JAAS

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/jaas

Novelty sentence:

Fast dissolution of gold-containing samples and chemically-based resolution of wash-in, wash-out problems for gold in ICP-based systems.

Rapid high-performance sample digestion for ICP determination by ColdBlock[™] digestion: part 2: Gold determination in geological samples with memory effect elimination

Yong Wang and Ian D. Brindle*

Department of Chemistry, Brock University, St. Catharines, Ontario, CANADA L2S 3A1

Abstract:

A procedure is described to tackle a weakness in laboratory analysis of geological materials, notably (1) systematic low gold recovery during wet sample dissolution using aqua regia, and (2) severe memory effect of gold during sample transportation and nebulization in conventional ICP/ICP-MS sample introduction systems. Modified aqua regia, in which hydrochloric acid is replaced by hydrobromic acid, was used to digest gold-containing ores with different mineralogical composition. Under these conditions, gold is more efficiently dissolved and is more stable in solution than it is from *aqua regia* treatment. A comparative study, directed to finding suitable matrix components to stabilize gold in dilute acid solution, was also conducted. A solution of 1% (m/v) L-cysteine and 1% HCl (v/v) was found to be effective in generating sensitive and stable gold signal in ICP-MS. This matrix also completely eliminates the troublesome gold memory effect. The combined effectiveness of these modifications was evaluated using six certified gold-containing reference materials (CCU-1D, SP-72, SP-73, SN-26, SG-14, and OxP116), comprising one sulphide-rich copper concentrate and five predominantly silica-based composite ores. With 0.5-2.0 grams of sample, and using digestion times of 10-12 minutes, 94-100% gold recoveries were achieved, using a total acid volume of 6-9 mL. Between-run reproducibility was in the range of 2-4%. Analytical results are close to those generated from INAA determination for one of the samples. Interestingly, for the samples studied in this work, the use of hydrofluoric acid in digestions conferred no benefits, in terms of gold recoveries and, in the case of the high-silicate samples, the use of hydrofluoric acid actually reduced gold recoveries.

1. Introduction

Accurate quantification of gold concentrations in gold-bearing ores has tremendous implications for the gold mining industry as the assessment of the viability of a gold mine, often expressed by the 'cut-off' grade of the ore, relies primarily on this process. As with the determination of other metals in most geological materials, determination of gold typically proceeds by a three-step procedure that involves physical treatment of the ore (sampling, crushing, pulverizing, sieving,

^{*} Corresponding author. Email: <u>ibrindle@brocku.ca</u>, Phone: +1 (905)688-5550, ext. 4559. Fax: +1 (905) 688-0748

homogenizing, etc.), chemical treatment (analyte extraction, pre-concentration or sample dissolution), and instrumental determination (AAS, ICP-OES, ICP-MS, etc.). Given the tendency to exhibit heterogeneous distribution, particularly noticeable with gold in rocks and soils, and usually called the "nugget effect", proper physical treatment of ore is a crucial prerequisite to render gold ore samples sufficiently fine and representative so as to minimize the "nugget effect". This step, from a mineral analyst's perspective, is largely accomplished by exploration geologists and milling technicians. It does, however, impact on the size of the sample that is taken through the digestion and analysis process and is an important consideration in the certification of Standard Reference Materials, where the minimum sample size to ensure representativeness of gold is specified on the certificate. This paper focuses on evaluating the next steps, namely the operating procedures that are routinely undertaken in the analytical laboratory after pulverized and homogenized ore samples are received and we propose convenient remedies to overcome limitations in the existing laboratory methodologies for gold analysis.

Although there is no shortage of gold extraction and determination methods, both published in the analytical literature and practiced in accordance with in-house methods, accurate determination of gold in geological materials, especially when low detection limit (DL) and high sample throughput are required, remains challenging for a variety of reasons. Various extraction and pre-concentration methods, such as solvent precipitation¹, organic extraction²⁻³, adsorption and ion exchange⁴⁻⁵ etc., have been reported. Not surprisingly, a number of these techniques find little application in commercial labs, due to high costs and operation complexity. Instrumental neutron activation analysis (INAA) is a well-known non-destructive method for the determination of gold and platinum group elements (PGE) and provides detection limits comparable with ICP-MS⁶. Its prohibitive capital cost and slow data acquisition, limit its use in commercial labs. There are three classical chemical treatment methods for the analytical treatment of gold ores; cvanidation, fire assay (FA) and acid digestion. Cvanidation is regarded as an obsolete technique in the analytical laboratory due to its health hazard. As a fusion technique, fire assay has dominated gold analysis for centuries due to its acceptance to deliver 'total recovery' of gold, regardless of the mineralogy of the host rock. While the technique is generally procedurally simple and straightforward, proper addition of various flux chemicals, such as lead oxide⁷ or nickel sulphide⁸, is often necessary. This requirement, together with the need to measure lower and lower gold concentrations in samples and control materials, often result in high blank readings and poor reproducibilities, despite the notion of "total recovery". Hoffman and Dunn⁹ reported that the method detection limit of fire assay sits typically at high part per billion levels, regardless of the choice of detection instrument. In addition, method reproducibility, expressed as relative standard deviation, ranges as high as 10-30%. As a result, these inherent limitations of fire assay can compromise the accuracy of gold values, particularly as method detection limits are approached.

