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1985/49. Gold analysis - a brief review

W.E. Baker

Abstract

Fire assay is the most widely accepted method for the determination of gold. At the trace level the technique is used for the concentration of gold which is then determined by an instrumental finish. Atomic absorption spectrophotometry is the common instrumental method although inductively coupled plasma-optical emission spectroscopy and neutron activation are also used. Other less widely applied procedures include constant potential coulometry, polarography, anodic stripping voltametry and ion chromatography.

Alternatives to fire assay concentration include extraction with aqua-regia, various acid-bromine mixtures and cyanide followed by solvent extraction or co-precipitation. Cyanide leaching of bulk samples is commercially available for exploration purposes and recently some success with large samples has been claimed for a system using dilute hydrochloric acid-bromine-amyl acetate.

INTRODUCTION

The literature on gold analysis is vast, and a comprehensive cover is beyond the scope of this review. Discussion will be limited to those methods published since 1965 which have survived the test of time and which may possibly be of use in the studies of gold contemplated by this department.

Fire assay continues to be the method against which all others are evaluated although it is not completely lacking in gremlins. At the trace level, the determination of gold is often undertaken by use of fire assay concentration followed by an atomic absorption finish. The inductively coupled plasma-optical emission technique and neutron activation have also been utilised as a finish to the fire assay procedure. Coulometry, polarography and ion chromatography have also been applied to the determination of gold. Whilst fire assay is generally accepted as the most efficient method of releasing gold from a sample other methods are quite effective (Chow, A.; Beamish, F.E., 1967). The alternatives include various acidic solutions, bromine in liquid or vapour phase and cyanide. These procedures are usually coupled with solvent extraction, co-precipitation or ion-exchange to concentrate the gold to a level which enables accurate determination.

FIRE ASSAY

Of all the methods of gold analysis, fire assay can be said to have stood the test of time since it had its beginnings in Asia Minor around 3000 BC (Haffty, J. *et al.*, 1977). In its modern form the method makes use of a flux consisting of litharge, sodium carbonate, silica, borax, potassium nitrate, calcium fluoride and flour or starch. The proportions of these components are varied according to the composition of the sample.

When an intimate mixture of the pulverized sample and flux is heated to 1000°C, the organic component reduces the litharge to lead which is dispersed through the mass as fine droplets. These alloy with the gold released from the sample particles which have been decomposed by other flux components. The accumulated lead is separated and may be subjected to scorification to reduce its amount before the final oxidising fusion

(cupellation) is used to recover the gold from the lead.

If the gold content of the sample is sufficiently high the cupellation stage will result in the production of a gold prill which can be weighed. Unlike instrumental procedures where uncertainty is mostly instrument dependant and generally accepted to be 2%, weighing is absolute. In the case of gold, the gravimetric procedure has an absolute error of ±0.3 ppm which is due in part to slight contamination of gold by silver and to difficulties inherent in the transfer and weighing of microgram quantities.

Whilst fire assay is the standard method of gold analysis the accuracy of results is highly dependant upon the skills of the analyst. Selection of fluxing agents to match the sample and management of the furnace stages are critical. Losses of gold to the slag and cupel (about 2% and 1% respectively) have to be carefully controlled and capable of correction in the final result.

