

Trace Analysis of Gold by Atomic Absorption – a Review

Application Note

Atomic Absorption

Author

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Introduction

Wide variations in the gold content of mineral and ore samples demand the development of both flame and furnace techniques to cover the required analytical range. Various methods have been published for the extraction of gold as a gold (III) complex from geochemical samples. It is generally concluded that an acid extraction, with aqua regia, is not a quantitative method since the gold recovery is only about 90–95%. Some methods are still used analytically, however, by treating standards in the same manner as the samples.

A variety of techniques have been used for separation and analysis. These include ion exchange, solvent extraction and chromatography. Precipitation techniques and fire assay methods are also commonly used. Many of these methods do not exclusively extract the gold, hence various interferences have been reported.

Organic solvent techniques have been reported and used successfully. These organic extractions also have the extra benefit of concentrating the final solution because the level of gold in the mineral sample is extremely low.

This paper reviews some analytical techniques which have been described for gold analysis.



Agilent Technologies

Acid Digestion Techniques

A simple technique has been described by Jon C. Van Loon [1] for the determination of gold in silver assay beads. Nitric acid was used for the dissolution, followed by small volumes of hydrochloric acid. The solution contained a final concentration of 1% added lanthanum which eliminated a variety of interferences,

Elliott and Stever [2] compared methods from two different laboratories. Laboratory A digested 30 g of ore with H_2SO_4 plus concentrated HCl.

The digested sample was filtered and analyzed by atomic absorption. Laboratory B treated two 4 g samples with aqua regia; one sample was spiked with a gold standard and both samples were analyzed by the method of standard additions. The authors used both of the above methods for their dissolution and compared the two procedures both with background correction, and without. The technique used for dissolution by Laboratory A was shown not to be as quantitative as the other method. Background correction was shown to reduce signal due to molecular absorbance and scattering, thereby improving the precision of the method.

Aluminium and calcium were the two principle interferents observed in the technique. Potassium, sodium, magnesium and iron interfered also, but to a lesser extent. The hotter temperature of the nitrous oxide-acetylene flame considerably reduced these interference effects.

Dissolution using aqua regia is perhaps the most common method used in analyzing gold [3]. In most procedures the gold is brought into solution using the hydrochloric and nitric acid mixture at some stage during the analysis.

Various analytical methods have been reported with furnace atomization techniques, [4,5,6,7] since many mineral and ore samples contain insufficient gold for the less sensitive flame methods.

Anion exchange resins [6] have allowed gold to be quantitatively separated from silicate ore samples. This method also minimizes many interferences from the matrix. With silicate rock samples it is desirable to remove silicon because of its known interference on all noble elements. Concentrated nitric, perchloric and hydrochloric acids, in equal volumes, were added to the finely powdered rock followed by hydrofluoric acid to remove the silicon as SiF_4 . The sample was taken to dryness and redissolved in hydrochloric acid (0.5 M) to be passed through an anion exchanger at a rate of 1 mL/min. Ammonia solution (2 M) was also passed through the column

at a rate of 1 mL/min and the eluent collected. After evaporation the residue was dissolved in aqua regia ready for injection into a furnace for atomization. The instrument conditions were: dry 110 °C ash 1000 °C, and atomize at 2250 °C. Detection limits using this method were as low as 0.2 ng/mL for gold in 1 g of rock sample.

Using other methods with the furnace atomic absorption technique, detection limits of 5.0 ng/mL have been obtained from a 10 μL sample volume [5]. The investigation included the effects of different parameters used, such as the ramp rate, the dry, ash and atomize temperatures and the different wavelengths available for gold analysis. The type of graphite tube used, either Massmann or West and Williams were compared. Interference effects from noble and other metals were also examined.

Detection limits using this method were as low as 0.2 ng/mL for gold in 1 g of rock sample with a 50 μL injection volume. The reproducibility of the results was shown to be about 1.6 %RSD. The shape of the absorption peak with respect to peak heights and peak areas was also examined. Where the possibility of interference from other elements arose, peak area was the mode of choice because the interferent either enhanced or depressed the peak height but the peak area signal remained stable. All of these factors were then compared with the corresponding flame technique for precision, accuracy and sensitivity.