Unlike fire assay, acid digestion of gold ores has increasingly garnered attention amongst research and commercial laboratories, due to a number of advantages. Acid digestion requires

significantly small amount of sample (typically from 0.5 gram to several grams) and less additional materials, and can thus dramatically reduce the cost of analysis per sample. In a general laboratory setting, acid digestion can take only a fraction of the time that is required for FA, enabling fast submission of prepared sample solution to analytical instruments. Moreover, the background noise in the running blank can drop 2-3 orders of magnitude thanks to negligible gold background in mineral acids. Consequently, lower detection limits and high sample throughput can be simultaneously achieved. To date, *aqua regia* (AR) is the most widely employed wet sample dissolution method for gold analysis.¹⁰

While low cost, fast turnaround, low detection limit and high accuracy are the four goals of modern gold analysis, *aqua regia* does not meet all these requirements. As an extraction method *via* acid parting, the one conspicuous shortcoming with AR is its limited ability to deliver "total recovery" of gold. Hall *et al.*¹¹ reported that gold values obtained from AR dissolution were in general 24-42% lower than those from INAA, which is considered the "non-sporting" method for the determination of concentrations of gold in samples[†]. FA values were lower than INAA to a lesser degree by 14-26%. Hoffman confirmed this disadvantage of AR, adding that silica encapsulation may be the main reason for low gold yields.¹² Senanayake argued that silica encapsulation and sulphide-rich gold ores limit the degree of gold leaching by various lixiviants even after fine grinding.¹³ Recently, Leybourne and Rice presented a preliminary mathematical correlation equation[‡] to illustrate the systematic bias of gold values between FA and AR, using more than 2000 rock and soil samples.¹⁴ They also stressed, however, that gold recovery also depends on the sample mineralogy and the mesh size of processed samples.

To explain consistent gold loss by AR is difficult and, in some cases, debatable. The notion of encapsulation of gold in silica often fails to explain gold loss, as some geologists reported no significant difference in gold data when HF was employed to unlock the refractory SiO₂ lattice.¹⁵⁻¹⁶ Another plausible explanation, that was extensively investigated by the US Bureau of Mines in 1971, is the high volatility of gold chloride (Au₂Cl₆) complexes at elevated temperatures.¹⁷ Significant gold losses, monitored at 200-250C, suggested that vaporization of Au₂Cl₆ could be a severe side effect of gold chlorination, which is proposed to be the reaction that liberates gold by AR.

Aside from difficulty with gold extraction efficiency, outlined above, another area of concern in gold determination is the severe gold memory effect, observed during sample transportation and nebulization in conventional ICP/ICP-MS sample introduction systems. Many elemental determination instruments, such as atomic absorption (AAS), or inductively coupled plasma optical emission (ICP-OES) or inductively coupled plasma mass spectrometers (ICP-MS), typically employ peristaltic pump-powered sample introduction and glass or silica-based aerosol

[†] INAA is performed on the solid sample and so avoids both losses during processing, due to encapsulated gold that is inaccessible to reagents, and contamination from reagents used to prepare the sample. The representativeness of the sample is the only critical parameter for this type of analysis.

 $^{^{\}ddagger}$ Au _{AR}=0.6332·Au _{PbFA}+0.00024 (ppm)

generation. Glass-based spray chambers and nebulizers tend to adsorb Au from solution and retain it on the glass surface, which results in a significant delay in the gold signal reaching a steady state and, after the sample is withdrawn, yet another delay during which the gold desorbs from the surface and gradually approaches the baseline. If handled with impatience and ineffective wash solutions, gold memory effects can lead to high background and produce erroneous results. A 2.4% *aqua regia* solution has become standard in some commercial labs as the wash solution for Au and other PGE group elements, but this approach does not eradicate these memory effects efficiently. Lam and coworkers provided a simple solution by replacing glass sample introduction system with a RytonTM counterpart, noting that the latter shows marked reduction in surface adherence of gold containing species.¹⁸⁻¹⁹ Brindle *et al.*, on the other hand, proposed a "chemical resolution" to eliminate the memory effect.²⁰ This approach, that is able to bring down the gold wash-in and wash-out times to less than 60 seconds, exploit the superior Au bonding ability by several complexing reagents, compared with bonding to glass surfaces. These reagents include thiourea and L-cysteine and, by using them, one can take advantage of the intrinsic efficiency of the cyclonic spray chamber.

