Studies on the determination of trace amounts of gold by chemical vapour generation non-dispersive atomic fluorescence spectrometry†

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Volatile species of Au in 0.72 mol l^{-1} HCl medium were generated at room temperature by reduction with 0.65% (m/v) KBH$_4$ using a programmable intermittent flow reactor and the detection system was used for the determination of trace amounts of gold by atomic fluorescence spectrometry. It was found that the presence of micro-amounts of DDTC greatly enhanced the generation efficiency of the volatile species and the flow rates of carrier and shield gas had a significant impact on the signal intensity of Au. In addition, high surface/volume ratio and rapid gas–liquid separation are essential for the generation of the volatile gold species. Based upon the results of the investigation, a detection limit of 0.23 ng ml^{-1} was obtained under optimized conditions and the precision of the measurements for 20 ng ml^{-1} of Au was 1.7% RSD. The method was successfully applied to the determination of gold in geological certified reference materials: the results were found to be in reasonable agreement with the certified values.

Introduction

Vapour generation has been proved to offer significant benefits as a method of sample introduction in atomic spectrometry. However, the elements that can be determined by this technique are still limited to a few elements such as As, Sb, Bi, Ge, Se, Te, Pb, *etc.*[1] Recently, other elements have been appended to this group: Pohl[2] reported the recent and novel developments in the chemical VG of volatile species of the transition and noble metals through the reaction of NaBH$_4$. In the past few years, some attempts were made to determine gold by a vapour generation technique.[3–9]

It is well known that vapour generation non-dispersive atomic fluorescence spectrometry (VG-AFS)[10–12] has been successfully and widely used for determination of hydride-forming elements because of its high sensitivity, wide linear dynamic range, speed of analysis, ease of use, low costs and less interference. However, to the best of our knowledge, the use of VG-AFS for the determination of trace amounts of gold has not yet been reported.

This technical note describes a sensitive method for the determination of gold utilizing the generation of volatile gold species in the presence of micro-amounts of DDTC aqueous solution using potassium tetrahydroborate as reductant. A commercial non-dispersive atomic fluorescence spectrometer, which was modified by the author, was used for the detection. The influence of experimental conditions on analytical performance was investigated and the method has been successfully applied to the determination of gold in geological samples.

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† Electronic supplementary information (ESI) available: operating parameters of the NDAFS instrument and optimum conditions for the generation of the volatile gold species with different spectrometric determination techniques. See DOI: 10.1039/b517553d

Experimental

Apparatus

A Model AFS2202 double-channel non-dispersive atomic fluorescence spectrometer (NDAFS, Beijing Hauguang Instrument Co., Beijing, China) was operated under conditions summarized in Table S1 †. The modified gas controller, which was operated at lower flow rates of carrier gas and shield gas, was used throughout this study. A gold hollow cathode lamp (HCL), which was specially designed for AFS, was used in this work. A programmable intermittent flow hydride generator, as described previously,[10] which was modified by adding carrier gas intake B (as shown in Fig. 1), was used throughout the work. The working program of the intermittent flow reactor used in this work is listed in Table 1.
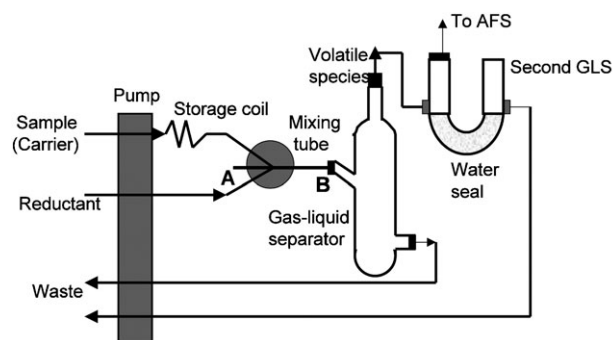

Fig. 1 Schematic diagram of intermittent vapour generator. Storage coil length 90 cm, i.d. 1.0 mm, PTFE tubing; Mixed tubing length 15 cm, i.d.3.9 mm, PTFE tubing; Perkin-Elmer type 1 gas-liquid separator (made of glass), height 8 cm, i.d. 10 mm; PTFE tubing (from the separator to the second separator) length 50 cm, i.d. 0.7 mm. The second gas–liquid separator constructed from glass with a U-shaped tube, height 5 cm, i.d. 6 mm; PTFE tubing (from the second separator to AFS atomizer) length 3 cm, i.d. 3.9 mm; A and B: carrier gas intake.

