Fresenius J Anal Chem (1997) 357: 308–313

ORIGINAL PAPER

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Novel dissolution procedure using a mixture of manganese dioxide and hydrochloric acid for the matrix-independent determination of gold

Received: 23 October 1995/Revised: 18 March 1996/Accepted: 23 March 1996

Abstract A mixture of manganese dioxide and hydrochloric acid has been used for the accurate and precise determination of gold in various gold-bearing matrices. Results of intermethod comparison studies, F-test on variances, Mann-Whitney U-test, Spearman rank correlation and regression analyses are presented. The recommended method can be applied to a quality control programme and for the evaluation of reference materials. Various standard reference materials (SRM) of diverse matrices have been examined to check the validity of the method and the results were found to be in very good agreement with the certified data. Sample decomposition is straight forward [1–10 g sample (roasted at 600–700 °C) + 5 g of MnO_2 + 30 mL of 2 mol/L HCl]. Gold is coprecipitated with potassium tellurite using tin (II) chloride solution. The precipitate is extracted into toluene and finally stripped back into aqua-regia solution for final nebulization into an air-acetylene flame for atomic absorption spectrophotometry. The method is very simple and easily adaptable, and more convenient than conventional methods involving aqua regia or a hydrobromic acid-bromine water mixture.

Introduction

In recent years, there has been great interest in the development of techniques for the determination of gold in geological and related materials, mainly as a result of the development of instruments of high sensitivity [1]. Both flame and graphite furnace AAS are now extensively used for this purpose. The disadvantage is that the sample must be brought into solution for analysis. This can be accomplished for gold using aqua regia ($HCl:HNO_3 = 3:1$) or a mixture of bromine water and hydrobromic acid [2] or by a suitable combination of both [3]. Over the years, many methods have been proposed and published for the determination of gold in complex geological and related matrices [4–8]. Dissolution involving aqua regia requires expulsion of excess of nitric acid in the subsequent stages. This is done by successive treatment with hydrochloric acid, sometimes resulting in loss of auric chloride (m.p. 290 °C) due to overheating [10]. Also, bromine vapours are extremely hazardous and difficult to handle in most of the laboratories. Tewari et al. [9, 10] have recently proposed a dissolution procedure for gold involving bleaching powder/potassium permanganate and hydrochloric acid. But the method was neither checked for SRMs nor was the composition of the materials used properly mentioned.

In continuation of our earlier communication [11] involving manganese dioxide (which has already been proved to be a very effective reagent for the decomposition of some acid resistant minerals), this paper reports a novel dissolution route for determination of gold in samples of diverse matrices and of a wide dynamic range (55–17 000 ppb or ng/g). The aqueous extract has been aspirated into the flame of an AAS for concentration measurement. A comparison of recoveries of the proposed method and of that involving bleaching powder clearly demonstrates the superiority of the former.

Experimental

All chemicals were of analytical reagent grade unless otherwise specified. Distilled water and solvent were used throughout. A gold solution (1 mg/ml) was prepared by dissolving chloroauric acid [BDH (now Merck), Poole, Dorset, UK] in 5% HCl. The gold solution was standardized by determination of gold as the metal (gravimetry) using hydroquinone [12]. By successive ten-fold

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Table 1 Reference samples and their composition

Sample	Constituent
Geol. Surv. Japan	
Stream Sediment JSd-2	SiO_2 – 60.27%, Fe_2O_3(T) – 11.51%, Cu – 1114 ppm, S – 1.33%, Zn – 2070 ppm
Analytisk Sporelement Komite (ASK)	
Sulphide Ore (ASK-3)	Fe_2O_3(T) – 51.26%, S – 41.5%, Cu – 1500 ppm, Zn – 9.2%, Pb – 2.1%
U.S. Geol. Survey	
Soil (GXR-6)	SiO_2 – 46.68%, Al_2O_3 – 33.4%, Fe_2O_3 – 7.89%
Copper mill Head (GXR-4)	SiO_2 – 66.19%, Al_2O_3 – 13.6%, Fe_2O_3(T) – 4.42%, S – 1.77%, Cu – 6520 ppm
Jasperoid (GXR-1)	SiO_2 – 48.57%, Al_2O_3 – 6.64%, Fe_2O_3 (T) – 33.8%, Bi – 1380 ppm, Cu – 1110 ppm
CANMET, Canada	
Cu-Ag-Au-Bearing Sulphide (CH-1)	Fe_2O_3 – 40.61%, S – 19.0%, Cu – 2.4%, Zn – 0.2%, SiO_2 – 27.82%
Gold Tailing (GTS-1)	SiO_2 – 49.86%, Fe_2O_3(T) – 8.64%
Gold Ore (MA-3)	SiO_2 – 53.68%, Fe_2O_3(T) – 6.65%, S – 1.17%, Al_2O_3 – 13.64%
Gold Ore (MA-lb)	SiO_2 – 52.18%, Al_2O_3 – 11.55%, Fe_2O_3 – 6.65%, S – 1.17%
CRPG, France	
Chromitite (CHR-Pt)	SiO_2 – 21.75%, MgO – 27.97%, Fe_2O_3(T) – 13.41%, Cr_2O_3 – 20.33%