In response to the growing interest within the gold mining sector for inexpensive and more reliable analyses, we present a modified acid digestion method, based on the ColdBlockTM technology, for fast and accurate gold determination with solution-based elimination of the gold memory effect.

2. Experimental

2.1 Design of sample preparation apparatus

Whilst most sample digestions have been conducted in hot-blocks or microwave ovens for decades, developmental advances in fast digestion and uncomplicated handling has not stopped. Recently a novel infrared (IR) radiation-based sample digestion device, known as the ColdBlockTM, has emerged that addresses many of the weaknesses in conventional sample digestion systems, such as lengthy digestion times, unsatisfactory reproducibilities, and consumption of large amounts of mineral acids. The working principles and detailed schematic designs of the ColdBlockTM (Fig 1.) were described in 2014 by Wang *et al.*²¹ Focused shortwavelength infrared energies are directly transmitted to the surface of sample particles in an appropriate acid medium, expediting sample breakdown by localized heating and acid attack. Although this device was initially validated using a series of environmental matrices, in-house experimental trials revealed that fast and essentially complete digestion of more refractory geological samples, such as iron ore, bauxite, and chromite, is also readily achievable. Therefore, in this study we continue to use the prototype of ColdBlockTM for the preparation of samples for the determination of gold.

A minor modification on the short-wavelength IR ring was made to the basic ColdBlockTM equipment. In the debut of the ColdBlockTM, the two IR rings were identically coated by ceramic

Journal of Analytical Atomic Spectrometry Accepted Manuscr

such that both rings emit infrared radiation horizontally towards the centre of the digestion tube, where the acid/sample mixture is situated (Fig 2a). Given the recalcitrant nature of many geological samples and the limited power capacity of the IR rings, if the IR radiation can be manipulated to generate higher intensity, the digestion may still be completed within a short timeframe, a desirable characteristic of this technology. In this regard, we altered the coating pattern of the upper ring, enabling its IR radiation to be focused downwards (Fig 2b). With this new radiation pattern of the IR rings, a larger volume of acid-sample mixture can be intercepted by the IR radiation and the energy intensity around the target zone is significantly increased.



Figure 1: The schematic design of the ColdBlock[™]

Page 7 of 18



Figure 2a: Original radiation pattern

Figure 2b: Modified radiation pattern

2.2 Analytical instrumentation

A PerkinElmer-SCIEX (Woodbridge, ON, Canada) ELAN[®] DRC[®] II ICP-MS was used for analyzing all samples and standards. The sample introduction system consists of a Meinhard[®] A3 type glass concentric nebulizer, a baffled quartz cyclonic spray chamber and a 2.0 mm (I.D.) quartz injector. Daily performance check was performed to ensure that the baseline elemental sensitivities recommended by the manufacturer were met. Other important operating parameters of the instrument are listed in Table 1.

Plasma RF power (W)	1200
Plasma gas flow (L min ⁻¹)	15.0
Auxiliary gas flow (L min ⁻¹)	1.2
Nebulizer gas flow (L min ⁻¹)	0.80-0.82 (optimized frequently)
Operating mode	Standard
Sample uptake (mL min ⁻¹)	~1.0
Interface	Pt sampler and skimmer cones
Auto lens calibration	On (Be 6.0 V, Co 7.0 V, In 8.0 V)
Detector	Dual
Scanning mode	Peak hopping

Table 1. Instrumental settings for ELAN ICP-MS:

Journal of Analytical Atomic Spectrometry Accepted Manuscr

Dwell time (ms)	500
Sweeps	1
Replicate	5

2.3 Reagents

Analytical-grade (single distilled) nitric acid (68-70% m/v) and hydrochloric acid (20-22% m/v) were purchased from Caledon (Georgetown, ON, Canada). Hydrobromic acid (47-49% m/m) and reagent-grade ammonium fluoride were acquired from Sigma Aldrich (Oakville, ON, Canada). Two gold 1000 μ g mL⁻¹ standard solutions were purchased from High-Purity Standards (Charleston, SC, USA). Thiourea and L-cysteine was manufactured by Amresco (Solon, OH, USA). All sample and working solutions were prepared with ultra-pure de-ionized water (18.2M Ω resistivity) from an Elgastat-Maxima purification system (High Wycombe, UK). Certified gold reference materials were obtained, CCU-1D from CANMET (Ottawa, ON, Canada), and SP-72, SN-26, SG-14, SP-73, and OxP116 from Rocklabs (Auckland, New Zealand). Research grade argon (99.998%) and nitrogen (99.999%) gases were supplied by Praxair (Hamilton, ON, Canada).

