Rapid Procedure for the Quantitative Determination of Gold and Base Metals by Graphite Furnace and Flame Atomic Absorption Spectrometry

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ABSTRACT

**A rapid and simple method has been developed for the determination of gold, copper, lead, zinc, nickel, cobalt, silver, and cadmium in soil and sediment samples at the sub ppb and sub ppm levels using graphite furnace and flame atomic absorption spectrometry. These samples were collected according to the procedures provided by the National Geochemical Mapping (NGCM) Project of the Geological Survey of India (GSI). In the present study, -200 mesh size samples were digested in a 500-mL poly tetra fluoro ethylene (PTFE) pressure vessel using an acid mixture for measurement of Au, Ag, Cd by graphite furnace atomic absorption spectrometry (GFAAS) and the base metals by flame atomic absorption spectrometry (FAAS). The gold was pre-concentrated by extraction in pre-equilibrated methyl isobutyl ketone (MIBK). The organic phase was directly measured by GFAAS for the quantitative estimation of gold. The bulk calibration standard was prepared by extraction in MIBK from

the acid mixture for the estimation of gold. Measurement of Cu, Pb, Zn, Ni, Co, Ag, and Cd was done by FAAS. Silver and cadmium were also measured by GFAAS using a bulk calibration standard. The efficiency of the method was compared by analyzing 13 international soil and sediment reference samples and very good agreement was observed with the certified values. In addition, 11 soil and sediment samples were collected according to the procedures provided by NGCM and analyzed by the proposed method. The results were compared with the standard *aqua regia* digestion procedure and excellent agreement was observed. An amount of 0.003 g pure gold was also dissolved by the proposed dissolution procedure to ensure the validity of the method. The present authors verified this method by analysis of pure gold. The recovery of gold was more than 95%. The limit of quantitation (10σ) achieved for Au, Cd, and Ag was 0.5, 2.0, and 5.0 ng/g, respectively and for all other elements it was 100 to 200 ng/g.

Elemental analysis in flame (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS) is normally carried out in the solution phase (2). Geological samples, e.g., soils, sediments, rocks, ores, minerals, etc., are usually brought into solution by mineral acid digestion. This dissolution procedure is a very important part of the analysis. Moreover, distribution of gold in geological samples is heterogeneous in nature. As a result, a large sample size is required to minimize the probability of getting an improper representation of gold in the samples under analysis. In this study, a 25-g of sample was used for the determination of gold. The sample was pulverized to -200 mesh size to reduce the probability of leaving the gold trapped in the silicate phase. The proposed method for gold determination consists of three parts: dissolution, pre-concentration, and measurement by GFAAS. For determination of the base metals, the method consists of two parts: dissolution and measurement by FAAS.

Dissolution of geological samples in order to bring gold into solution is an important part of the analysis. An almost quantitative recovery of gold by *aqua regia* has been reported by several authors (3-5).

Iron, copper, chromium, and lead interfere in the determination of gold by GFAAS (6). Thus, a pre-concentration method is required to minimize these interferences and to reach detection levels in the ppb range. Pre-concentration of gold has been performed using ion exchange separation (7-8), precipitation on tellurium (9-11), and sol-

INTRODUCTION

Gold can be present as alloys, sulphides, arsenides, and also in its native state as discrete phases in geological materials. Gold, like other metals, is present in silicate rocks normally in the nanogram

range (1). Crustal abundance of gold is 4 ng/g (1). The Geological Survey of India has accepted to determine 66 elements in soil and sediments below their crustal abundance levels using the National Geochemical Mapping (NGCM) guidelines for sampling. In this study, the present authors have chosen to determine eight elements (Au, Ag, Cd, Co, Cu, Ni, Pb, Zn) as part of this project. An accurate, precise, simple, and rapid method is required to fulfil this need.

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vent extraction (12-14), while in the present study, MIBK was used.