ALTERNATIVE EXTRACTION AND CONCENTRATION PROCEDURES

Various acid extraction systems have been used in the determination of gold. Many procedures make use of aqua regia followed by extraction with an organic solvent such as methyl isobutyl ketone (MIBK) (Hall, S.H., 1979). With the advent of carbon furnace atomic absorption (CFAS) some rapid methods involving dissolution with aqua regia and determination not requiring solvent extraction have come into use (Kontas, E., 1981). The slight solubility of MIBK in aqueous solutions requires that all reagents used in conjunction with this solvent be first saturated with it if accurate results are to be achieved. An alternative system makes use of dibutyl sulphide in toluene to provide a less water soluble system for extraction (Rubeska, I. *et al.*, 1977). In the geochemical unit of this department our applications make use of CFAS which requires only small solvent quantities and allows use of amyl methyl ketone which is expensive but water insoluble (Baker, W.E., in press). The aqua regia system is sound where free gold exists in the sample but it is likely to be less efficient where the metal is protected by quartz and other minerals. In such cases preliminary treatment with hydrofluoric acid is required. The presence of sulphides is also undesirable due to the production of elemental sulphur which creates difficulties at the solvent extraction stage. Generally the presence of sulphides requires that the sample be roasted before acid digestion.

The problems with some applications of the aqua regia system have led to the development of alternative methods for the extraction of gold. The susceptibility of gold to attack by bromine is the basis of several methods of gold dissolution (Van Sickle, G.H.; Lakin, H.W., 1968). Mixtures of sodium bromate-hydrobromic acid, bromine-hydrobromic acid and bromine-ether have all been used to effectively dissolve gold. The most recent development in this type of dissolution procedure claims 100% efficiency for the extraction of gold from finely ground samples suspended in dilute hydrochloric acid by a mixture of bromine and amyl acetate (Haddon, M.J.; Pantony, D.A., 1980). It is a method which promises much and it may be worthwhile having it checked by chemists of this department.

Cyanide extraction of gold has been used in analytical chemistry but has not been overly popular because of the extreme toxicity of the reagent concerned. It has had a revival of recent times as a possible solution to the problem of variable gold distribution in geochemical samples. The metallurgical procedure of cyanide extraction has been adapted to the processing of 5 kg samples in what has become known as the

Otter method (Scott, P.A., 1983). The extraction of gold from samples is more variable than would generally be accepted in analytical procedures but appears to be adequate for geochemical exploration. Currently it is offered by at least two commercial laboratories.

Co-precipitation procedures have been used for the recovery of gold after processing of solid samples (Das, A.K., 1980) and of river waters (McHugh, J.B., 1983). Ion exchange has been used to remove interfering ions in flame atomic absorption (FAS) determination of gold but this procedure appears to be more relevant to mill concentrations of gold rather than those found in geochemical samples (Kohn, N.; Van Loon, J.C., 1978). It is possible that ion exchange coupled with X-ray fluorescence or CFAS could be developed as a geochemical procedure.

INSTRUMENTAL DETERMINATION OF GOLD

Flame atomic absorption spectrophotometry is the most widely used instrumental method of gold analysis and as noted above is used as a finish to fire assay procedures where the gold content of the sample is too low to result in a prill that can be weighed. The recommended range of concentration of gold in a solution for aspiration in FAS is about 3 to 15 µg/ml and the detection limit will depend upon sample preparation. The real world differences between fire assay-gravimetric finish (absolute error ±0.3 ppm) and fire assay-FAS finish (relative error ±2%) becomes apparent if the processing of two ore concentrates is considered. If we have a copper concentrate carrying 30 ppm gold it would have a value of $6 million ±$60,000 by gravimetric finish and $6 million ±$120,000 by FAS finish. A consignment carrying 9 ppm gold would be worth $1.8 million ±$60,000 by gravimetric finish and $1.8 million ±$36,000 by FAS finish. Hence the need for gold umpires when dispute arises. Where gold values decrease to the ultra-trace level the CFAS technique is one of very few available to determine these low concentrations. This technique has an absolute detection limit of about 2 ng/ml when loaded as a 5 µl sample. Multiple loading can be used to further lower this detection limit.

The development of the inductively coupled plasma (ICP) has resulted in a resurgence in optical emission spectrometry (OES; Wemyss, R.B.; Scott, R.H., 1978). Detection limits are comparable with FAS and the method which has a wide range capability from ppm to percent levels of analyte concentration, is relatively free of matrix effects. It has a considerable advantage over FAS in that it is a multi-element technique although its high price is a deterrent.