2.4 Method of sample dissolution and preparation

Due to the semi-closed design of the ColdBlockTM device, it was observed that significant gold loss occurred using traditional *aqua regia* attack. Changes in the HCl/HNO₃ (AR) mixture were required to (a) minimize the formation of volatile gold chloride species, (b) form a new acid mixture that retains strong oxidizing ability, and (c) stabilize new Au-containing species that do not volatilize at relatively high temperatures. Earlier investigators suggested that hydrobromic acid might be a suitable AR component as the new HNO₃/HBr mixture demonstrated improved performance in Au extraction,²²⁻²³ though the volatility of AuBr₃/Au₂Br₆ species, the major Aucontaining products of HNO₃/HBr attack, was not investigated. This method was not favoured in the past at commercial scales mainly due to the high cost of the reagent.²⁴ These concerns were largely addressed by investigations into the ColdBlockTM digestion and optimization of digestion protocols in the current study.

Appropriate use of acids during sample dissolution requires knowledge of samples' physical and chemical nature, as well as the analytical goals of the analysis. The six gold CRMs investigated in this study comprised two different mineralogies. CCU-1D is a copper concentrate which consists chiefly of chalcopyrite (CuFeS₂, 66.8%), pyrite (FeS₂, 20.5%), pyrrhotite (Fe_xS_y, 3.8%), and sphalerite ((Zn, Fe)S, 3.8%). For such a sulphide-rich material, roasting is a common sulphur removal practice in many commercial labs. Prior to conducting HNO₃/HBr digestions, conventional AR attack was attempted without any form of roasting. Small sulphur beads,

floating at the top of the resulting digestates, made black by incorporation of unreacted sample, suggest that roasting may be a necessary step if HNO₃/HCl was to be used. When replaced with HBr, however, the HNO₃/HBr mixture exhibited a very different result as a clear yellow brown solution formed with no sign of elemental sulphur. It is possible that the reason of the low gold yield of CCU-1D with HNO₃/HCl may be due to the incorporation of some gold inside the sulphur beads, in addition to the loss via vaporization.

The matrices of the other five gold CRMs are mainly basalt and feldspar that are high in silicate (55-65%). No increase of Au recoveries was observed from our tests employing HF and so HF was eliminated from the acid mixture used for these samples. A two-stage acid addition approach was adopted. All CRMs were received with sufficient homogeneity (screened to eliminate the 'nugget effect') that allowed the use of relatively small samples (0.5-2 grams per sample) for gold determinations. The detailed acid treatment procedure and the durations of IR heating are listed in Table 2. It can be seen that both the time required to complete the digestion and the volume of total acid used are advantageous compared with existing methods. All digestions were carried out in a well-vented fume hood for safety reasons. The resultant digestates were diluted to 25 mL with ultra-pure water and filtered with a syringe-filter of 0.45 µm porosity. All filtrates were further diluted, with appropriate dilution factors to ensure that gold concentrations are comfortably bracketed within the calibration range (0-20 ppb).

Journal of Analytical Atomic Spectrometry Accepted Manuscrip

Sample ID	CCU-1D	SP-72	SN-26	SG-14	SP-73	OxP116
Step 1						
$HNO_3(mL)$	4	5	5	8	6	6
HBr (mL)						
35% (min)	4	5	5	7	7	7
Step 2						
$HNO_3(mL)$	3					
HBr (mL)		1	1	1	1	1
30% (min)					3	3
33% (min)		5	5	5		
35% (min)	4					
Step 3	Step 3					
$HNO_3(mL)$						
HBr (mL)	1					
40% (min)	4					
Total acid (mL)	8	6	6	9	7	7
Total time (min)	12	10	10	12	10	10

Table 2. ColdBlock TM digestion program	n for four gold certified reference materials
----------------------------------------------------	-----------------------------------------------

2.5 Matrix selection, calibration, detection limit, and quality control

Severe memory effects for gold were observed using dilute nitric or hydrochloric acids as sample diluents. A comparative investigation was conducted to examine the performance of various solutions with respect to gold memory effect during ICP-MS determination. Amongst four candidate matrix solutions (0.5% HNO₃, 1% HCl, 1% L-cysteine in 1% HCl, and 1% thiourea in 1% HCl), both L-cysteine and thiourea solutions are capable of eliminating the gold carry-over effect satisfactorily. Gold standards, prepared in a thiourea matrix, delivered declining signals over a timespan of several days, suggesting that the Au-thiourea complex undergoes decomposition and requires fresh preparation for day-to-day determination. L-cysteine, on the other hand, stabilized the gold in solution and Au standards prepared in this matrix lasted several weeks without any observable drop in signal intensity. Therefore, a matrix solution containing 1% (m/v) L-cysteine and 1% (v/v) HCl was prepared to serve all sample and working standard preparation purposes.

