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# Determination of gold and silver in geological samples by focused infrared digestion: A re-investigation of *aqua regia* digestion



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## ARTICLE INFO

## Article history:

Received 10 August 2015

Received in revised form

4 November 2015

Accepted 5 November 2015

Available online 6 November 2015

## Keywords:

Gold

Silver

Infrared

Sample digestion

*Aqua regia*Reverse *aqua regia*

ICP-MS

## ABSTRACT

Focused infrared radiation-based digestions, for the determination of gold and silver, can be achieved in a timeframe as short as 10–15 min, making it an attractive candidate technology for the mining industry, where very large numbers of samples are analyzed on a daily basis. An investigation was carried out into gold and silver dissolution chemistry from geological samples using this novel digestion technique. This study investigated in-depth the issue of low recoveries of gold from *aqua regia* (AR) digestions, reported by a number of researchers. Conventional AR digestions consistently delivered gold recoveries in a range of 69–80% of the certified values for the four certified reference materials (CRM) employed (CCU-1d, SN26, OREAS 62c, and AMiS 0274), while silver recoveries were satisfactory. By gradually shifting the HCl:HNO<sub>3</sub> ratio (v/v) from 3:1 to a reversed 1:3 ratio, recoveries of gold and silver exhibited inverse trends. At a HCl:HNO<sub>3</sub> ratio of 1:3, complete recovery of gold was achieved with excellent reproducibility in all CRMs. Meanwhile, silver recoveries plunged significantly at this ratio in samples with higher silver concentrations. Silver values were recovered, however, when the silver was re-solubilized by adding a small volume of concentrated HCl to the cooled reverse *aqua regia* digests. Recoveries of base metals, such as Fe and Cu, were satisfactory throughout and were much less sensitive to changes in the digestion medium. Using four CRMs and five real-world gold/silver containing samples, the utility of the proposed reverse *aqua regia* was systematically studied. The uncomplicated nature of the digestion methods reported here, that are fast, effective and inexpensive, may be useful to analysts developing/optimizing their methods for the rapid determination of Au and Ag in a variety of mineral phases, particularly where rapid results are desirable, such as in prospecting and mine development.

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## 1. Introduction

Accurate quantification of gold and silver in geological samples provides vital information to exploration geologists in the decision-making process of whether a mine should be developed, maintained, or closed. The analytical procedure demands near-total recovery of both elements for an accurate estimation of the economic potential of the mine. Laboratory determination of the two elements, however, largely depends on both the efficiency of extraction methods, and on the mineralogy of the rock samples. In current practice, both AR and a more aggressive acid attack, with the addition of hydrofluoric acid and perchloric acid, are routinely employed to serve general sample preparation purposes, with the latter being termed as “total digestion (TD)”, or a “four-acid”

digestion. *Aqua regia*, in particular, has been employed as the preferred sample preparation method, capable of digesting various sample types since medieval times [1]. The performance attributes of the acid mixture fit well with the criteria of elemental analysis of geological materials, such as wide commercial availability, strong oxidizing ability to bring metals into solution, and relatively low cost. One of the many analytical applications developed historically, and still a prevalent and effective method in modern day operations, is its use in extracting precious metals, such as silver and gold, and/or strategic metals from rocks and ores in a wet dissolution process [2].

Amongst popular gold and silver extraction and determination methodologies for geological materials, AR competes primarily with fire assay (FA) [3–5]. The main reason FA has been a trusted gold extraction method within the geological community is twofold: (a) it is assumed to be a ‘total’ recovery method, and (b) past experience suggests that using a large sample size, that can be accommodated readily by the FA process. Sample size typically

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ranges from 30–50 g, and effectively reduces the risk of the ‘nugget effect’\*. It should be noted that, despite being the preferred method for gold and precious metals extraction, the performance of FA remains laboratory- and technician-dependent. Its ability to extract total gold from geological materials has also been found less satisfactory, as gold recovery by FA can sometimes be 14–26% lower than the values obtained by instrumental neutron activation analysis (INAA) [6]. INAA is an essentially non-destructive and matrix-independent technique. It offers reporting of total metal concentrations in contrast to AR, which is a leaching process. The use of INAA is limited, particularly where time of analysis is an important factor, since other activated elements, notably sodium, must be allowed to undergo nuclear decay for approximately seven days before the measurement of gold can take place [7]. Aside from the need to gain access to the beam lines of a nuclear reactor, the turnaround time for analysis fails to justify its use in high-sample throughput mining operations. Acid digestions for gold determination serve the purpose where a cheaper but relatively reliable method is sought. This approach, however, requires samples to be sufficiently homogenized so that a smaller sample size can be used. In the case of commercial gold reference materials, a maximum particle size that passes through a sieve of 200-mesh or finer is recommended to mitigate the extent of gold encapsulation and the nugget effect. Gold results reported previously by various acid treatments and sample types, however, suggest that the determination of gold in geological materials can be more complex than other metals and must be dealt with on a case-by-case basis. For instance, one study employed as little as 0.1–0.2 g of relatively coarsely ground samples (~170  $\mu\text{m}$ , or 90-mesh), and claimed excellent precision for gold and silver recoveries [8]. Where gold is measured in soils and alluvial deposits, Ward and coworkers suggested that the gold nugget effect can be greatly reduced by performing a clay-size separation of soil and till prior to the AR digestion [9]. On the other hand, an investigation using 0.5–1 g of reference materials (SARM-7, SU-1a) in closed-vessel low-pressure microwave digestion yielded unsatisfactory gold recoveries and reproducibilities [10]. Other reports suggest that encapsulation of gold in silicates samples, another source of variation in the determination of gold in mining samples, may not be as common a phenomenon as previously thought, as little difference was found in gold concentrations between AR and TD methods [11,12]. In the past, there was also a lack of consensus on the minimum number of replicates (at a given set of conditions) required, which inevitably contributes to the overall uncertainty of gold determination by acid digestion.