Table 2 Results of different dissolution procedures, concentration ng/g or ppb

sample	MnO_2 + HCl			Bleaching powder			Literature value
	Mean	RSD (%)	Std. error	Mean	RSD (%)	Std. error	
JSd-2	59.00	9.13	1.62	61.60	22.62	4.19	54.00
ASK-3	60.10	5.46	0.98	62.20	18.33	3.42	60.00
GXR-6	94.90	5.76	1.64	81.30	14.81	3.61	95.00
CH-l	245.10	3.57	2.63	217.00	7.93	5.16	250.00
GTS-1	346.30	1.96	2.04	321.10	7.75	7.47	346 ± 16
GXR-4	461.00	2.40	3.32	438.00	5.44	7.15	470.00
GXR-1[a]	3.29	1.52	0.01	3.13	2.87	0.03	3.30
CHR-Pt[a]	4.33	1.62	0.02	4.17	4.02	0.05	4.30
MA-3[a]	7.42	0.94	0.02	7.03	2.42	0.05	7.49
MA-lb[a]	16.95	1.06	0.05	16.52	2.00	0.08	17.00

[a] Values are expressed in µg/g or ppm; RSD (%) = relative standard deviation (%); Std. error = standard error; number of replicates = 10

dilutions with 5% HCl, standard solutions of 100, 10 and 1 µg/ml were obtained. The compositions of the SRMs, used in the current work are shown in Table 1, their descriptions are available elsewhere [13–16].

Instrumentation. The analyses were carried out using a Varian Techtron AA-1475 spectrometer, equipped with deuterium arc background correction system coupled with an Epson LX-800 printer and Varian DS-15 data station. The instrumental parameters were as follows: wavelength 242.8 nm; slit-width 1.0 nm; lamp current 4.00 mA; integration time 2 s; air-acetylene flame (oxidizing).

Procedure. Accurately weigh 5–10 g of powdered sample into a flat porcelain basin and roast at 600–700 °C for 1 h. Transfer the roasted sample into a 250 ml borosilicate beaker. Add 5 g of MnO_2 powder and 30 mL of 2 mol/L HCl. Cover the mouth of the beaker and keep it on a hot plate (temperature 150 °C) for 1 h. Then add 5 mL of HCl

Table 3 Mann-Whitney U-test (T), Spearman correlation coefficient (r′), t-test from pooled variance model and F_9^9 for various samples

Sample	T		r′	t	F_9^9
	(MnO_2 + HCl)	Bleaching powder			
JSd-2	23	20	0.73	0.55	6.69
ASK-3	23	23	– 0.13	1.08	13.88
GXR-6	65	– 1	– 0.19	3.23	4.84
GXR-4	57	6	– 0.47	4.56	3.86
GXR-1	84	1	0.44	3.07	13.40
CH-1	54	– 5	– 0.22	2.75	4.63
GTS-1	70	11	– 1.00	5.08	3.24
CHR-Pt	56	3	– 0.13	2.73	5.89
MA-3	75	– 3	– 0.14	6.67	6.67
MA-1b	72	4	0.30	3.67	3.67

(11.6 mol/L) and digest on a hot plate for 1 h. Repeat this step for another 30 min. Add 30 ml of HCl (2 mol/L) and filter through Whatman No. 40 filter paper. Wash the residue with 1 mol/L HCl. Reduce the volume of the combined filtrate to about 80–100 mL. Add dropwise tin (II) chloride (20%, w/v) until colourless. For chromite and nickel bearing samples, the solution becomes green. Add to the solution 5 mL of aqueous potassium tellurite (0.2%, w/v) and boil for 1 min.