Four gold calibration standards were prepared at 1.0, 5.0, 10.0, 20.0 μ g L⁻¹ levels and the ICP-MS instrument was frequently calibrated to eliminate the potential for drift to compromise the results. Calibration curves were blank subtracted (linear through zero) and presented a minimum correlation coefficient of 0.9999. Method detection limit[§], based on 8 continuous measurements of the blank, was determined at 6.8 pg L⁻¹. Procedural blanks were also analysed and the gold concentrations were found insignificant (below the limit of detection). All measurements were frequently checked with QC solutions that were made from a separate Au stock solution from High-Purity.

3. Results and discussion

3.1 Performance evaluation of HNO₃/HBr mixture in sample digestion

A mixture of HNO₃/HBr oxidizes elemental Au in a similar manner as its HNO₃/HCl counterpart.

 $HNO_3 + 3HBr \rightarrow NOBr + Br_2 + 2H_2O$ (1)

 $2Au + 2Br^{-} + 3Br_2 \leftrightarrow 2AuBr_4^{-}$

Although nitric acid alone is a strong oxidant, it does not oxidize sulphide (S^{2-}) to $S^{(4+)}O_2$; neither does nitrosyl chloride, a major product of the *aqua regia* reaction. Even treated with an excess of HNO₃/HCl and extended digestion time, beads of sulphur, formed during the digestion, persist

(2)

 $^{^{\$}}$ Calculation was based on a slope of 11255 cps/pg mL⁻¹, an average blank reading of 52.4 cps, and σ of 8.0 cps.

and sequester sample particles and render them inaccessible to the digesting acid mixture. Mass spectroscopy later confirmed that the beads were elemental sulphur. The HBr *aqua regia*, on the other hand, shows very different behavior. No sulphur beads form during the digestion. No precipitate was observed when the diluted reaction matrix was treated with a solution of barium chloride, suggesting that the sulphide was not oxidized to sulfate. It is possible that the sulphur is volatilized as S_2Br_2 since this compound, which readily forms between sulphur and bromine, has a relatively high vapour pressure at the temperatures that are used in the digestion. Hydrolysis of S_2Br_2 is reported to deliver H_2S and SO_2 .²⁵

Full conversion and stabilization of gold, in the form of AuBr₄⁻ in acidic solutions, is nevertheless a delicate process. Maintenance of some elemental bromine in the solution is critical in this process and it can be easily lost via vaporization, despite the powerful *in-situ* cooling by the Peltier unit. If HBr is added simultaneously with HNO₃, rapid vaporization of Br₂ leads to a need to increase the amount of HBr to achieve good gold recovery, which releases more bromine to the environment and increases the cost of the procedure. When added after HNO₃, gold recoveries are in line with the certified values, as long as the digestion temperature and time are properly set and that a residual bromine concentration remains in solution. Reaction 2 appears to favour the reversed fashion if the IR rings operate at high powers. Long digestion time may also be detrimental to the gold recovery because the free Br₂ in the digestates will be exhausted, likely leading to decomposition of AuBr₄⁻ and resulting in decreased gold in solution. Maintaining a slight excess of free Br₂ is therefore the key to complete extraction of Au into solution. Excellent gold recoveries, using moderate IR heating and digestion times, with minimal consumption of HBr, were achieved. Our in-house data suggest that gold recoveries could drop 10-20% where there is no dissolved bromine in solution. Journal of Analytical Atomic Spectrometry Accepted Manuscrip

