. Tanner and V. I. Baranov, *J Am Soc Mass Spectr*, 1999, **10**, 1083-1094.
16. S. D. Tanner, V. I. Baranov and U. Vollkopf, *Journal Of Analytical Atomic Spectrometry*, 2000, **15**, 1261-1269.
17. C. C. Chang, H. T. Liu and S. J. Jiang, *Analytica chimica acta*, 2003, **493**, 213-218.
18. J. W. Olesik and D. R. Jones, *Journal Of Analytical Atomic Spectrometry*, 2006, **21**, 141-159.
19. L. A. Simpson, M. Thomsen, B. J. Alloway and A. Parker, *Journal Of Analytical Atomic Spectrometry*, 2001, **16**, 1375-1380.
20. W. Guo, S. H. Hu, X. F. Li, J. Zhao, S. S. Jin, W. J. Liu and H. F. Zhang, *Talanta*, 2011, **84**, 887-894.
21. W. Guo, S. H. Hu, X. J. Wang, J. Y. Zhang, L. L. Jin, Z. L. Zhu and H. F.

Zhang, *Journal Of Analytical Atomic Spectrometry*, 2011, **26**, 1198-1203.

22. W. Guo, S. H. Hu, Y. F. Xiao, H. F. Zhang and X. J. Xie, *Chemosphere*, 2010, **81**, 1463-1468.
23. W. Guo, S. H. Hu, J. Y. Zhang, Z. C. Hu, H. F. Zhang and Y. X. Wang, *Talanta*, 2012, **91**, 60-64.
24. W. Guo, S. H. Hu, J. Y. Zhang, L. L. Jin, X. J. Wang, Z. L. Zhu and H. F. Zhang, *Journal Of Analytical Atomic Spectrometry*, 2011, **26**, 2076-2080.
25. W. Guo, S. H. Hu, J. Y. Zhang and H. F. Zhang, *Sci Total Environ*, 2011, **409**, 2981-2986.
26. W. Guo, S. H. Hu, J. A. Zhao, S. S. Jin, W. J. Liu and H. F. Zhang, *Microchemical Journal*, 2011, **97**, 154-159.
27. W. Guo, S. H. Hu, Y. X. Wang, L. Y. Zhang, Z. C. Hu and J. Y. Zhang, *Microchemical Journal*, 2013, **108**, 106-112.
28. P. Allain, L. Jaunault, Y. Mauras, J. M. Mermet and T. Delaporte, *Anal Chem*, 1991, **63**, 1497-1498.
29. Z. C. Hu, S. Gao, S. H. Hu, H. L. Yuan, X. M. Liua and Y. S. Liu, *Journal Of Analytical Atomic Spectrometry*, 2005, **20**, 1263-1269.
30. Z. C. Hu, S. H. Hu, S. Gao, Y. S. Liu and S. L. Lin, *Spectrochim Acta B*, 2004, **59**, 1463-1470.
31. E. H. Larsen and S. Sturup, *Journal Of Analytical Atomic Spectrometry*, 1994, **9**, 1099-1105.
32. G. C. Y. Chan and W. T. Chan, *Spectrochim Acta B*, 2003, **58**, 1301-1317.
33. G. Grindlay, L. Gras, J. Mora and M. T. C. de Loos-Vollebregt, *Spectrochim Acta B*, 2008, **63**, 234-243.
34. J. Machat, V. Kanicky and V. Otruba, *Analytical and bioanalytical chemistry*, 2002, **372**, 576-581.
35. J. Machat, V. Otruba and V. Kanicky, *Journal Of Analytical Atomic Spectrometry*, 2002, **17**, 1096-1102.
36. Z. Arslan, V. Yilmaz and L. Rose, *Microchemical Journal*, 2015, **123**, 170-178.
37. B. Hattendorf and D. Gunther, *Spectrochim Acta B*, 2003, **58**, 1-13.
38. J. M. Dyke, A. M. Ellis, M. Feher, A. Morris, A. J. Paul and J. C. H. Stevens, *J Chem Soc Farad T 2*, 1987, **83**, 1555-1565.
39. NIST, Search for Species Data by Chemical Formula, http://webbook.nist.gov/chemistry/form-ser.html.
40. E. G. Rauh and R. J. Ackermann, *J. Chem. Phys.*, 1974, **60**, 1396-1400.
41. G. K. Koyanagi, D. Caraiman, V. Blagojevic and D. K. Bohme, *J Phys Chem A*, 2002, **106**, 4581-4590.
42. R. M. Olivas, C. R. Quetel and O. F. X. Donard, *Journal Of Analytical Atomic Spectrometry*, 1995, **10**, 865-870.
43. C. D. Pereira, E. E. Garcia, F. V. Silva, A. R. A. Nogueira and J. A. Nobrega, *Journal Of Analytical Atomic Spectrometry*, 2010, **25**, 1763-1768.
44. M. Pettine, B. Casentini, D. Mastroianni and S. Capri, *Analytica chimica acta*, 2007, **599**, 191-198.