Digest on a boiling water bath for 5 min and allow to cool. Transfer the solution into a separatory funnel and wash the sides of the beaker with HCl (2 mol/L). Add 5 mL of toluene and shake for 2 min. Reject the lower aqueous part. Add 1.5 mL of freshly prepared aqua regia and shake for 1 min. Collect the lower aqueous layer in a calibrated test tube. Repeat this operation once more. Heat the tube in a burner carefully until the solution becomes clear. Dilute the volume to 5 mL with water. Further dilution, if required, should be performed with 2.5% v/v aqua regia. Aspirate the aqueous solution into an acetylene flame of the AAS system. Calculate the gold content directly from a calibration graph prepared under identical conditions. In case of bleaching powder add 5 g powder, 20 mL of distilled water and 20 mL HCl (2 mol/L). After 1 h, add twice 10 mL of HCl of the same strength within an interval of 30 min. Proceed as described before.

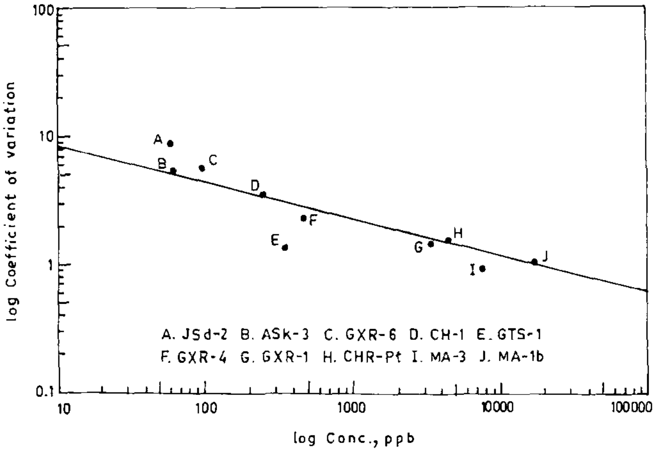


Fig. 1 Concentration of samples plotted against the coefficient of variation using the MnO$_2$ + HCl mixture

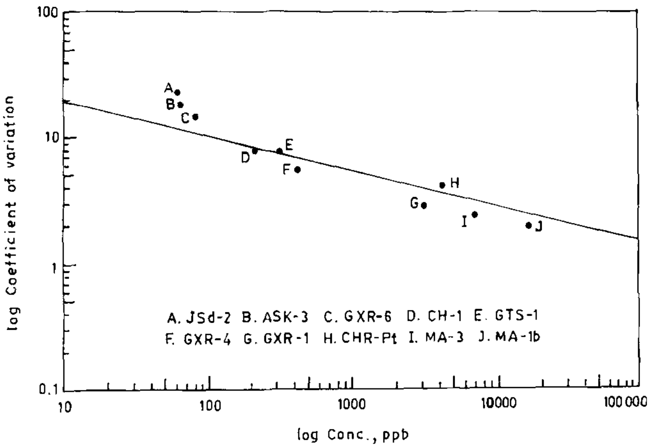


Fig. 2 Concentration of samples plotted against the coefficient of variation using bleaching powder