3.2 Elimination of gold memory effect

In the determination of gold by ICP-MS, it is important to know whether the determinations are compromised by carry-over from previous samples. For most elements, carry-over is minimal and determinations can readily be made in most samples and standards, prepared in dilute nitric or hydrochloric acids. In routine geological sample preparation practices, these matrices do not, however, deliver reliable gold signals in a fast and reproducible manner. This failure is due to lengthy wash-in and wash-out times, particularly for gold. Fig 3a illustrates the slow climb of the gold signal over a time period as long as 10 minutes, when the sample is presented in 0.5% (v/v) HNO₃. Dilute HCl solution does help reach a stable gold signal in a faster manner, but its overall time for analysis per sample (3-5 minutes) is still far from acceptable in commercial operations (Fig 3b). In the determination of gold, these solutions are evidently unsuitable to serve as the matrix solution for sample and standard preparation, as well as the wash solution between sample runs. Brindle *et al.* pointed out that sulphur-containing ligands, for instance, thiourea and L-cysteine, form stable co-ordination complexes with gold.¹⁹ They observed that the memory effect of gold was completely resolved when samples and working standards were prepared in 1%

Journal of Analytical Atomic Spectrometry Accepted Manuscr

(m/v) solution of either of the two co-ordinated matrix solutions, instead of using them as wash solutions^{**}. An L-cysteine matrix also showed extraordinary wash-in and wash-out times when complexed with Au in acidic solutions (Fig 3c). L-cysteine solution can maintain high sensitivity of Au for several weeks at room temperatures, whereas thiourea was found to be relatively unstable: the Au-thiourea complex tends to decompose over a relatively short time, resulting in reduction of the signal.



Figure 3a: 1 ppb Au in 0.5% (v/v) HNO₃ solution

^{**} Residual bromine, remaining in solution after digestion, will react with either _L-cysteine or thiourea. Coordination of excess _L-cysteine or thiourea stabilizes the gold in solution, making handling of the samples easier, and eliminating fugitive emissions of bromine from the prepared sample solution, prior to its being introduced to the spectrometer.





Figure 3b: 1 ppb Au in 1% (v/v) HCl solution



Figure 3c: 1 ppb Au in 1% (m/v) L-cysteine and 1% (v/v) HCl solution

Journal of Analytical Atomic Spectrometry Accepted Manuscri

The other aspect of the memory effect, due to the potential adsorption of Au to the quartz reaction tube, was also investigated.^{††} After removing the digestates for filtration, the quartz tube was rinsed several times with deionized water and a final wash by dilute _L-cysteine matrix solution was collected for background Au scan. The insignificant Au readings suggest that, during the preparation of samples, using the ColdBlockTM, the combination of acids, bromine, and bromide that react with the sample also work to keep the gold in solution, and prevent it from adsorbing onto the surface of the silica tube. The quartz tube can be readily cleaned with the aid of conventional detergent and no noticeable Au carryover has been observed.

3.3 Validation of analytical performance

Analysis of copper concentrate CRM CCU-1D

As indicated in Table 2, digestion of this sulphide-rich copper concentrated sample can be completed in as little as 12 minutes, without the requirement of roasting or other sulphur removal treatments, thanks to the superior heating and *in-situ* cooling functions of the ColdBlockTM. Excellent gold recoveries were obtained, with between-run reproducibilities of 2.4% (reported as relative standard deviation). For method comparison purpose, duplicate samples of CCU-1D sample were also sent out to a commercial lab, for INAA quantification. It can be seen (Table 3) that the current work is able to produce gold data that align well with results from INAA, with significant savings in turnaround time and analytical costs. In order to evaluate the overall performance of the proposed digestion method, a separate aliquot of the digestate was diluted, prepared in 0.5% HNO₃ solution, and sent for determination by an ICP-OES spectroscopy (PerkinElmer DV 3300). Major elements analyzed, including Cu, Fe, Pb, and Zn which returned satisfactory recoveries and RSDs, indicating that the adopted leaching procedure is analytically efficient.

		-	-	-		
CCU 1D		Certified values ^{‡‡}	ColdBlock™ (HNO ₃ /HBr, n=3)		INAA (n=2)	
CCU-ID	$(\mu g g^{-1})$	Measurement	Recovery (%)	Measurement	Recovery (%)	
	Au	14.01±0.18	13.2±0.3	94.0	12.1±0.8	86.4
С	^c u (%)	23.99±0.04	24.3±0.5	101.2	-	-
F	e (%)	29.3±0.4	29.9±0.3	102.4	29.8±0.5	101.7
Р	b (%)	0.262±0.005	0.267±0.008	102.0	-	-
Z	(%)	2.63±0.04	2.69±0.08	102.1	2.67 ± 0.08	101.5

Table 3. Analytica	l results of CCU	J-1D by ColdBlo	ock [™] digestion
--------------------	------------------	-----------------	----------------------------

^{tt} The authors thank the referee, who asked to have the question of adsorption of gold to the reaction tube clarified.

[#] Published in the certificate of the reference material and also accessible from Natural Resource Canada's website.