Table 1 Working program for the intermittent flow reactor

Step	Flow rate/ ml min^{-1}	Time/s	Function
1	Sample: 6 Reductant: 3	8	Insertion of sampling tube into sample solution
2	Sample: 0 Reductant: 0	3	Change over of sampling tube into carrier solution
3	Carrier: 6 Reductant: 3	16	Readout
4	Carrier: 0 Reductant: 0	3	Return to step 1

Reagent

All reagents were of analytical grade, and de-ionized water was used throughout. About 0.5–2.5% (m/v) potassium tetrahydroborate was prepared daily by dissolving KBH_4 in 0.3% (m/v) of potassium hydroxide. A 1% (m/v) sodium diethyldithiocarbamate (DDTC) was prepared by dissolving 1 g of DDTC in 100 ml of water.

An intermediate 100 mg l^{-1} stock solution of Au was prepared by dilution of a 1000 mg l^{-1} stock standard solution (National Standard Material Center of China) with 20% (v/v) *aqua regia*. A series of standard solutions of Au were prepared by three-stage dilution of the 100 mg l^{-1} stock solution.

Procedures

At the beginning of first step, the sampling tube was placed in the test solution, and then the pump propelled the solution into the storage coil. Second, the pump was stopped for 3 s, thus allowing the sampling tube to be changed over to the carrier solution. At this stage, the sample stayed in the storage coil that was in front of the mixing joint of the manifold and consequently no reaction occurred between the sample solution and the reductant. Third, the carrier solution was propelled, pushing the sample and the reductant into the mixed coil and gas–liquid generator. At this stage, the volatile species were formed and transported to the quartz furnace. In a hydrogen–argon–air entrained micro-flame, the gaseous molecular compounds were atomized and determined by AFS. After the third step, the pump was stopped again and made ready for the next determination.

Sample pretreatment

20.0 g of geological sample was baked in muffle furnace at 600 °C for 4 h and transferred into a 300-ml glass beaker, 80 ml of *aqua regia* (1 + 1) was added, and then it was digested on a hot-plate at boiling temperature for approximately 90 min. After cooling, the solution was transferred into a 200-ml volumetric flask and diluted to volume with water. After 4–6 h, 100 ml of the upper liquid was transferred into a 200-ml conical flask and approximately 0.5 g of thiourea resin[13] was added; the flask was then put into a horizontal rotator shaker and shaken to adsorb Au for 1 h. The resin was separated and transferred into a 25-ml test tube; the sorbed Au was statically eluted with 15 ml of 0.5% (w/v) thiourea in a boiling water-bath for 40 min. After cooling, 4 ml of HCl (1 + 1) and 1 ml of 1% (w/v) DDTC were added and diluted to 25 ml with water for a subsequent measurement by VG-AFS.

Results and discussion

Optimization of AFS instrument parameters

Studies on the influence of lamp current show that an increase in the lamp current significantly improves the signal intensity of Au. However, higher lamp current would produce higher signal noise, and reduce the lifetime of the lamp. A current of 60 mA was used as a compromise in this work. Similarly, higher voltage of PMT would produce higher signal intensity and noise; a voltage of 340 V was used in this work.

The carrier gas flow rate influences the overall efficiencies of analyte generation, gas–liquid separation, analyte transport and atomization. In the present work, the flow rate of carrier gas was found to have a significant impact on the signal intensity of Au. The sensitivity of Au remains a maximal plateau when the flow rate of carrier gas is in the range of 100–250 ml l^{-1}, and a remarkable decrease is observed when the flow rate of carrier gas exceeds 250 ml l^{-1}. 200 ml l^{-1} of carrier gas was used as a compromise.

In this work, the relationship between the flow rate of shield gas and the normalized intensity was studied and the flow rate of shield gas has a significant impact on the signal intensity of Au. The results reveal that a shield gas flow rate of 400 ml l^{-1} is optimal for giving higher signal intensity and a better signal-to-noise ratio; the sensitivity of the determination is greatly decreased when higher or lower flow rates are used.

Otherwise, it can be clearly seen that a lower flow rate of the carrier gas and shield gas as compared with that used in the determination of other hydride-forming element (*e.g.*, As, Sb, Bi and Se in ref. 10) are needed to obtain satisfactory results. The differences may be due to the reason that higher atomization temperature is needed for volatile gold species and a significantly longer residence time is required in the atomizer for sufficient atomization of volatile gold species. At higher flow rates, a short residence of the analyte species in the atomizer would be dominant, leading to a reduction of the atomization efficiency of Au and resulting in the decrease of the signal intensity of Au.

