بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

Sudan University of Science And Technology
College of Graduate Studies

Evaluation Of Atomic Absorption Spectrophotometric Determination Methods Of Gold In Its Ores After Aqua Regia Digestion, Cyanide Leach (NaCN) or Fire Assay Method Fusion

تقويم طرق تحديد عنصر الذهب في خاماته بواسطه مطيافية الامتصاص الذري بعد الهضم بالماء الملكي او التمرير بالسيانيد او بالصهر بطريقة مقايسة النار

A thesis submitted in partial fulfillment of the requirements for the Degree of M.Sc. in Chemistry

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DEDICATION

To my parents Elamin and Aisha
my Family
And my brothers and sisters
With my love.

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I thank God almighty for giving me the health to accomplish this work,
My appreciations are due to my supervisor Dr.Mohamed El mukhtar for his guidance,
valuable advice and supervision throughout this work.

ABSTRACT

In the persent research study three analytical methods used in Sudan based on the atomic absorption determination of gold after aqua regia digestion (AR), cyanide leach (NaCN) or fire assay method fusion (FA)were evaluated.

The efficiency of the sample pre-treatment procedures (crushing, splitting and grinding) and size of the subsample was also evaluated using both the AR leach and the cyanide leach methods.

Two ore samples [1] and [2] from Abouhmd area (north of Sudan) and four ore samples [3],[4],[5] and [6] from Umtrambesh area (north of Sudan) were collected,analysed and their results were compared with those of Reference Samples Material (RSM).

After crushing, the samples were ground to two grades of fineness (<0.03 and<0.06 mm) and were analysed for gold using the three analytical methods. Each determination was performed five times.

According to t-tests on the FA results of the two splits, crushing and splitting produced samples containing equal gold content. Grinding to a finer grain size did not give a significant difference in Au results except for the ore sample [5]. Greater than 95% recoveries were obtained for all samples except sample [1] (87% recovery) by the AR leach method assuming that the FA results represent 100% recovery of gold . Recoveries of over 95% by the NaCN leach method for samples [3],[4], and [5] were obtained, whereas recoveries for the other three samples varied between 73% and 92%. The AR leach also was performed on 1-g samples; the NaCN leach was performed on 250-g samples. For three of the ores samples, decreasing sample size from 20 g to 1 g did not cause a significant difference in the variance of the Au results. Increasing the sample size from 20 g to 250 g significantly improved the representatively of only the sample [5]. For the [4], [5] and [6] ores, a sample larger than 250 g was needed to obtain a precision equivalent to that for reference samples.

المستخلص

تم في هذه الدراسة تقييم ثلاث من طرق التحليل الكيميائي المتبعة في السودان لتقدير عنصر الذهب في خاماته بإستخدام مطيافية الامتصاص الذري بعد الهضم بالماء الملكي(AR) او التمرير بالسيانيد (NaCN) او بالصهر بطريقة مقايسة النار(FA) وتم تقييم فعالية كل عمليات تجهيز العينات قبل المعالجة النهائية من طحن وسحن وتقسيم بالإضافه لحجم العينة.

جمعت ستة عينات من مناطق شمال السودان ،عينتين خام [1]وخام [2] من منطقة أبوحمد واربعة عينات [3]و[4]و[5]و[6] من منطقه ام طرامبيش ،وتم تحليل كل العينات المذكورة مع عينات خام مرجعية (RSM) ومقارنه النتائج .

بعد عملية الطحن للعينات الجافه تم سحنها وتقسيمها إلي درجتين من الاحجام (0.03>و 0.06> mm)، وتم تحليل كل العينات بطرق التحليل الكيميائي الثلاثة وتم وتكرار كل قراءة خمسة مرات.

وفق نتيجة تطبيق ال(t-tests) علي نتائج طريقة الصهر (FA) عند درجتي السحن والتقسيم لم يوجد إختلاف واضح في قراءة الذهب بين درجتي السحن للعينة الواحده ماعدا تلك في عينة خام [5]. باعتبار طريقة (FA) كمرجعية (قيمة الأسترجاع 100%) وجدت قيمة الأسترجاع في نتائج طريقة (AR) اعلي من 95% لكل العينات ماعدا تلك عينة خام [1]حيث كانت 87%، وكانت قيمة الأسترجاع في نتائج طريقة (NaCN) أعلي من 95% لعينات خام كل من [4]و[3]و[5] اما باقي العينات فتراوحت بين 73% و 92%.