Analysis of pulped rock and ore blends

Five pulped gold CRMs (SP72, SN26, SG14, SP73, and OxP116) were specifically designed and prepared by Rocklabs to serve as quality control materials in routine laboratory gold determinations. Following the proposed steps in Table2, HNO₃/HBr treatment was able to extract maximum gold values from these high silicate samples in 10 minutes (Table 4). Gold results from HF digestions were also reported. Although the amount of residual silicate was reduced significantly due to the HF attack, gold recoveries did not improve and the authors decided that it was not necessary to employ HF for the samples studied in this investigation. Having said that, it is worth noting that HF may be added to the digestion if the analyst is uncertain about the gold mineralogy in silicate-rich samples or a 'total digestion' is required for analysis.

Table 4. Analytical results of SP72, SN26, SG14, SP73, and OxP116 by ColdBlock[™] digestion

	Current method (n=3)			HNO ₃ /HB1	HF digestion (n=3)
Au ($\mu g g^{-1}$)	Measured	Certified ^{§§}	Recovery (%)	Measured	Recovery (%)
SP72	18±1	18.16±0.10	98.6	16.0±0.6	88.1
SN26	8.5±0.3	8.54±0.07	99.0	7.2±0.2	84.0
SG14	0.99±0.03	0.989±0.019	99.7	0.84±0.03	84.6
SP73	17.9±0.4	18.17±0.12	98.4	16.5±1.0	90.5
OxP116	14.9±0.5	14.92±0.11	99.6	13.0±0.3	87.1

Journal of Analytical Atomic Spectrometry Accepted Manuscri

3.4 Other considerations

Aside from the use of the IR based ColdBlockTM digester and the successful application of metalligand chemistry to address gold memory effect, the authors note that appropriately pre-treated samples, submitted in an well-ground and homogenized form prior to the digestion, are also a key factors to enable fast sample digestion and good reproducibility of gold. The importance of particle size must be stressed in gold analysis because this factor not only influences reaction kinetics, in that the rates of digestion reactions are directly affected by the degree of sample exposure to mineral acids, but also the representativeness of the sample, a critical parameter determining the required amount of sample for accurate analysis. Based on our experience, a minimum 200-mesh of sample milling may be recommended to the analytical community for

^{§§} Published in the certificate of the reference materials and also accessible from Rocklab's website.

wet dissolution practices where gold is the primary analyte of interest. Together with the adoption of a minimum 1 gram of sufficiently blended sample, the risk of experiencing the gold nugget effect can be significantly reduced.

Care should also be taken when samples of unknown elemental composition are submitted for ICP-MS analysis. Although sitting at the high end of atomic weights, the mono-isotopic gold ion, ¹⁹⁷Au⁺, could also suffer from potential polyatomic interferences from species, such as 116 Cd⁸¹Br⁺, 116 Sn⁸¹Br⁺, 118 Sn⁷⁹Br⁺, 157 Gd⁴⁰Ar⁺, 181 Ta¹⁶O⁺ and 180 Hf¹⁶OH⁺.^{***} To investigate this possibility, individual 100 ppb solutions of Cd, Sn, Gd, Ta, and Hf were prepared in 0.1% HBr, mimicking the levels of these interference-contributing elements in prepared real-world samples. and analyzed them in standard mode ICP-MS. The corresponding peaks of 197, where the monoisotopic Au signal is located, showed intensities close to baseline values for Cd, Sn, and Gd solutions. Tantalum and Hafnium do form di- or tri- atomic ions²⁶ that can interfere with the ¹⁹⁷Au⁺ signal. Since Au is often determined at ppb and sub ppb levels, if Ta and Hf are present in relatively significant amounts, this may lead to positive reporting errors. A preliminary scan on elements such as Rh, Ta, Hf, Tl, and Bi is recommended to help the analyst develop appropriate and effective ICP-MS methods for gold determination. For instance, in CCU-1D, significant concentrations of Rh, Tl, and Bi were found, indicating that these elements are not suitable candidates to serve as internal standards. If Ta and Hf are found abundant in samples, a dynamic reaction cell (DRC) or collision cell (CC)-based method may become necessary to eliminate aforementioned polyatomic interferences. As a result of scanning all prepared solutions of the adopted CRMs, no DRC method was necessary in the current study due to insignificant presence of Ta and Hf in those samples.

Finally, it is worth noting that the significant savings in time would, in an automated system, offset the additional cost of HBr and _L-cysteine, and would deliver good quality data in a timely fashion for the gold-mining industry.