The use of an intermittent flow reactor allows raising of the pump rate (carrier flow rate) at the third step to enhance the signal.[14] In this work, the influence of the flow rates of carrier on the fluorescence signal of gold was studied. Contrary to the report by Guo,[14] the decrease of fluorescence signal with increasing pumping rate may be due to the slow formation of volatile gold species. In order to further evaluate this supposition, a rapid generation device was used for the generation of volatile gold species and compared with the present intermittent hydride generator. The experimental result revealed that substitution of the rapid generation device for the intermittent hydride generator attenuated the signal by 2.7-fold. In addition, silica gel and PTFE tubing of different inner diameters and lengths were tested as the mixed tubing (reaction coil). It is shown that PTFE tubing of 3.9 mm id and 15 cm length was preferential for the formation of Au volatile species. With longer mixed tubing the fluorescence signal was clearly diffused and the intensity of peak height dropped gradually. With narrow-bore PTFE tubing (1.8 mm id), a 3.8-fold decrease in the peal area response occurred, which might be attributed to the fact that the generated analyte

Table 2 Percentages of gold in various parts and efficiencies of vapour generation for gold (100 ng ml^{-1} of Au, $n = 3$)

	Percentages and efficiencies (%)	
	Absence of DDTC	Presence of DDTC
Deposit[a]	9.7 ± 1.1	3.4 ± 0.4
Waste effluent	15.9 ± 2.7	58.2 ± 4.2
Deposit[b]	74.3 ± 7.2	27.4 ± 1.2
Efficiencies of VG	<1	$11\pm$

[a] Deposit coated in the mixed tubing. [b] Deposit separated from the waste effluent.

species were highly unstable in the aqueous solution and rapid gas–liquid separation of volatile product was essential, but the narrow-reaction space decreased the efficiency of this process and using a better reaction space offered a high surface/volume ratio for efficient escape of the volatile product. Changing the carrier gas intake from A to B (Fig. 1) caused a 5.2-fold decrease in the peak area response, which further showed that Au hydride was highly unstable in the aqueous solution and rapid gas–liquid separation was necessary.

PTFE tubing of different inner diameters were tested as a transfer line between the first and second gas–liquid separator. It is shown that PTFE tubing of 0.7 mm id was preferential for the transfer of volatile gold species. The fluorescence intensity slowly dropped with longer transfer line length. However, too short a length caused very high standard deviations (RSDs) and worsening detection limits, while the RSDs of three replicate measurements ranged from 11% to 2% when a 40 cm length of PTFE tubing took the place of 10 cm of PTFE tubing as transfer line. Taking into consideration the sensitivity and precision of the method, a transfer line length of 50 cm was employed as a compromise.

Optimization of the conditions for the generation of the volatile gold species

The previous report showed that the generation efficiency of gold volatile species depends strongly on the acidity of the reaction medium.[7] In this work, using an intermittent reactor and performing the reaction in 0.04% DDTC medium with 0.65% KBH$_4$ as reagent, the influence of HCl concentration on the signal of Au was studied. The results show that the intensity increases significantly within 0.24–0.48 mol l^{-1}: a maximum is reached and remains a plateau in the range of 0.48–1.2 mol l^{-1}, and a decrease is observed when exceeding 1.2 mol l^{-1}. For HNO$_3$ and *aqua regia*, the highest intensities for Au are reached at the same concentration of 0.24 mol l^{-1}; however, sensitivities are 10% and 30% lower when HNO$_3$ and *aqua regia* are used, respectively, and the signal of Au remains constant in a narrow range, which is difficult to control in practical analysis. In this work, considering the sensitivity and manoeuverability of the method, 0.72 mol l^{-1} HCl (6%, v/v) was used as the optimal acidity.

The relationship between the potassium tetrahydroborate concentration and the peak area signal obtained was tested. The potassium hydroxide concentration (0.3%, m/v) was kept constant for different reductant concentrations in this study. Generation of gold volatile species can be carried out with a KBH$_4$ concentration from 0.5% to 1.5% (m/v). The highest intensity is reached at a KBH$_4$ concentration of 0.65% (m/v).