The *aqua regia* method is widely used for the estimation of gold. Beamish et al. (15) reported that nascent chlorine and NOCl are responsible for its dissolution. In the *aqua regia* method, loss of gold occurs in the form of auric chloride during evaporation of the solution.

In this paper, a simple and rapid dissolution procedure has been developed for the determination of gold, silver, cadmium, copper, lead, zinc, nickel, and cobalt in geological samples collected in accordance with the NGCM guidelines (16). The acid mixture used in the present study produces nascent chlorine and NOCl under pressure at 120 °C and brings gold into solution. Ichinose (13) and Beamish et al. (15) also reported the successful MIBK extraction of gold from an acid mixture.

For geochemical mapping, the total concentration of elements is required to be estimated. These data have a multipurpose use, i.e., for mineral exploration and environmental investigative studies of basic geology (17). Nitric acid digestion has been most commonly used in exploration geochemistry for many years, but it does not always provide total extraction as reported by Chao and Sanzalone (18). Balaram et al. studied *aqua regia* digestion and extraction for some base metals resulting in a 95-99% extraction (19). Roy et al. did a comparative study using a different dissolution procedure for the measurement of copper, lead, zinc, nickel, cobalt, silver, and cadmium and concluded that HF-HClO₄-HNO₃ digestion is most suitable for complete extraction of these metals (20).

In this study, the limit of quantitation (10σ) for the estimation of gold, silver, and cadmium was

found to be 0.5, 5.0, and 2.0 ng/g, respectively, and for the other elements it was from 100 to 200 ng/g, which is much less than the crustal abundance level and also the required detection level for geochemical mapping. This method was compared with the results of 13 standard reference materials (SRMs).

EXPERIMENTAL

Instrumentation

All analyses were performed using a Varian 220 FS (fast sequential) atomic absorption spectrophotometer (Varian, Palo Alto, CA, USA). The analytical parameters used for the determination of Au, Ag, Cd, and the base metals by GFAAS and FAAS are listed in Tables I and II. The temperature profile for the measurement of Au, Ag, and Cd are listed in Tables III, IV, and V, respectively.

Reagents

All reagents used were of analytical reagent (AR) grade.

Gold Standard

The gold standard was prepared from gold strip which was obtained

from Johnson and Matthey Chemical Ltd., Royston, U.K.

Copper, lead, zinc, nickel, cobalt, silver, and cadmium standards were prepared from copper foil, lead oxide, zinc powder, nickel powder, cobalt sponge (metal), silver powder, and cadmium powder (Johnson and Matthey Chemical Ltd., Royston, U.K.).

The acid mixture (consisting of 1100 mL of concentrated HCl, 1150 mL distilled water, and 250 mL concentrated HNO₃ was placed into a 2.5-L amber bottle and well shaken.

The gold standard solution (100 ppm) was prepared by dissolving 0.1 g pure gold (24 carat) in 20 mL *aqua regia*. The solution was then made up to 1000 mL volume with 2N HCl.

The copper, lead, zinc, nickel, cobalt, silver, and cadmium standards (500 ppm) were prepared by dissolving 0.25 g copper foil, 0.2693 g lead oxide, 0.25 g zinc powder, 0.25 g nickel powder, 0.25 g cobalt sponge (metal), 0.25 g silver powder, and 0.25 g cadmium powder in 20 mL (1:1) nitric acid, respectively, which

TABLE I
Instrumental Parameters of Au, Ag, and Cd for GFAAS Measurement

	Au	Ag	Cd
Wavelength (nm)	242.8	328.1	228.8
Slit width	1.0	0.5	0.5
Lamp current (mA)	4.0	4.0	4.0
Background correction	On	On	On
Sampling mode	Auto mix	Auto mix	Auto mix
Calibration mode	Conc.	Conc.	Conc.
Measurement	Peak Height	Peak Height	Peak Height
Replicates	3	3	3
Total volume (μL)	20	25	15
Sample volume (μL)	15	20	10
Bulk concentration (μg/L)	50	20	10
Volume reduction factor	5	5	5