Kontas [7] found that complexing the gold with mercury proved to be a simple and rapid way to determine the level of gold in geochemical samples. Hydrochloric and nitric acids were added to the sample and allowed to stand overnight. After centrifuging the sample, SnCl_2 and $\text{Hg}(\text{NO}_3)_2$ were added causing the formation of a mercury-gold complex. This precipitate was collected and dissolved in water and hydrogen peroxide before running through the furnace atomizer. A typical absorbance of 0.08 was obtained for 1.0 ng of gold.

The traditional method for the analysis of the noble metals is by fire-assay techniques followed by atomic absorption measurement [8,9]. Potassium (or sodium) cyanide is used to quantitatively complex the gold and, in addition, provide a high concentration of readily ionized atoms to reduce the possibility of ionization of gold. Prior to the addition of the cyanide salt the sample was dissolved in nitric acid followed by aqua regia. The solution was heated to dryness to remove all traces of acid. Note that the cyanide solution must not be added to acids. Measurements of as little as 0.08 $\mu\text{g/mL}$ of gold have been made with a precision of approximately 1 %RSD by flame AA.

Chromatographic separation has greatly reduced the interference from other elements in a typical ore sample [10]. Digestion of the sample, with aqua regia, on a hot plate took place followed by the addition of hydrochloric acid. The solution was filtered and passed through a column of Amberlite XAD-7 in hydrochloric acid. Base metals likely to cause interference were removed by rinsing the column initially with hydrochloric acid. Acetone and hydrochloric acid were mixed and passed through the column at a rate of 2 mL/minute to elute the gold.

The sensitivity of the method was 0.1 µg Au/mL with a precision of 1 %RSD.

Solvent Extraction Techniques

When organic solvents are aspirated through an atomic absorption instrument or injected into a furnace for atomization, a few important points must be observed. Flammable solvents are a potential hazard if treated carelessly and all relevant safety practices must be followed [11]. Containers for storage of samples and standards must be kept tightly closed at all times to prevent evaporation. It is good analytical procedure to prepare all solutions just prior to analysis.

If flame AA is to be used the analyst should be aware that the organic solvent will change the air:fuel ratio in the flame. Thus the composition and temperature of the flame will be affected. Always use an adjustable nebulizer to reduce sample uptake and adjust the fuel conditions accordingly.

When analyzing an organic sample always ensure that the composition of the standards and samples is comparable. If the solutions contain a different solvent composition, the air-acetylene flame could be affected by the differing viscosities and surface tensions which result in different flows through the capillary. If chromium is to be analyzed, for example, the flame stoichiometry is critical for the best sensitivity. Hence any change in the solvent content could change the stoichiometry of the flame. This could result in poor sensitivity, a loss of precision, or a combination of both.

When using furnace atomization, conditions for both drying and ashing must be carefully established since variations from optimum conditions can have a marked effect on sensitivity, accuracy and precision.

Solvent extraction methods for the determination of gold in ores have long been recognized. Methyl isobutyl ketone (MIBK), di-isobutyl ketone (DIBK) and toluene are the solvents of choice. Other solvents are used but these three are

the more common solvents for gold extraction. Dibutyl sulphide (DBS) and other alkyl sulphides have been used in conjunction with toluene for gold separations [12,13,14]. Xylene or octane can be substituted for toluene.

Either flame or carbon rod techniques are feasible [12] depending on the level of gold in the sample. In that study a 25 g sample was mixed with NH_4NO_3 and heated, both over a Bunsen burner and in a muffle furnace. To stabilize the gold complex, sodium chloride and hydrochloric acid were added and left to stand. Nitric acid addition followed. The solution was allowed to evaporate to wet salts over a water bath followed by redissolution into hydrochloric acid. The undissolved residue was separated while hot using a centrifuge. For extraction into the organic solvent a solution of 0.2 M DBS in toluene was prepared. A volume of 5 mL was used to extract the gold followed by measurement by AAS. When 25 g of ore sample is extracted into 5 mL of organic solvent it is possible to determine 20 ng/mL Au by flame techniques, 1 ng/mL by furnace techniques.