At higher KBH$_4$ concentrations ($>0.65\%$), the fluorescence intensity rapidly drops due to dilution, a consequence of the increased hydrogen production and shorter residence time of volatile gold species in the atomizer; lower concentrations of KBH$_4$ ($<0.5\%$) could not sustain the atomizer flame. In this work, 0.65% KBH$_4$ was used as reductant.

It can be clearly seen that the optimum conditions for the generation of volatile gold species differ between the present method and literature values (see Table S2 †). The previous literature[4,8] explained the factors that caused the differences. However, I think that various detection systems and atomization types are among the reasons for the different conditions of Au vapour generation. In the vapour generation AFS, the atomizer is a hydrogen–argon–air entrained micro-flame. The fitting HCl and KBH$_4$ concentrations not only provide the optimum conditions for the generation of volatile gold species but also sustain the atomizer flame; too low concentrations could not produce enough hydrogen gas to sustain the flame.

Effect of DDTC concentration

Ma *et al.*[8] found that diethyldithiocarbamate (DDTC) had a positive effect on the generation of the volatile gold species. The influence of the concentration of DDTC on the atomic fluorescence intensity was studied. The results reveal that in the presence of DDTC, the sensitivity of the determination is greatly increased. A concentration of 0.04% w/v DDTC in the final test solution is recommended for the determination. Compared with the absence of DDTC, the sensitivity of Au was increased 27-fold. In order to understand the role of DDTC, a gold containing solution was mixed with DDTC solution using the intermittent flow reactor under the same conditions suggested above: no signal was found in the test. The experiment revealed that no volatile species was formed by the reaction of gold and DDTC. For further studies, the inner-wall of the mixed tubing eventually became coated with a black deposit for the reaction of gold and KBH$_4$. The black deposit was dissolved with *aqua regia* and the solution was used for the determination of gold by an ICP-MS. In addition, the concentrations of gold in waste effluent and the deposit, which was separated from the waste effluent with a mixed cellulose ester membrane and dissolved by *aqua regia*, were also determined. The percentages of gold in various parts are summarized in Table 2. The experimental results indicated that the role of DDTC in this work was as the complexing agent of Au(I), thereby preventing the formation of Au^0 and enhancing the yield of gold volatile species.

Evaluation of interferences

It is well known that the transition metal ions (*e.g.*, Cu^{2+}, Ni^{2+}) are potential interferents in hydride generation methods. Other possible interferents are hydride-forming elements, which may cause gas phase interference especially when AAS and AFS are used for the determination. In this work, the effects of 37 diverse ions on the generation of the volatile species were tested and the results are listed in Table 3. It can clearly be seen that among the coexisting ions, Ni^{2+}, Cu^{2+}, Te^{6+}, Bi^{3+}, Ag$^+$, Pd^{2+} and Hg^{2+} cause the most serious interference on the determination of Au by VG-AFS. The methods for elimination of the interferences were investigated. The interferences from Fe^{3+}, Ni^{2+} and Pb^{2+}

Table 3 The effect of various ions on the determination of gold by VG-AFS[a] (40 ng ml^{-1} of Au)

Coexisting ion	Concentration/μg ml^{-1}	[M][b]/[Au]	Signal change (%)
Fe^{3+}	20	500	−2
	100	2500	−10, −3[c]
Ni^{2+}	1	25	−4
	5	125	−45, −2[c]
Cu^{2+}	1	25	−80, −8[d]
Pb^{2+}	20	500	−6
	100	2500	−3[c]
Hg^{2+}	1	25	−10
	5	125	−63, −3[d]
Te^{6+}	0.1	2.5	−58, −8[d]
Bi^{3+}	0.5	12.5	−37, −5[d]
Ag^{+}	1	25	−60, −4[d]
Pd^{2+}	1	25	−65, −2[d]
Mo^{6+}	1	25	−3
	5	125	−15

[a] No interferences were found for the following ions with the concentrations (μg ml^{-1}) cited in parentheses: Al^{3+}, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}(5000), Zn^{2+}, La^{3+}, Rb^{+}, Sr^{2+}, V^{5+}, Mn^{2+} (100), As^{3+}, Sb^{3+}, Sn^{2+}, Cd^{2+}, Cr^{6+}, Tl^{+} (20), Co^{2+}, Ge^{4+}, Se^{6+} (5), Ga^{3+}, In^{3+}, Rh^{4+}, Ir^{4+}, Pt^{2+} (1), Os^{6+}, Ru^{3+} (0.2). [b] Interferent concentration. [c] 2 mg ml^{-1} of EDTA in KBH$_4$ solution was used. [d] 4 mg ml^{-1} of thiourea in the final test solution was used.

were eliminated when EDTA (2 mg ml^{-1}) was added in the potassium tetrahydroborate solution, and adding thiourea (4 mg ml^{-1}) in the final test solution decreased the interferences from Cu^{2+}, Hg^{2+}, Te^{6+}, Bi^{3+}, Ag^{+} and Pd^{2+}.