4. Summary

Fast, accurate, and cost-effective gold determination is achieved with a novel laboratory method comprised of significant modifications in the digestion hardware, dissolution chemistry, and instrumental analysis. The proposed digestion method, using ColdBlockTM digester and HNO₃/HBr acid attack, recovers gold efficiently. The use of L-cysteine in the sample matrix prevents the notorious gold memory effect, safeguarding the data output. These modifications may be readily implemented in the standard operating procedures in many analytical laboratories for data accuracy and quality control purposes.

^{***} The authors are grateful to a reviewer for drawing our attention for the potential for the species ${}^{116}Cd^{81}Br^+$, ${}^{116}Sn^{81}Br^+$, ${}^{118}Sn^{79}Br^+$, ${}^{157}Gd^{40}Ar^+$ to interfere with the ${}^{197}Au$ signal.

Acknowledgements

Financial support for this Collaborative Research and Development (CRD) project was provided by the Ontario Centres of Excellence (OCE), the Natural Sciences and Engineering Research Council of Canada (NSERC), the Centre of Excellence for Mining Innovation (CEMI), Barrick Gold, and Chemquant Technologies under grants numbered OCE 11537 and NSERC CRDPJ 445997-12 is gratefully acknowledged. Barrick Gold is thanked for providing three gold reference materials and to Jack Biln of the Barrick Technology Centre, Vancouver, British Columbia, Canada, for helpful discussions. The Canada Foundation for Innovation and the Ontario Research Fund provided funds for the purchase of the SCIEX Elan ICP-MS (DRC II). The authors would also like to extend their appreciation to our undergraduate summer student, Laura Boudreau, who executed rigorous sample digestions.

- 1. A. Diamantatos, Analyst, 1986, 111, 213.
- 2. P. Chattopadhyay and B.N. Sahoo, Analyst, 1992, 117, 1481.
- 3. J.M. Vermeulen, JAAS, 1989, 4, 77.
- 4. H. Zhang and D.B. Dreisinger, Hydrometallurgy, 2002, 66, 67.
- 5. M.J. Nicol and G. O'Malley, Journal of Metals, 2002, 54, 44.
- 6. E. Hoffman, Journal of Geochemical Exploration, 1992, 44, 297.
- 7. A. Diamantatos, Anal. Chim. Acta, 1984, 165, 263.
- 8. K.E. Jarvis, J.G. Williams, S.J. Parry, and E. Bertalan, Chemical Geology, 1995, 124, 37.
- 9. E. Hoffman and B. Dunn, Sample Preparation and Bulk Analytical Methods for PGE, in *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements*, Canadian Institute of Mining, Metallurgy and Petroleum, 2002, p1-11.
- 10. T.T. Chao and R.F.J. Sanzolone, Journal of Geochemical Exploration, 1992, 44, 65.
- G.E.M. Hall, J.E. Vaive, J.A. Coope, and E.F. Weiland, *Journal of Geochemical Exploration*, 1989, 34, 157.
- 12. E.L. Hoffman, Exploration and Mining Geology, 1998, 7, 155.
- 13. G. Senanayake, Mineral Engineering, 2004, 17, 785.
- 14. M. Leybourne and S. Rice, *Explore*, 2013, **158**, 1.
- 15. A. Chow and F.E. Beamish, Talanta, 1987, 14, 219.
- 16. V. Balaram and K.V. Anjaiah, J. Indian Chem. Soc., 1997, 70, 581.

- 17. Gold Transport by Complex Metal Chloride Vapors, *Bureau of Mines Report of Investigation 7489*, March 1971, US Department of Interior.
- 18. Y-L Feng, R.E. Sturgeon, and J.W. Lam, JAAS, 2003, 18, 1435.
- 19. Y-L Feng, R.E. Sturgeon, J.W. Lam, and A. D'Ulivo, JAAS, 2005, 20, 255.
- 20. W.C. Chen, P. Wee, and I.D. Brindle, JAAS, 2000, 15, 409.

- 21. Y. Wang, R. Kanipayor, and I.D. Brindle, JAAS, 2014, 29, 162.
- 22. M.F. Benedetti, A.M. De Kersabiec, and J. Boulegue, Geostandards Newsletter, 1987, 11, 127.
- 23. J.B. Hiskey and V.P. Atluri, Mineral Processing & Extraction Metallurgy Review, 1988, 4, 95.
- 24. J.O. Marsden and C.I. House, *The chemistry of Gold Extraction (2nd Edi.)*, 2006, Society for Mining, Metallurgy, and Exploration Inc., Littleton, Colorado, USA. p287.
- 25. Clement J. Leaper, Materia Photographica, Iliffe and Son, London, UK, 1891, p90.
- 26. S.A. Yim, M.S. Choi, and J.S. Chae, J. Am. Soc. Mass. Spectrom., 2012, 23, 171.