أظهرت الدراسة أيضاَ أن وزن العينه المأخوذه (1,20,250)جم لا توثرعلي نتائج الطرق الثلاثة عدا عينة خام [5] عند تحليلها بطريقه (NaCN) حيث كانت أدق مع زيادة الوزن من 20جم الي 250جم.بالنسبة للعينات [5]و[4]و[6] كانت هناك حاجه لزيادة الوزن أعلي من 250جم للحصول علي مستويات دقه أقرب إلي دقه العينات المرجعية (RSM).

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List of Abbreviations

FA	Classical lead fire assay
AR	The aqua regia leach
(Aliquat336)	Trialki methyl ammonium chloride
MIBK	Methyl isobutyl ketone
DIBK	Diisobutyl ketone (2, 6-dimethyl-4-heptanone)
FAA.S	Flame Atomic Absorption Spectroscopy
AFS	Atomic Fluorescence Spectroscopy
AES	Atomic Emission Spectroscopy
GFAAS	GraphiteAtomization Atomic Absorption Spectroscopy
ICP	Inductively Coupled Plasma
LOQ	Limit of Quantification
HSE	Health, Safety and the Environment
SPE	Solid Phase Extraction
AOAC	Association of Official Analytical Chemists
RSD	Relative Standard Deviation
g	Gram
m^3	cubic meters
ug/ml	micrograms per milliliter
mg/l	milligrams per liter
ppm	parts per million (weight by weight)
ppb	parts per billion (weight by weight)

CHAPTER ONE

1. INTRODUCTION

1.1 Gold Occurrence

Native gold is an element and a mineral. It is highly prized by people because of its attractive colour, resistance to tarnish and its many special properties - some of which are unique to gold. Its rarity, usefulness and desirability make it command a high price. Trace amounts of gold are found almost everywhere but large deposits are found in only a few locations (Table (1)). Although there are about twenty different gold minerals all of them are quite rare. Therefore, most gold found in nature is in the form of the native metal (Figure(1)and Figure(2). (Gold.org 2003). Gold occurs in hydrothermal veins deposited by ascending solutions; as disseminated particles through some sulphide deposits and in placer deposits.

1.2 Uses of gold

Most of the gold that is newly consumed or recycled each year is used in the production of jewellery. About 10% is used in coinage or in the financial stores of governments. The remaining 12% is consumed in a wide range of other uses which include electronics, medicine, dentistry, computers, awards, pigments, guiding, and optics.(Gold.org 2003). Of all the minerals mined from the Earth, none is more useful than gold. Its usefulness is derived from a diversity of special properties (Table (2)). Gold conducts electricity, does not tarnish, is very easy to work, can be drawn into wire, can be hammered into thin sheets, alloys with many other metals, can be melted and cast into highly detailed shapes and has a wonderful color and a brilliant luster. Gold is a memorable metal that occupies a special place in the human mind.

Table (1) 2011 Gold Production

Estimated gold production in metric tons. Data from USGS Mineral Commodity Summaries.

Country	Metric Tons
China	355
Australia	270
United States	237
Russia	200
South Africa	190
Peru	150
Canada	110
Indonesia	100
Ghana	100
Uzbekistan	90
Mexico	85
Papua New Guinea	70
Brazil	55
Chile	45
Other Countries	630

When Spanish explorers first arrived in the "New World" they met the native South Americans. These two cultures had been separated by a vast ocean, they had never touched one another, they spoke different languages and lived entirely different lives. Yet they had one thing in common - they both held gold in highest esteem and used it to make some of their most important objects. Throughout the history of our planet almost every established culture has used gold to symbolize power, beauty, purity and accomplishment. Today we continue to use gold for our most significant objects: wedding rings, Olympic medals, Oscars, Grammys, money, crucifixes and ecclesiastical art. No other substance of the same rarity holds a more visible and prominent place in our society. (GoldPrice.org 2000)

Table (2) Physical Properties of Gold

Chemical Classification	native element
Color	gold yellow
Streak	gold yellow
Luster	Metallic
Diaphaneity	Opaque
Cleavage	None
Mohs Hardness	2.5 to 3
Specific Gravity	19.3
Chemical Symbol	gold, Au
Crystal System	Isometric
Uses	Numerous uses in jewellery; coinage; bullion; currency backing; an electrical conductor used in computers, circuits, appliances, cell phones, etc.; dental work, gilding.