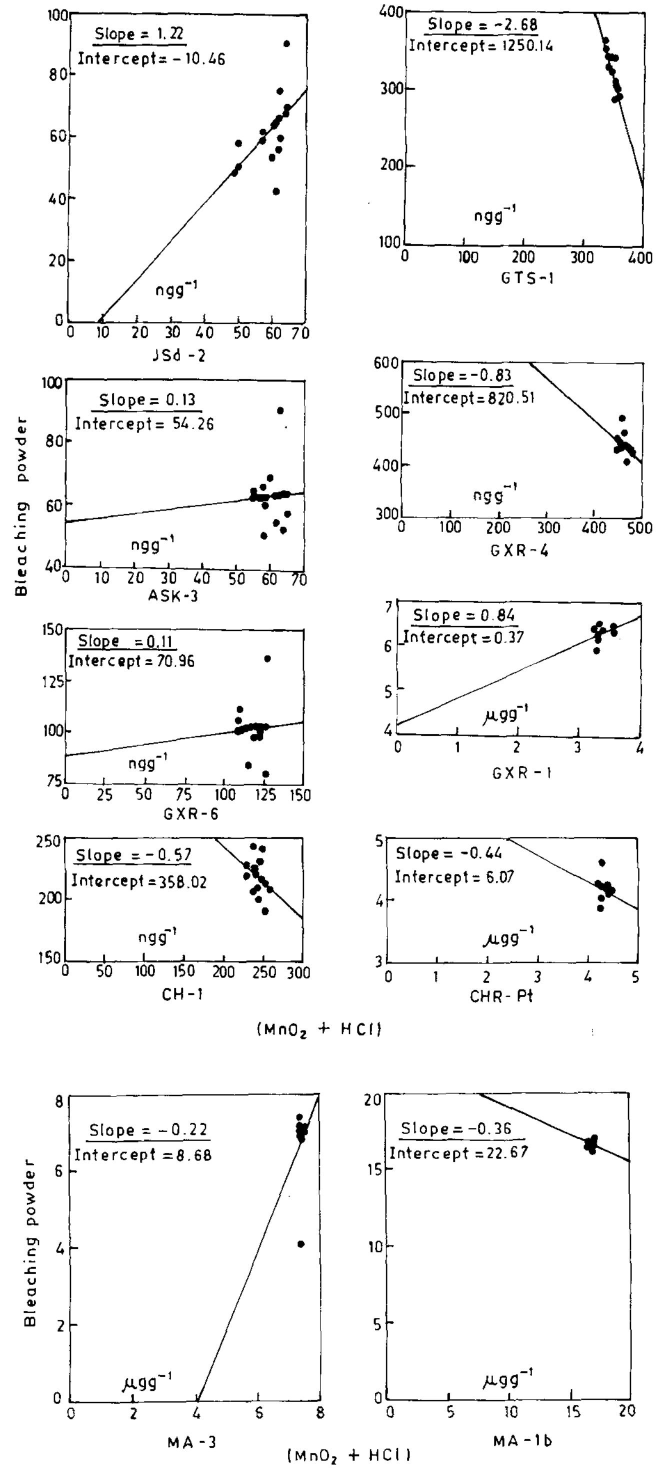
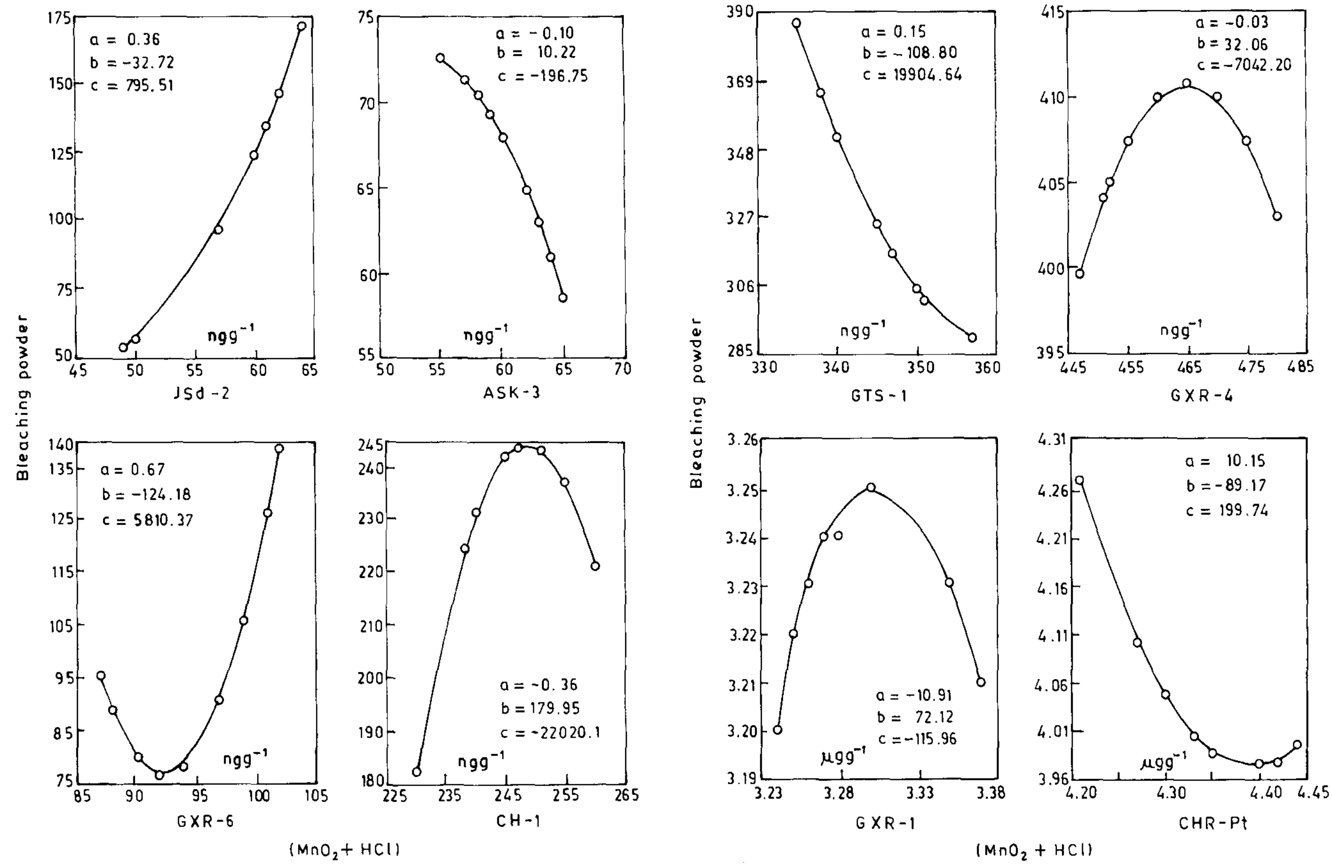