TABLE II
Instrumental Parameters
for FAAS Measurement

Element	Wave-length (nm)	Slit Width (nm)	Lamp Current (nm)	Background Correction
Cu	324.8	0.5	4.0	On
Pb	217.0	1.0	10.0	On
Zn	213.9	1.0	5.0	On
Ni	232.0	0.2	4.0	On
Co	240.7	0.2	7.0	On
Ag	328.1	0.5	4.0	On
Cd	228.8	0.5	4.0	On

TABLE III
Temperature Profile for Gold Measurement

Step	Temp (°C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	95	20.0	3.0	Normal	No	No
2	120	5.0	3.0	Normal	No	No
3	500	5.0	3.0	Normal	No	No
4	700	2.0	3.0	Normal	No	No
5	700	8.0	3.0	Normal	No	No
6	700	4.1	0.0	Normal	No	Yes
7	2600	1.0	0.0	Normal	Yes	Yes
8	2650	2.0	0.0	Normal	Yes	Yes
9	2700	2.0	3.0	Normal	No	Yes

TABLE IV
Temperature Profile for Silver Measurement

Step	Temp (°C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	30.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	700	25.0	3.0	Normal	No	No
5	700	2.9	3.0	Normal	No	No
6	750	2.9	0.0	Normal	No	Yes
7	2100	0.8	0.0	Normal	Yes	Yes
8	2100	2.0	0.0	Normal	Yes	Yes
9	2150	2.0	3.0	Normal	No	Yes

TABLE V
Temperature Profile for Cadmium Measurement

Step	Temp (°C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
1	85	5.0	3.0	Normal	No	No
2	95	30.0	3.0	Normal	No	No
3	120	10.0	3.0	Normal	No	No
4	300	30.0	3.0	Normal	No	No
5	300	2.5	3.0	Normal	No	No
6	400	2.5	0.0	Normal	No	Yes
7	2000	0.8	0.0	Normal	Yes	Yes
8	2000	2.0	0.0	Normal	Yes	Yes
9	2100	2.0	3.0	Normal	No	Yes

were placed into a 500-mL flask and made up to volume with de-mineralized water.

Calibration Standard

A 50-ppb bulk calibration standard was prepared first by dilution with the acid mixture and then by the extraction of gold from the standard solution maintaining the same procedure as adopted for the analyte solution. The calibration standards for silver, cadmium, and the base metals at ppm and ppb levels were prepared by appropriate dilution of the 500 ppm standards with de-mineralized water.

Dissolution Procedures for Geological Samples and Pure Gold

Geological Reference Samples

A 25-g sample of each of the standard reference materials (Canadian GTS-2; Chinese GSS-4, GSS-5, and GSS-6; and USGS Geochemical Exploration GXR-6) was taken into 500-mL PTFE pressure vessels, respectively, and 250 mL of the acid mixture was added to each. The PTFE pressure vessels were closed with a screw cap and heated in an air oven at 120°C for about three hours, then were left standing overnight at room temperature. An aliquot of 150 mL was taken by decantation and used as the stock solution. A 100-mL aliquot of the

stock solution was used for extraction of the gold. Silver, cadmium, and the base metals were measured from the remaining 50-mL stock solution.

Sample of Soil Mixed With Pure Gold

A 25-g amount of pre-tested soil sample free of gold and 0.003 g of pure gold were placed into a 500-mL PTFE pressure vessel and 250 mL of the acid mixture was added. The PTFE pressure vessel was closed with a screw cap and heated in an air oven at 120°C for about three hours, then it was left standing overnight at room temperature. An aliquot of 100 mL was used for the extraction of gold.

Gold Extraction

After dissolution of the geological samples, an aliquot equivalent to 10 g was put into a 250-mL separating funnel and 10 mL MIBK (methyl isobutyl ketone) with the acid mixture as listed above was added. The solution was shaken for about two minutes, allowed to settle, and the aqueous layer discarded. The organic layer was again shaken with 30 mL of 0.1N HCl for about one minute and allowed to settle. Then the aqueous layer was discarded and the MIBK layer used for GFAAS measurement of gold.