Torgov and Khlebnikova [14] used a method where the extractant was a 0.1 M solution of petroleum sulphides (b.p. 212-265 °C; sulphide sulphur content 14.4%) in toluene. In practice, extraction is carried out for an organic:aqueous phase volume ratio of 1:20 to 1:30 obtaining a 98–99% extraction. Detection limits for this extraction procedure, based on a sample weighing of 10 g, are 20 ng/mL for flame and approximately 5 ng/mL for the furnace. In the case of the flame technique a 5 mL extract volume was used.

An extract volume of 2–3 mL provided sufficient sample volume for the graphite furnace technique. The sample is further concentrated when using a smaller extract volume. Comparison of the developed methods for assay indicates that no systematic error exists.

Men'shikov et al [13] dissolved the ore sample in aqua regia. After heating, hydrochloric acid was used to redissolve the salts. The extraction medium was 0.2 M DBS in toluene. This method gave a sensitivity of 1 ng/mL.

Galanova et al [15] also used DBS in toluene. They found that if the ore contained approximately 20-30% iron the concentration of the DBS had to be increased from a 0.2 M solution to 0.4 M solution. To reduce the effect of the DBS on the flame, the extract was diluted 1:1 with alcohol. Gold can be extracted quantitatively from both hydrochloric acid and aqua regia, with the extraction efficiency being about 100%. The behaviour of some 23 elements was investigated during the extraction of gold using the DBS techniques [16]. Silver was the only element extracted to any appreciable extent (about 10%).

As well as using toluene as the basis for analysis by DBS, Parkes and Murray-Smith [17] have used DIBK with a few modifications to increase sensitivity and throughput of samples. The detection limit obtained was 0.012 $\mu\text{g/g}$. The samples were first roasted at 600 $^{\circ}\text{C}$ to remove any sulphur, followed by hydrochloric and nitric acid attack to dissolve the gold, palladium and any other metals. Then they were treated with the organic solvent and aspirated into an air-acetylene flame.

The extraction of the gold (III) from a chloride medium into DIBK containing either trioctyl methyl ammonium chloride or trioctylamine was quantitative up to a pH of 4 [18]. The same method of extraction from an aqueous cyanide solution was quantitative up to a pH of 10. The range of the method is from 0.01 to 50 $\mu\text{g/mL}$. This technique has been applied to ore samples successfully and found to be free of interferences.

Figure 1 shows a series of standards and samples of gold in DIBK. A Varian CRA-90 was used for the analysis with the conditions as shown in Table 1.

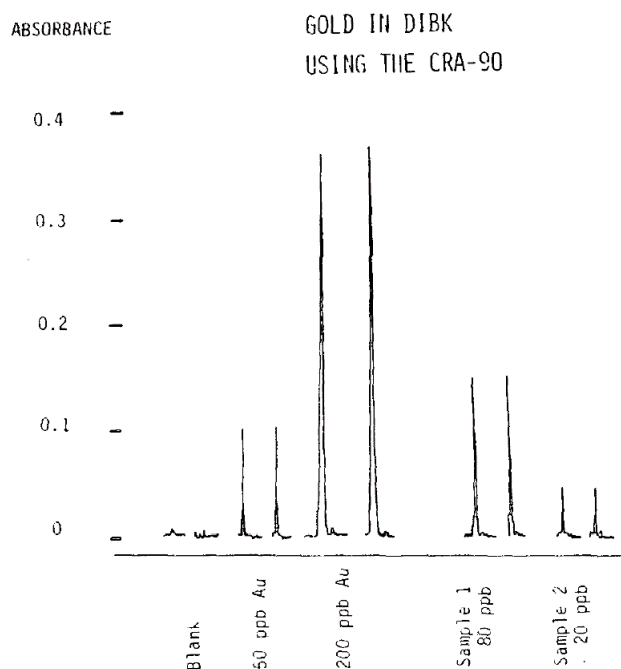


Figure 1.

The use of MIBK as the organic solvent has been found to be successful when analyzing copper ores or geochemical samples where the copper level is relatively high [19,20,21].