1.3Future Uses of Gold

Gold is too expensive to use by chance. Instead it is used deliberately and only when less expensive substitutes can not be identified. As a result, once a use is found for gold it is rarely abandoned for another metal. This means that the number of uses for gold have been increasing over time,It is truly a metal of the future.

Figure(1) Vein quartz with gold attached to basalt from California. This specimen is approximately 1 inch (2.4 centimeters) across.(Gold.org 2003).

Figure (2) White "vein quartz" with gold from Colorado. This specimen is approximately one inch (2.5 centimeters) across.(Gold.org 2003).

1.4. Chemical analysis of gold

1.4.1. Analytical requirements

Regional, large-scale geochemical projects demand special requirements for chemical analysis:

i. the analytical methods used must be sufficiently sensitive to allow detection of a wide range of determinands in all of the sample media at background levels;
ii. the analytical precision must be good, preferably significantly better than natural geochemical variation;
iii. the analytical accuracy must also be good, preferably even better than that achieved in most national geochemical surveys; and
iv. all data and other records pertaining to the analysis and testing must be fully documented and traceable.

Total element concentrations are most relevant for geochemical interpretation of data. For solid materials, this means that the silicate matrix either needs to be fully decomposed by mixed acid digestion before instrumental analysis, or a solid sampling technique such as X-ray fluorescence needs to be used. However, to address the needs of national and European level environmental authorities, information on leachable concentrations of the elements was also considered to be important. In environmental chemistry, a slightly unscientific and non-specific term, 'near total', is often used to describe the maximum concentration of an element that can be liberated from a material in its natural environment. An aqua regia leach(AR) or digestion is normally used for simulating this characteristic in the laboratory, although, unfortunately, almost every laboratory has its own standard operating procedure for carrying out aqua regia leaching (AR). (Crosby & Indu 1995), (Bennett,V.(1987).

1.4.2. Sampling

Sampling and sample preparation are the most critical processes contributing to the overall uncertainty budget. A special homogeneity test protocol was established for the project to demonstrate the quality of the sample preparation. Approximately one per cent of the prepared samples were split into four sub-samples.

Uncertainty in chemical analysis, although often significantly less than that associated with sampling and sample preparation, is nevertheless essential to understand and control.

In order to assess the precision of the chemical analysis relative to the variation due to sample preparation and sampling, duplicate samples and repeat measurements were taken. Approximately 5% of all sites were sampled in duplicate. The duplicate samples were prepared independently of each other and analysed randomly along with all other samples, with each duplicate sample also analysed in duplicate to allow estimation of sampling uncertainty. (Eller & Tobschall 1989), (Mauri ‘et al.’ 1990), (Furman, N.H. (1995)

1.4.2.1. Sampling solid materials

Solid samples are characterised by even larger variability than liquid samples. Typical solid materials sampled for analysis include: raw materials for industry/manufacturing, soils, sediments, snow and ice, wastes (industrial, municipal, hazardous, etc.), biological plant material, electro filter dusts, road dusts, tissues and organs of animals, etc. Analysis can give reliable results only if a sample has the same quantitative and qualitative composition as the material studied. Even the most accurate analysis of the test sample is useless if primary samples are not correctly collected and a gross sample is not representative of the material studied. The same importance should be given to sampling as is usually given to subsequent steps of an analytical process. Also, a quality assurance program is required for this step to ensure that information derived from analytical data is correct.(Likhareva, N.et al. (1988).

When preparing the sampling plan the following questions should be answered: - What kinds of samples are needed? - When, where and how should samples be collected? - What containers should be used to collect samples? - How should the samples be preserved? - What preparations are necessary for sample analysis? - What precision of sampling is required? Each sampling protocol should specify the number and size of samples. They depend on many factors, including lot size, material granulation, analytical method to be used, variability within and between particles, concentration of the component of interest, etc. The related problems should be discussed individually for each sampling task. If the product to be sampled is in packages, a specified number should be randomly selected from the lot, i.e. from the total amount of material which is to be characterised. One of the factors determining the number of sampled packages is the number in the lot; generally, if it is less than five, samples should be taken from each package in the lot. (Crosby & Indu 1995), (Rajah & Raju 1974), (Dvoryak & Pronin 1981), (Plant J.A et al 1996).