Analytical performance

Under optimized operating conditions, based on the five experimental points of the calibration curve, the relationship between the relative intensity of atomic fluorescence (I_f) and the concentration of gold (C, ng ml^{-1}) was found to be $I_f = 43.8C$, with a linear correlation coefficient of 0.9997. The limit of detection (LOD) and relative standard deviation (RSD) of the procedure, as well as their comparison with those of the hyphenated vapour generation spectrometric procedures for the determination of Au, are summarized in Table 4. The LOD, which was simply calculated as three times the standard deviation of eleven sample blank values, of 0.23 ng ml^{-1} is not only superior to those obtained by VG-AES and quartz tube atomizer VG-AAS, but also lower than those by in-atomizer trapping VG-ETAAS. In addition, a RSD ($n = 7$) value of 1.7% at the 20 ng ml^{-1} level was obtained, which was a substantial improvement as compared with those obtained by the other methods in Table 4.

Table 4 The limit of detection and precision of the present procedure as compared with some of the repored data

Method	LOD (ng ml^{-1})	RSD (%) (ng ml^{-1})[b]	Refs.
VG-AAS	420	20 (1000)[b]	3
VG-ICP-AES	0.8	N.D[c]	6
VG-AAS	24	2.0 (2000)[b]	7
VG-GFAAS	0.8	2.2 (50)[b]	8
VG-AAS	2.8	2.5 (400)[b]	9
VG-ICP-MS	0.004	10.8 (91)[b]	15
VG-AFS	0.23[a]	1.7 (20)[b]	This procedure

[a] $3\sigma_{n-1}$ of 11 runs of the sample blank. [b] Concentration level at which the RSD value was obtained. [c] No data available.

Table 5 The determination of Au content in geological certified reference materials by VG-AFS ($n = 3$)

CRMs (unit)	Certified	Found
GAu-1/ng g^{-1a}	13 ± 1	12.7 ± 0.5
GAu-4/ng g^{-1a}	36 ± 2	36.5 ± 1.2
GAu-6/ng g^{-1a}	25 ± 2	24.3 ± 0.9
GAu-7/ng g^{-1a}	87 ± 4	86.2 ± 1.9
GBW07299/μg g^{-1b}	5.72 ± 0.22	5.63 ± 0.11
GBW (E) 070012/μg g^{-1b}	0.30 ± 0.02	0.29 ± 0.01
GBW (E) 070013/μg g^{-1b}	1.09 ± 0.03	1.07 ± 0.03
GBW (E) 070019/μg g^{-1b}	0.42 ± 0.03	0.41 ± 0.02

[a] The ministerial trace gold CRMs (soil) of the original geological ministry of China. [b] The national CRMs (gold ore) of China.

The developed analytical procedure was critically evaluated by analyzing 8 geological certified reference materials from the Institute of Geophysical and Geochemical Prospecting, People's Republic of China. Concentrations of Au determined by VG-AFS in these reference materials are reported in Table 5. It can be clearly seen that the results of Au in the various CRMs agreed very well with the reference values.

Conclusions

Gold can react with tetrahydroborate in aqueous solution to form volatile species which can be subsequently determined by AFS with a low detection limit (0.23 ng ml^{-1}, 3σ) and good precision (1.7% RSD at 20 ng ml^{-1} of Au). To the best of our knowledge, this has not been reported previously. Compared with the CVG systems for Au proposed by previous reports,[3-9] this procedure has the advantages of high sensitivity, low cost and ease of operation. The key points for performing the reaction are: (1) the addition of a micro-amount of DDTC in the final test solution; (2) the lower flow rates of carrier and shield gas; (3) the fitting inner diameter of mixed tubing; (4) the optimization of chemical conditions. Xu and Sturgeon[9] have reported that the micro-amount of NaBEt$_4$ in K(Na)BH$_4$ solution as mixed reductant could enhance the chemical vapour generation efficiency of gold. Regrettably, the enhanced efficiency of a mixed reductant was not investigated for lack of NaBEt$_4$. It is a possibility that very low detection limits will be obtained when the mixed reductant is used in this work.

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