Fig. 3 First order regression lines for comparing the two methods

Results and discussion

Typical results for the determination of gold in various samples are presented in Table 2. Results of the Mann-Whitney U test (T), the Spearman correlation coefficient (non-parametric correlation, r′) [17], the t-test



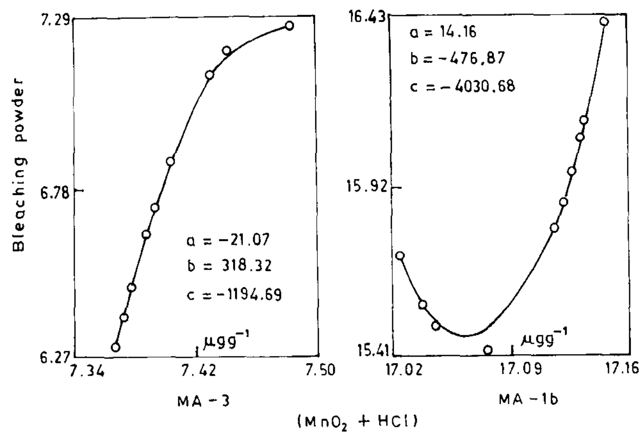


Fig. 4 Second order orthogonal regression lines for comparing the two methods

using the pooled variance model [18] and the F-test values are shown in Table 3.

The limits of two critical areas for T are found from the table described elsewhere [17] as $T_{\alpha/2}$ and nm–$T_{\alpha/2}$. When $\alpha = 10\%$ these limits are 28 and 86, since in the present case both n and m = 10 (i.e. number of replicates). The statistic test using (MnO_2 + HCl) falls within the critical region for most samples; so this test suggests that extraction of the analyte from the matrices would be independent of their composition. A similar conclusion cannot be drawn when bleaching powder is used for sample dissolution.

Spearman's rank correlation (r′) is analogous to r in that it varies from + 1.0 (perfect correspondence between the ranks) to − 1.0 (perfect inverse relationship between the ranks). A rank correlation of r′ = 0.0 indicates that the two sets of ranks are independent. A weakly positive relationship does exist between the two methods in case of GXR-1 (r′ = 0.44) and MA-1b (r′ = 0.30) and quite strongly in case of the sediment sample (JSd-2, r′ = 0.73). A significance level of $\alpha = 0.05$ would be appropriate to test the correlation between the methods under investigation. The upper critical value corresponds to $1 - \alpha/2 = 0.975$ or 0.6364 for n = 10 and the lower critical value corresponding to $\alpha/2 = 0.025$ is − 0.6364. Computed correlation, in most of the samples, falls beyond either of these limits; so it can be concluded that two methods are independent of one another.