The notion of encapsulation of silver, though rarely reported in the literature, may also be case-dependent, as is the case with silver in the Veladero mine, described below. Ore Research and Exploration (ORE) has released a series of silver-containing certified reference materials, representing a range of frequently encountered ores, and compared data from various extraction methods such as AR, TD, and fusion (FU). The certificates reported no statistically significant differences in silver values between these methods (Table 1), suggesting that encapsulation of Ag in those materials is not likely a common mineralogy, or the amount of encapsulated silver appears analytically negligible at the given particle sizes. Results obtained from some real-world mining samples, however, suggest that there are exceptions that require

\* The nugget effect is usually described as being due to the occurrence of discrete particles, often of pure gold in the sample. The number of these particles required to make up the concentration of gold is relatively small. Thus, from a probabilistic perspective, a relatively large sample size is needed to provide an appropriate number of these particles to give a subsample that is representative of the whole and therefore generate a reasonably accurate concentration of gold. Gold is also difficult to grind in conventional comminution equipment, since it is ductile and malleable and is likely to smear on the grinding equipment, leading to losses from the sample.

**Table 1**  
Comparison of recovered Ag ( $\mu\text{g g}^{-1}$ ) by different sample preparation techniques<sup>a</sup>.

CRM	AR <sup>b</sup>	TD <sup>b</sup>	FU <sup>b</sup>	Maximum particle size ( $\mu\text{m}$ )	Description
OREAS 37	5.19	–	5.0	30	Sulfidic
OREAS 131a	29.5	30.9	30.2	30	Siliceous Zn–Pb–Ag ore
OREAS 134b	204	209	206	30	Siliceous and sulphidic
OREAS 926	2.97	2.92	< 3 <sup>c</sup>	75	Siliceous copper ore
OGGeo08	20.2	20.4	19.8	30	Granite-based ore blend

<sup>a</sup> Data taken from Ore Research and Exploration data sheets.

<sup>b</sup> AR: *aqua regia*, TD: total digestion, FU: fusion, sodium peroxide or lithium borate.

<sup>c</sup> Reported as lower than method reporting limit.

case-by-case analytical scrutiny. For instance, in 2007 Barrick Gold offered a \$10 million “Unlock the Value” program to release silver from a silicate-encapsulated silver deposit in their Veladero mine, in which more than 90% of the silver was encapsulated [13].<sup>†</sup> It appears that the silver mineralogy of this deposit may be uncommon as the total leachable silver by a regular AR attack accounts for only a small portion of total silver.

Although AR is clearly effective for silver extraction from geological materials [14–16], the interpretation of gold values generated by AR leaching should be interpreted with caution, since gold recoveries can be broadly lower than the values determined by FA [17]. This observation has been replicated in our laboratory, regardless of the sample types and choice of digestion method (hotblock or ColdBlock). Hall and coworkers reported that AR typically produces negative reporting biases in a range of 24–42%, compared with INAA [6]. Wang and Brindle discussed this limitation of AR and suggested that the reduced gold recoveries with the AR method, using a conventional HCl/HNO<sub>3</sub> ratio of 3:1, are likely associated with the volatility of the gold chloride species, Au<sub>2</sub>Cl<sub>6</sub>, at elevated temperatures [18]. This notion was originally reported by the US Bureau of Mines in 1971 [19].

It occurred to the authors that the ratio of HCl:HNO<sub>3</sub> in AR, although sometimes modified in in-house methods for particular extraction purposes, has not been investigated systematically, and that it may have a profound impact on extraction efficiency for Au and Ag. General trends in silver recoveries, as a function of HCl:HNO<sub>3</sub> ratio (v/v), were discussed in environmental samples by Link et al. [20]. They proposed that silver recoveries may increase proportionately to the concentration of free chloride ions, which react with insoluble AgCl to form soluble AgCl<sub>2</sub><sup>-</sup>. When the acid ratio is reversed, however, the recovery quickly plummets as a consequence of the chloride being exhausted by its oxidation to volatile chlorine and nitrosyl chloride. In this paper, we present our investigations into the determination of Au, Ag, and major base metals by AR dissolution in various acid ratios, with the addition of HF where necessary, using four commercial CRMs and five real-world mining samples that represent significantly different mineralogies and ore types. Together with our continuing effort to develop fast and accurate digestion methods using the infrared-based ColdBlock digester, we present data that will be useful to analysts in developing or optimizing methods for rapid and accurate determination of Au and Ag in mining samples.

<sup>†</sup> Typically, mines grind ores to a much coarser mesh than analytical facilities do, so the potential for the silver to be associated with the groundmass of the ore, rather than encapsulation into a silica matrix, must also be considered. The authors thank Mr. Russ Calow, Vice President of Global Analytical Services, SGS, Lakefield, Ontario, Canada, for this valuable insight.

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