1.4.2.2. Sampling Soils

Different definitions of soil are presented in the literature. Depending on the aim of the analysis and the kind of soil, different approaches are used to sampling procedure and design. Special care should be taken and an appropriate approach applied to sample soil for preparation of soil matrix reference materials. Again, a proper sampling approach is needed. Substantial differences can be observed in approaches to profile sampling and sampling different layers and types of coverage. Sampling depends also on the kind of compounds to be studied. Special care is required, for example, when volatile organic compounds are to be determined. Quite recently, comparative studies (15 European participants) on soil sampling for three-dimensional pollution assessment were conducted. Participants used their own sampling procedures. The results obtained show that this step of soil analysis needs harmonisation throughout Europe.

1.4.2.3. Sampling site selection

The average sample should represent the area of agricultural land of close natural conditions (soil type, soil textural group, topographic features, etc.). For similar areas with respect to soil, topographical features, etc... Sampling sites should be selected along a zigzag line or along a diagonal (Fig. 3). The approaches presented schematically in Fig (4) are also proposed. They include normal sampling, test sampling, diagonal sampling, and cross sampling. (Keith‘et al.’1983), (Kratochvil & Taylor 1981), (Rump, H.H.Kirst, H.H (1988)

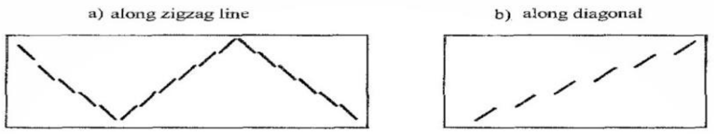

Fig. 3.8. Zigzag and diagonal arrangement of sampling points for soils (based on Ref. [29]).

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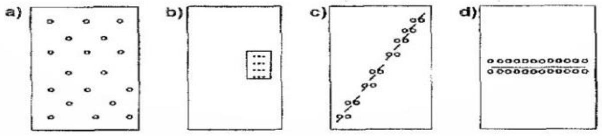

Fig. 3.9. Arrangement of soil sampling sites proposed by Rump and Kirst [30]. (a) Normal sampling, (b) test sampling, (c) diagonal sampling, (d) cross sampling.

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Composite sample: a mixture of samples collected from more than one sampling location, or at the same location more than once. Gross sample: a portion of a material composed of all primary samples collected from the same lot. Heterogeneity: a situation when values of a given property or composition of material in one place of a lot differ from values in other places of the same lot. Heterogeneity is random if a property value in one portion of the population studied is independent of the values in neighbouring portions and independent of the position in the whole bulk of the material; heterogeneity is directional when a property value changes along a specified direction in non-random way; heterogeneity is periodic when a property value fluctuates periodically around an average value. Laboratory sample: a sample prepared from primary, gross or composite samples intended for testing or analysis. The laboratory sample must retain the composition of an original sample. Often reduction in particle size is necessary in the course of reducing the quantity; it should be packed and stored in such a way as to protect its identity. Lot: a quantity of bulk material of similar composition whose properties are under study. Primary sample: an individual portion of material collected by a single operation of a sampling device from one site of an unpacked material or from a one site in a single package. Profile sampling: collecting soil samples from individual layers or horizons of a soil profile. Representative sample: a sample that closely resembles, or is subset of, the population being measured. Sampling: an attempt to choose and extract a representative portion of a physical system from its surroundings. Segregation: a process or state in which a substance or particles undergo distribution throughout a bulk material in a non-random way. Test sample: a sample prepared from a laboratory sample, e.g., by means of grinding, reduction, etc. Portions of test sample, termed test portions, are taken for single measurements Unit sample: a portion of a material composed of all primary samples collected from one package. (Crosby & Indu 1995), (Kratochvil & Taylor 1981).