Intermethod comparison studies are necessary in the development and evaluation of new methods. From individual means and standard deviation a 'pooled' standard deviation and t-value are calculated [$t = (x_1 - x_2)/S\sqrt{(1/n_1 + 1/n_2)}$; x_1 and x_2 are means; n_1 and n_2 are the numbers of replicates; S = pooled variance]. The observed t is compared to the critical value t_c as obtained from Student's t-table [18]. If $t > t_c$

Table 4 Fe, Cu, Ni and Pb in the final extract determined by FAAS

Sample	Fe/μg mL^{-1}	^{m}Fe:^{m}Au	Cu/μg mL^{-1}	^{m}Cu:^{m}Au	Ni/μg mL^{-1}	^{m}Ni:^{m}Au	Pb/μg mL^{-1}	^{m}Pb:^{m}Au
MA-1b	21.00	1.23	2.32	0.14	0.10	–	0.75	0.04
MA-3	24.75	3.30	0.97	0.13	1.05	0.14	0.75	0.10
CHR-Pt	5.79	1.34	1.68	0.39	2.76	0.64	0.15	0.35
GXR-1	31.46	9.53	7.15	2.17	1.57	0.47	1.56	0.47
ASK-3	4.63	77.17	1.30	21.67	0.19	3.17	1.63	27.17
GXR-4	35.76	76.06	13.00	27.66	0.23	0.50	0.62	1.33
CH-1	12.50	50.00	45.45	181.80	0.82	3.30	1.75	7.02

a given confidence level, then we have the given confidence that the averages are different, i.e., the methods are not equivalent [18]. For JSd-2 and ASK-3, experimental t-values are greater than 2.101 and 2.878 (which are the t_c at 95% and 99% confidence level, respectively), at a degree of freedom $(10 + 10 - 2)$ indicating that both methods are equally effective. F^{9}_{9} is 3.18 at 5% significance level [19] and the F-ratios for all the samples are greater than the theoretical value; this test further suggests that the bleaching powder route is significantly less precise than the proposed one $[F = S_1/S_2 > 1]$; here s_1 and s_2 are the standard deviations for the (bleaching powder + HCl) and (MnO_2 + HCl) route, respectively.

The t-test on paired means is more sensitive than that on means of two methods of analyses. The test on paired means yielded t-values of 0.23, 0.56, 3.19, 2.64, 2.46, 2.57, 6.72, 6.90 and 3.41, for JSd-2, ASK-3, GXR-6, CH-1, GTS-1, GXR-4, GXR-1, MA-3 and MA-1b, respectively. At the 5% level, t with (10–1) degrees of freedom is 2.26; hence the differences are significant for various matrices, excepting JSd-2 and ASK-3. This test suggests that there must be something very different about the two decomposition routes under which the first and second series of determinations were carried out [19].

Regression analysis evaluates the relationship between one variable and another that may be affecting it, e.g. the time taken for a chemical to dissolve and the amount of stirring needed. Generally, an inverse relationship exists between the concentration of an element and the precision expressed by the coefficient of variation. An average quality of analysis [19] is shown in Figs. 1 and 2 using (MnO_2 + HCl) and (bleaching powder + HCl), respectively. The samples below the line are easier to analyse at the plotted concentration and those above the line harder.

Linear regression involves the fitting of points to a straight line function such that the sum of the squares of the deviations from the points to the 'best straight line' is minimized [18]. This means that the overall deviations between the observed and calculated points are such that the sum of the deviations (+ and −) is zero. In Fig. 3 first order regression lines for all the samples [21] are shown which reveal that the routes under investigation are not linearly related (excepting JSd-2). An orthogonal regression of second order $(y = ax^2 + bx + c)$ has been found to be much more appropriate and hence better fit, as shown in Fig. 4.

When the ^{m}Fe:^{m}Au mass ratio exceeds 100, than the gold absorbance signal decreases to 88% [20]. The amount of concomitant elements present in the final extract (as shown in Table 4) did not affect the gold signal under the conditions investigated.

The results of the analyses of reference samples indicate that the proposed method provides accurate results for gold in diverse matrices. The MnO_2 + HCl mixture is much better than the other two commonly used oxidizing leaches (aqua regia and Br_2-HBr mixture) in a sense that it can be handled easily and is less labour intensive. Geological, metallurgical and mineral beneficiation laboratories require an accurate and rapid method for gold analyses and this method would certainly fulfil their requirements.

Acknowledgements The Director, Regional Research Laboratory, Bhubaneswar, is thanked for granting permission to publish the results of this work. The authorities of US Geological Survey, Geological Survey of Japan, Analytisk Sporelement Komite, Norway, and Canada Centre for Mineral and Energy Technology are thanked for sending sufficient amounts of reference materials and associated documents in time, without which this work could have never been complete. Mr. P.N. Sethi is thanked for extending generous secretarial assistance.

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