Neutron activation analysis (NAA) is also used by a number of laboratories as a finish to fire assay concentration procedures and also for the direct determination of gold at trace levels (Hoffman, E.L.; Scott, R.H., 1975). The method requires the use of nuclear facilities and sophisticated counting equipment and as a result is expensive. It offers very low detection limits (claimed to be 0.1 ppb) which is competitive with the capability of CFAS.

Constant potential coulometry (Werbicki, J.J., 1982) is an electrodepositional process which is not widely used in routine gold analysis. It is however the most accurate method available and is used as a reference for other procedures. The method involves the deposition of gold onto a platinum electrode at constant potential. The quantity of gold plated out is given by the number of coulombs passing through the solution during electrolysis. An accuracy of ±0.1% and standard deviation of 0.05% is possible with this method.

Polarography has been slow to develop as a means of routine analysis because early equipment was complicated and unreliable. Solid state electronics have now made the method attractive. In this technique gold is deposited onto a dropping mercury cathode and the cell current generated at a fixed potential is proportional to the gold concentration. Detection limits are similar to FAS. A recent development allied to polarography is anodic stripping voltametry. In this procedure the gold is plated out and the current associated with its subsequent stripping is a measure of the concentration. The method is capable of low detection limits but has not seen wide application to date.

Ion chromatography is a comparatively new technique in analytical chemistry (Rocklin, R.D., 1984). The method involves the application of high performance liquid chromatographic (HPLC) equipment to ion exchange separations. In the HPLC unit, concentration of the desired species ($AuCl_4^-$ in the case of gold) is effected on an anion concentrator column whilst interfering species are eluted. The retained anions are passed to a separator column and the eluant monitored by a variety of detectors (most commonly ultraviolet) and amperometric). The detection limit for gold is 50 ppb.

ANALYSIS OF GOLD FOR GEOCHEMICAL EXPLORATION

A recent review (Bumstead, E.D., 1984) found that no commercially available gold analysis met the criteria for quality geochemical analysis of ±10% or better and ore reserve quality of ±5%.

The study yielded a mean precision of ±15% for fire assay-FAS and ±30% for aqua regia/MIBK-FAS. It would appear that for exploration purposes at least we have to live with this situation since to correct it would involve intensive sample preparation and analytical control and the high costs inherent in such procedures.

The department's fire assay routine is adequate for both in-house and commercial analyses. For rock analysis where gold is not vein style the hydrofluoric acid/aqua regia-FAS or CFAS finish could be a useful development. In exploration practice where the chance is high that gold is of variable distribution we need to have a method such as 'Otter' in place. An alternative to the former method may be the hydrochloric acid/bromine/amyl acetate procedure noted earlier. Table 1 lists results of gold analysis from various sources. Unfortunately it is fragmented as there is no encompassing study of gold analysis but it serves to illustrate the variability of results according to the procedure.

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TABLE 1. COMPARATIVE RESULTS OF GOLD ANALYSIS*

SAMPLE	Fire Assay	Fire Assay - FAS	HF/Aqua regia - FAS	Cyanide - FAS	Hydrobromic acid/ Bromine - FAS	Bromine/ether - FAS	ICP - OES	Polarography	Neutron Activation	Coulometry
Geochemical Survey North Carolina										
Saprolite		0.3		0.1	0.3	0.26				
Red Soil		0.5		0.1	0.6	0.18				
Cellular Gossan		5.5		3.2	5.6	6.8				
Pyrite rock		4		3.8	4	4.7				
Sulphide ore		7		0.5	3.9	4.6				
Ore Samples										
Ashley	19.842		28.332						20.619	
Buffalo	14.586		12.844						13.124	
Electroplating Solutions										
Acid	1548	1648	1580				1592	1661		1555
Cyanide	970	927	933				908	995		1014
Stripper	1835	1940	1885				1804			1885

* All values ppm