RESULTS AND DISCUSSION

For this study, five Canadian, Chinese, and U.S. standard reference samples (SRMs) of soil and sediment (GTS-2, GSS-4, GSS-5, GSS-6, and GXR-6) were used for the determination of gold. Excellent agreement was found with the certified values and the results are listed in Table VI. In addition, 11 real soil and stream sediment samples (Table VII) were analyzed, collected from the Reamal area, Orissa, India (Toposheet No. 73C/11) in

accordance with the NGCM guidelines. These samples were dissolved by the proposed dissolution technique as well as with the standard *aqua regia* method. Both analytical techniques were compared and good agreement was found. This confirms the complete dissolution of gold in these soil and sediment samples. The comparative results obtained by the standard *aqua regia* method and the proposed dissolution techniques of these 11 samples are listed in Table VII.

In this study, the proposed dissolution technique by analysis of pure gold was also verified. The recovery of gold was more than 95% and the results (listed in Table VIII) obtained for pure gold was the mean of six determinations. The *aqua regia* dissolution method was also applied for the five SRMs and the comparative results are listed in Table VI. The resulting data infer that the acid mixture effectively dissolves the gold and is equally as effective as *aqua regia*. Table VI shows that the recovery of gold for the five SRM soil and sediment samples is excellent when compared to the certified values and was almost

equal for both methods. The values of the *aqua regia* method were slightly lower. This loss is probably due to the evaporation of *aqua regia* during dissolution of the samples.

The standard calibration curve for gold analysis is shown in Figure 1. The absorbance value of 10 ppb gold solution was 0.1974 and the characteristic concentration was 0.22 ng/mL. That is, a solution containing 0.22 ng/mL gold will give 1% absorption. The detection limit (10σ) for the quantification of gold was 0.50 ng/g, which is below the crustal abundance level. The RSD% for this analytical methodology was <10%. Eight SRMs of soil, sediment, and geochemical exploration samples (see Table IX) were analyzed for Ag, Cd, and the base metals Cu, Pb, Zn, Ni, and Co using the proposed dissolution and the *aqua regia* method. It can be seen that the values obtained for all of the elements is very close to the certified values of the standard reference materials. Complete extraction of these elements was obtained using the acid mixture dissolution procedure. It can, there-

TABLE VI
Results of Gold Determination of
Five SRMs by GFAAS

Sample No.	Sample I.D.	Certified Values (ng/g)	*Mean Observed Values Aqua regia (ng/g)	Acid mixture (ng/g)
1.	GTS-2	260	253	268
2.	GSS-5	260	255	256
3.	GSS-6	(9)	4	6
4.	GXR-6	(95)	73	105
5.	GSS-4	(5.5)	7	8

*Mean of six determinations.

TABLE VIII
Recovery of Gold by Proposed Method

Amount of Gold	*Amount recovered
0.003 g	0.0027 g

*Mean of six determinations.

TABLE VII
GFAAS Results of Gold Estimation in
11 Soil and Sediment Samples Collected Using
the National Geochemical Mapping Guidelines

Sample No.	Sample I.D.	Sample Nature	*Mean Observed Values Aqua Regia (ng/g)	Acid Mixture (ng/g)
1.	6613-5	Soil	800	850
2.	6613-6	Soil	290	310
3.	6620-9	Stream Sediment	115	125
4.	6620-31	Stream Sediment	104	95
5.	6663-2	Soil	4	5
6.	6663-3	Soil	60	68
7.	6663-4	Stream Sediment	78	75
8.	6663-9	Soil	48	50
9.	6663-15	Stream Sediment	110	116
10.	6663-17	Soil	24	26
11.	6663-19	Soil	6	7

*Mean of six determinations.

fore, be stated that this methodology can be very effectively used for the determination of these elements for geochemical exploration work. The standard calibration curves for

Ag and Cd measurements are shown in Figures 2 and 3, respectively. The absorbance value for 2 ppb Ag solution was 0.050 and for 2 ppb Cd solution it was 0.100.