The general procedure was to heat the sample, either over a hotplate or by roasting, depending on the nature of the sample. The residue was then taken up in hydrochloric acid

Table 1.

ELEMENT : GOLD		
λ	242.8 nm	
SBW	1.0 nm	
LC	3.5 mA	
Matrix DIBK		
Sheath Gas	N_2	6 L/min
Sample Size	2 μl	
BC off		
STAGE	$^{\circ}\text{C}$	TIME
Dry	95	30
Ash	500	15
Atomize	2400	0
Ramp Rate	400 $^{\circ}\text{C/sec.}$	

and heated. After a series of acid digestions the sample solution was transferred to a separating funnel for the gold to be extracted into MIBK followed by filtration through a phase separating paper. The sample was then aspirated into a very lean air-acetylene flame. There was no apparent interference from copper, iron or nickel. The range measured was from 0.1 to 40 $\mu\text{g/mL}$.

Hildon and Sully's method [20] was also based on dissolution of the sample in acid followed by extraction into MIBK. After the addition of hydrochloric and nitric acid, the sample was baked in order to decompose any nitrates. The solution was redissolved with water and hydrochloric acid, keeping the acid concentration at about 10% v/v. Then, a 2.5 g/L tellurium solution in 10% hydrochloric acid was added, followed by 20% w/v hydrazine dihydrochloride solution. This mixture was brought to the boil to coagulate the precipitate. After a series of evaporation steps with hydrochloric acid and aqua regia, the sample solution was extracted into 5 mL of MIBK to be analyzed by AAS. The range of the analysis was from 2 ng/mL up to 25 $\mu\text{g/mL}$. A precision of 5 %RSD was achieved.

A simple technique was used to extract gold from platiniferous materials.

The sample was dissolved in a hydrochloric/nitric acid mixture. After a series of evaporation steps the final solution was made up to 6 M hydrochloric acid. MIBK was then added to extract the gold, back-washing to ensure quantitative results. This MIBK extract was then run through a lean air-acetylene flame.

When it is necessary to measure parts-per-billion levels, it is essential to use graphite furnace techniques. Bratzel et al [22] used an Agilent M-61 carbon rod atomizer for their analysis of gold in geological and metallurgical samples. The sample References was leached with a series of aqua regia additions, boiling to dryness after each addition. A third aliquot was then added and heated to near boiling and cooled slowly. Gold was extracted as a chloro complex into MIBK. The sample was then injected into the CRA for analysis. The furnace conditions were determined experimentally to obtain a detection limit of 6×10^{-13} g (or 0.6 pg) of gold.

Amyl acetate was used in a method developed by Haddon and Pantony [25]. Samples, with a mesh size of 150 μ m, were suspended in dilute hydrochloric acid, and shaken for up to three hours with amyl acetate containing a small proportion of bromine. The addition of bromine forms bromoaurate complexes which are then extracted quantitatively into the amyl acetate. The authors discussed the choice of organic solvents, the efficiency, effect of shaking and many other variables which produce the overall accuracy of the method.

Many of the articles available on gold analysis mention the possible interferences that can be expected for each method [23,24,26]. The mutual interferences between the noble metals themselves has caused concern to analysts. This has necessitated the development of gold-specific separation methods. Others have investigated different ways of overcoming these problems [22]. When flame analysis is used the interferences have been either removed or greatly reduced by using the dithizonates of these metals instead of the chlorides. The gold is taken up in aqua regia, expelling the excess of nitric acid by evaporations with hydrochloric acid. Extractions were made with a 0.015% w/v solution of dithizone in MIBK.

Agilent has recently introduced a new graphite furnace, the GTA-95. It has been determined that, by using argon as the inert gas and 2400 °C atomization temperature, the characteristic concentration is 4 pg. When using a 20 μ L volume of aqueous solution the analytical working range is from 2–40 ng/mL of gold.

Summary

In summary, many techniques are available for gold analysis. Before a method is chosen, the analyst must decide the length of time he has available for the analysis, the type of sample that is to be analyzed, and the expected concentration of the gold complexes in the geochemical sample.

The use of solvent extraction techniques and also furnace atomic absorption methods have permitted the measurement of very low levels of gold by atomic absorption.

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