45. E. H. Evans and L. Ebdon, *Journal Of Analytical Atomic Spectrometry*, 1990, **5**, 425-429.

Abstract graphic

Direct determination of Au in geological samples using a combination of ion molecule reaction ICP-MS and CH_4 plasma modifier technique

Figure captions

Fig. 1 Effects of O_2 gas flow rate on the signal intensities (at m/z 197) of Au + matrix, matrix blank, and SBR. The concentration of Au was 1 ng mL^{-1}. A solution of 700 ng mL^{-1} Ta, 5,300 ng mL^{-1}Hf, and 2 % aqua regia was used as the matrix blank.

Fig. 2 Effects of O_2 gas flow rate on ion signal intensities of $^{181}Ta^+$, $^{181}Ta^{16}O^+$, $^{213}TaO_2^+$, $^{229}TaO_3^+$, and $^{245}TaO_4^+$. The concentration of Ta was 700 ng mL^{-1}.

Fig. 3 (a) Normalised signal (to that without CH_4 plasma modifier) of ^{197}Au as a function of the added CH_4 gas flow rate; (b) normalised signals (to that without CH_4 plasma modifier) of Au and background in ion molecule reaction ICP-MS with 2 mL min^{-1} CH_4 plasma modifier as a function of nebulizer gas flow rate. Au concentration was 1 ng mL^{-1}. A solution of 700 ng mL^{-1} Ta, 5,300 ng mL^{-1} Hf, and 2 % aqua regia was used as the background.

Table 1 Potential interferences in target Au analysis *via* ICP-MS

Target	Relative abundance (%)	Content in the crust (ng g^{-1})	m/z	Potential interferences					Required resolution
				Element	Relative abundance (%)	Content in the crust (ng g^{-1})	Oxide ions	m/z	
^{197}Au	100	1.3	196.97	^{181}Ta	99.99	900	^{181}Ta^{16}O^{+}	196.94	8335
				^{180}Hf	35.08	5300	^{180}Hf^{16}OH^{+}	196.95	12492

Table 2 Instrument operating parameters

ICP-MS instrument	Perkin-Elmer ® NexION® 300D ICP-MS
Sample introduction	PFA-400 MicroFlow nebulizer
Spray chamber	Cyclonic spray chamber (PC^3 Peltier Chiller)
Injector tube	1.0 mm id quartz
RF power, W	1,300
Plasma gas flow, L min^{-1}	16
Auxiliary gas flow, L min^{-1}	1.00
Nebulizer gas flow, L min^{-1}	0.82 (Ar-plasma) 0.80 (CH_4-Ar mixed plasma)
Optional gas (CH_4), mL min^{-1}	2.0
Reaction gas O_2, mL min^{-1}	2.0
Rejection parameter, q	0.80
Rejection parameter, a	0
Autolens	on
Dwell time, ms	50
Sweeps	20
Readings	1
Replicates	3
Monitored ratios	$^{197}Au^+$
Internal standard	$^{205}Tl^+$

Table 3 Comparison of the signal to background ratio (SBR), and limit of quantification (LOQ) of the five different methods

Analytical methods	SBR [a]	LOQ [c] (ng g^{-1})
DRC Ar-CH_4 mixed plasma-MS (this work)	1200	0.008
Conventional ICP-MS	0.16	0.6
DRC ICP-MS	150	0.02
ICP-MS after NiS fire assay and Te co-precipitation [9]	– [b]	0.053 (MLOD [d])
ICP-MS after microwave digestion, alkali fusion and cation-exchange chromatography [12]	– [b]	2.0

[a] The ratio of the signal intensity (at 197 amu) of 1 μg L^{-1} Au and the simulated background matrix (a mixture of 700 ng mL^{-1} Ta, 5,300 ng mL^{-1} Hf, and 2 % aqua regia).

[b] No available.

[c] The LOQ was the limit of quantification (LOQ, ten times the standard deviation of produce blank), which is taken into account the dilution factor (200).

[d] Method detection limit (MLOD).