1.4.3. Sample Preparation

Samples are dried if necessary and then reduced size to 0.25 inch with a jaw crusher. The jaw crusher is cleaned with compressed air between samples and barren material between sample batches. The sample is then reduced to 90% -10 meshes with a rolls crusher. The rolls crusher is cleaned between samples with a wire brush and compressed air and barren material between sample batches. The first sample of each sample batch is screened at10 mesh to determine that 90% passes 10 meshes. Should 90% not pass, the rolls crusher is adjusted and another test is done. Screen test results are recorded in the log book provided for this purpose. The sample is then riffled using a Jones type riffle to approximately 300gm. Excess material is stored for the client as a crusher reject. The 300gm portion is pulverized to 90% -200 meshes in a ring and puck type pulverizes, the pulveriser is cleaned between samples with compressed air and silica sand between batches. The first sample of each batch is screened at 200 meshes to determine that 90% passes 200 meshes. Should 90% not pass, the pulverizing time is increased and another test is done. Screen test results are recorded in the log book provided for this purpose.(Hoffman 1998),(Mauri 'et al.' 1990),(GariaOlalla & Aller 1991),(Rady, G. and Erdy, L. (1967).

1.4.4. Analytical Methods

Element concentrations are most relevant for geochemical interpretation of data. For solid materials, the solid needs to be fully decomposed and digested before determination by instrumental analysis.

1.4.4.1 Methods of decomposition and digestion

(A) Acid leachable element

In addition to the total concentrations of the elements, the acid leachable portion of selected elements were analysed after hot aqua regia leach (AR) by ICP-AES-AAS instrument. As a rule, acid digestion procedures are employed for the determination of elements in solids subsequent to sampling and mechanical sample preparation in order to completely transfer the analyses into solution so that they can be introduced into the determination step (e.g., ICP-AES, ICP-MS, AAS or palaeography) in liquid form. The goal of every digestion process is therefore the complete solution of the analytes and the complete decomposition of the solid (matrix) while avoiding loss or contamination of the analyte. There is an additional need to ensure that the digestion is safe, reproducible and simple, that is, that it can be performed without excessive manual effort. Since sample preparation typically also consumes the largest share of task time, this process also has economic significance. (Ol'khovich, PF.and Pilipenko (1970)

In this context, wet chemical digestions utilizing various mineral acids (e.g., HCl, HNO_3, HF, H_2SO_4, etc.), hydrogen peroxide and other liquid reagents is carried out in either an open system, that is, under atmospheric pressure, or in closed vessels. Further, the samples may be heated in convection or microwave ovens. Accordingly, these processes are described in the relevant literature more-or-less synonymously as acid digestion and pressure digestion or microwave digestion (microwave decomposition) and microwave pressure digestion. The advantage of the closed procedure in comparison with open digestion in a recycling device or with the traditional "hot plate", lies in the significantly higher working temperatures which can be achieved.

While operating temperatures in open systems are limited by the boiling point of the acid solution, closed digestion vessels typically allow temperatures in the range of 200-260 °C to be reached.Samples were digested in aqua regia(open system) by weighing (1-20) g of sample in a polyethylene tube and adding (for 1 g) 6 ml HCl and 2 ml HNO_3. The samples were left for 15 minutes at room temperature before heating in an aluminium block at 95°C for 60 minutes. After cooling, the samples were filtered and made up to 50 ml in a polyethylene flask. (Hoffman 1998), (Gawlik & Muntau 1999), (Christian, G.D. and Epstein, M.S. (1998).

(B) Sodium cyanide leach

A basic cyanide solution is known to leach Au from rock samples upon the oxidation of Au and the formation of the easily soluble [Au(CN)$_2$]complex. Leaching with a basic solution of NaCN has been used widely in Au production since the turn of the century. Quantitative determination of Au can also be based on the cyanide leach. The method has been used, for example, in the analysis of siliceous limestone ores and in geochemical exploration for Au. The NaCN leach was introduced as an analytical method for Au at the Geological Survey of Finland (GSF) in 1995, to enable the use of a large sample size, 250–1000 g. (Hoffman 1998),(Groenwald,T.1968).

(C) Organic Concentration Methods for Spectroscopy

Extraction is a technique used to eliminate background interference or enhance absorbance for atomic absorption spectrophotometry. Gold is preferentially absorbed by an organic solvent which has been agitated with the sample solution. This organic phase is separated for AAS analysis. Absorbance is enhanced by using less extractant than sample, and interference is reduced when interfering elements are not extracted with the gold.