The characteristic concentrations for Ag and Cd were 0.176 and 0.088, respectively. The detection limits (10σ) for the base metals using the proposed method were from 100 to 200 ng/g; while for silver and cadmium they were 5.0 and 2.0 ng/g, respectively.

CONCLUSION

The proposed dissolution technique is simple, quick, cost-effective and less hazardous, without any possibility of loss of analyte elements in comparison to using *aqua regia*. The limit of quantification achieved was much below the crustal abundance of gold and the other elements. This method is routinely followed by the Geological Survey of India for the quantitative analysis of gold in soil and sediment samples and the recovery achieved was more than 90%. The determination of gold consists of three parts: dissolution, pre-concentration, and measurement by GFAAS. The determination of the base metals consists of two parts: dissolution and measurement by FAAS. The estimation and extraction of gold and the base metals in soil and sediments was achieved using a single decomposition procedure.

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Fig.1. Calibration Curve of Gold by GFAAS (ng/g).

Fig.2. Calibration Curve of Cadmium by GFAAS.

Fig.3. Calibration Curve of Silver by GFAAS

TABLE IX
FAAS and GFAAS Determination of Cu, Pb, Zn, Ni, Co, Ag, Cd in SRMs

SRM	Cu (µg/g)			Pb (µg/g)			Zn (µg/g)			Ni (µg/g)			Co (µg/g)			Ag (µg/g)			Cd (µg/g)		
	PDP	ARDP	C.V.	PDP	ARDP	C.V.	PDP	ARDP	C.V.	PDP	ARDP	C.V.	PDP	ARDP	C.V.	PDP	ARDP	C.V.	PDP	ARDP	C.V.
GSS-4	40.20	40.66	40 ±4	52.45	46.46	58 ±7	204	194	210 ±19	63.50	57.04	64 ±7	22.45	24.40	22 ±3	0.085	0.065	0.070 ±0.016	0.320	0.310	0.35 ±0.08
GSS-6	382	378	390 ±22	301	294	314 ±20	99.4	104	97 ±9	55.60	56.60	53 ±5	7.79	7.88	7.6 ±1.7	0.215	0.230	0.20 ±0.03	0.125	0.120	0.13 ±0.04
GSS-7	96.12	95.30	97 ±9	13.82	11.80	14 ±4	145	135	142 ±17	277	270	276 ±23	98	101	97 ±9	0.065	0.045	0.057 ±0.016	0.098	0.072	0.08 ±0.033
GSS-11	66.20	68.56	65.4	2750	2800	2700	3825	3835	3800	25.40	27.54	24.2	12.25	13.68	11.6	5.58	5.38	5.4	27.8	27.10	28.20
GSD-2	5.5	4.6	4.9 ±0.7	33.6	24.24	32 ±8	50.1	47.9	44 ±7	5.8	4.32	5.5 ±2.1	2.5	2.8	2.6 ±1	0.069	0.045	0.066 ±0.015	0.079	0.065	0.065 ±0.016
GSD-12	1235	1215	1230 ±51	275	248	285 ±16	508	512	498 ±27	13.40	10.78	12.8 ±1.9	9.02	8.60	8.8 ±1.1	1.19	1.18	1.15 ±0.16	3.84	3.70	4.0 ±0.4
GXR-1	1135	1080	1110	715	705	730	745	705	760	42.60	38.50	41	8.11	7.60	8.20	32.20	28.50	31	3.23	3.10	3.3
GXR-6	67.40	64	66	109	95	101	112	105	118	26.82	26.50	27	13.65	12.20	13.8	1.25	1.20	1.3	0.97	0.95	1.00

PDP=Results with proposed dissolution procedure.

ARDP=Results with aqua regia dissolution procedure.

C.V.=Certified value.

Observed values are the mean of six determinations.

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