Table 4 Au in ten geological standard reference materials (SRMs), ng g^{-1}

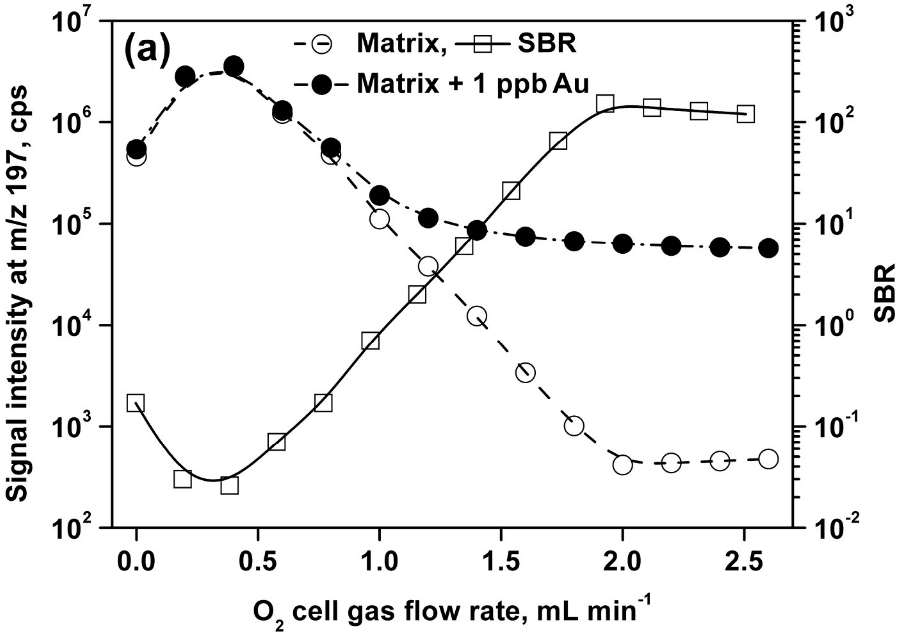
SRM	This method (n =5 [a])	Reference value	ICP-MS [b]	ICP-DRC-MS [c]	ICP-MS with addition of CH_4 [d]	Ta	Hf
AGV-1, andesite	0.60 ± 0.04	0.62	2.70 ± 0.22	0.72 ± 0.16	1.43 ± 0.18	885	5020
BCR-2, basalt	0.68 ± 0.05	0.66	2.73 ± 0.18	0.80 ± 0.16	1.30 ± 0.12	765	4850
GBW07107, shale	1.06 ± 0.12	1.0	3.25 ± 0.22	1.43 ± 0.27	2.82 ± 0.20	852	2750
GBW07108, argillaceous limestone	0.94 ± 0.09	0.94	1.96 ± 0.25	1.19 ± 0.16	1.45 ± 0.15	405	1820
GBW07309, stream sediments	1.32 ± 0.12	1.3	9.40 ± 1.05	1.58 ± 0.25	4.36 ± 0.66	1250	9610
GBW07311, stream sediments	3.55 ± 0.20	3.6	19.6 ± 1.2	4.10 ± 0.72	9.40 ± 0.86	5660	5360
GBW07805, trace gold ore	0.84 ± 0.03	0.85 ± 0.05	8.25 ± 0.45	1.06 ± 0.12	3.35 ± 0.25	955	3220
GBW07806, trace gold ore	3.12 ± 0.14	3.10 ± 0.20	16.4 ± 2.2	4.10 ± 0.56	7.54 ± 0.65	1060	5290
GBW07242, trace gold ore	0.48 ± 0.04	0.50 ± 0.10	9.42 ± 0.92	0.65 ± 0.10	3.15 ± 0.26	795	5860
GBW07243a, trace gold ore	1.58 ± 0.08	1.60 ± 0.10	10.5 ± 0.6	1.76 ± 0.18	3.50 ± 0.43	886	4547

[a] The interval estimation is calculated from 5 independently dissolved sample portions (method repeatability).

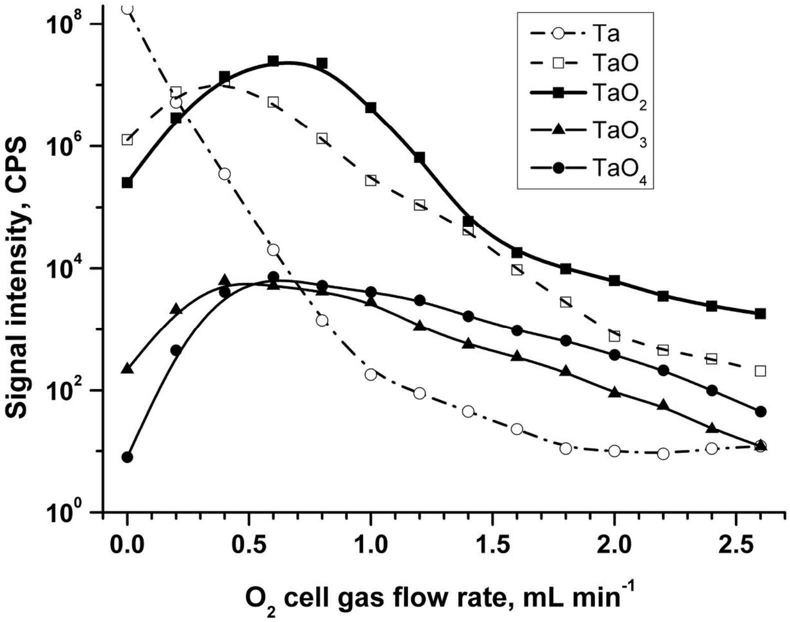
[b] The conventional ICP-MS method after closed acid digestion procedure (Seen in ESI† Table S1).

[c] DRC-ICP-MS with O_2 as reaction gas method (no CH_4 added to the plasma) after closed acid digestion procedure (Seen in ESI† Table S1).

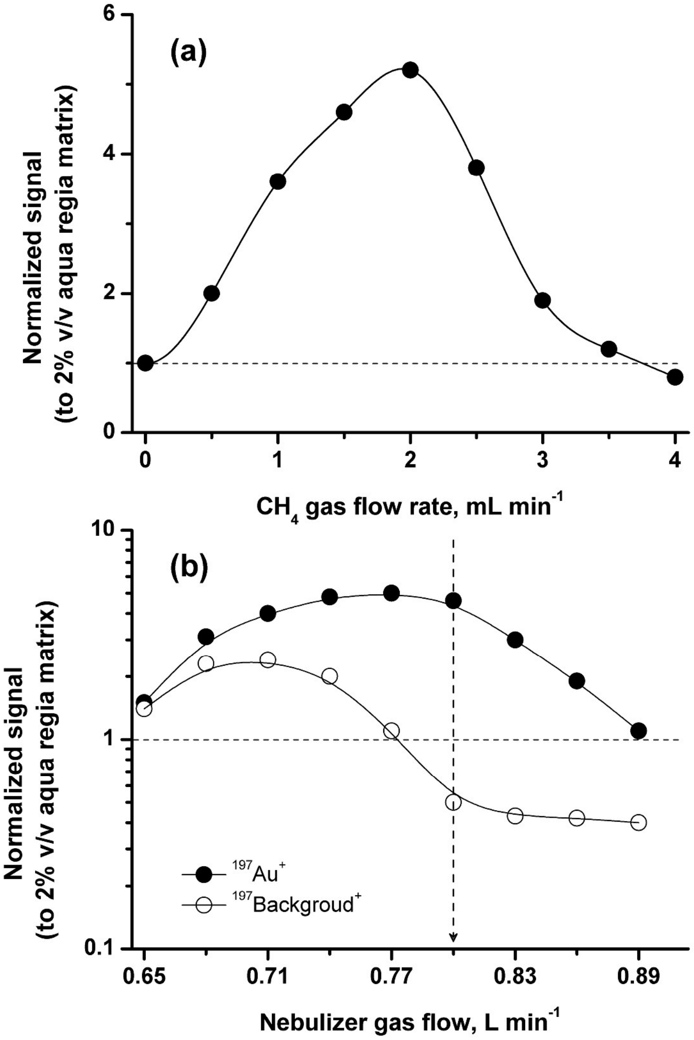
[d] ICP-MS with addition of the CH4 plasma modifier method (no O_2-DRC) after closed acid digestion procedure (Seen in ESI† Table S1).



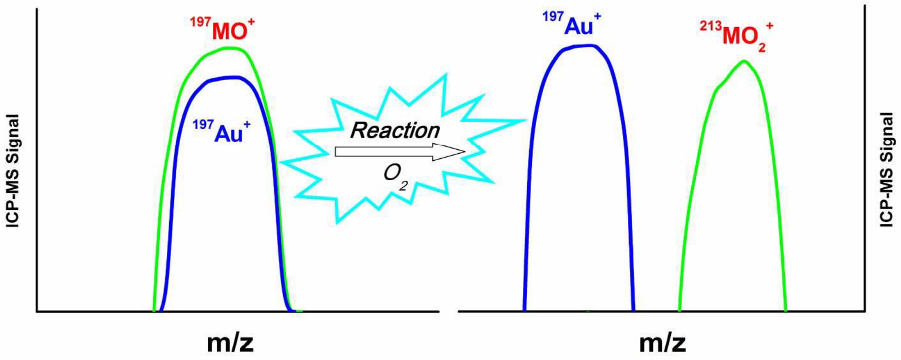
209x148mm (300 x 300 DPI)



209x148mm (300 x 300 DPI)



296x419mm (300 x 300 DPI)



201x141mm (300 x 300 DPI)