The first method uses MIBK as the organic extractant. MIBK affinity for the gold ions and complexes found in Rocks, ores and other geological materials is limited, so the method requires that sample must be acidified in a hood prior to the addition of MIBK for extraction and separation.

The second method uses a solution of DIBK and trialkyl ammonium chloride (Aliquat 336) to extract solutions over pH ranges of 11-12.5. The method differs from first method by adding salt solution to the sample to optimize extraction. Higher concentration ratios than those in the MIBK extraction method are possible if quality standard solutions can be obtained. The extreme stability of gold in this extractant gives extracted samples a longer shelf life if this is required. (Keith‘et al.’1983),(Parks & Mtirry Smith 1979).

The third method uses a solution of xylene with dibutyl sulfide as the extractant. It is not in current mining use. Solutions require acidification before extraction and should be handled in a hood. The strong odor which is associated with dibutyl sulfide requires ventilation. (Seward, P.D. and Gilbert, lT.J.(1984).

(D) Inorganic Concentration (Fire Assay) Methods

Fire assay methods they are a group of analytical techniques which use high temperature selective reduction of precious metals and lead from a molten solution (fusion). Precious metals are separated qualitatively by selective oxidation (cupellation) for gravimetric or instrumental analysis.

Fire assay methods are more labor intensive but are preferred for checking primary reference solutions or solutions which might contain uncorrected interference factors. These methods are considered to be relatively immune to chemical, elemental or physical interference factors which, in instrumental methods, can cause unrecognized false determinations. Reference standard solutions are not required, but control samples are recommended.

A general fire assay method has been included for reference. The fire assay practice outlined will produce accurate determinations for "fire assay as normal". It assumes that fusions will be with a fluid pouring, slightly acid fusion and cupellation will involve 25 or more grams of lead.

Assay comparisons between analytical labs are recommended to detect errors in technique. Although the reference method and reference sources give a good basis in fire assaying, safe and accurate results depend on an experienced assayer.(Parks & Mtirry Smith 1979), (Bugbee , E.E. (1984).

(F) Copper Sulfate Methods

The Copper Sulfate Method uses a solution of copper sulfate and sulfuric acid to precipitate gold and silver from solution. This precipitate is filtered, dried and either scorified or fired to produce a lead button for cupellation.

The Pinson assist the filtration method uses potassium ferrocyanide and sodium sulfite to formation of the gold precipitate and flocculent to aid the precipitate.

The Freeport Method does not use fldcculent or potassium ferrocyanide. It is believed that ferrocyanide increases the amount of copper in the precipitate without an improvement in gold values for the type of sample solutions used. sodium sulfite is used to assist precipitate formation.

The Golden Sunlight Method combines copper sulfate, sodium hydroxide and sodium cyanide to make a precipitation solution. Potassium ferrocyanide is used to assist gold precipitation, and sodium sulfite is not used in the precipitation process. Flocculent is not used with filtration.

(F) Chiddey Method (Composite) Chiddey is a term applied to a zinc precipitation method used to collect gold from solution for fire assay cupellation. Three variations of this method were submitted which were essentially identical. This is a composite of all three methods.

(G) Lead Acid Method (Composite)

Gold ions from an HCl-acidified sample solution replace lead atoms granulated lead. The gold-loaded granulated lead is dried for cupellation by standard fire assay techniques. Three essentially identical methods were submitted. Battle Mountain Gold's method is the primary model for this composite.

(H) Direct Assay Method (Newmont Method)

The direct assay method is only used on high-grade solutions. A small aliquot of solution is dried in a crucible filled with standard flux and fire assayed by "normal" techniques. The procedure included here was submitted by Newmont Gold Company. No other labs are currently using direct assay.

(I) Potentiometric titration

A direct potentiometric titration method for the determination of gold in ores and alloys is described. It is based on the reduction of Au(IIl) with iodide ions yielding accurate and reproducible results. Detection limit and sensitivity were 0.06 and 0.032 mg/1 Au, respectively. The linear response range was between 0.1 and 120 mg/1 Au. The method can be used for the routine assay of gold in different kinds of samples.

Gold determination in alloys, minerals and soils is usually carried out by spectrometric methods .All these methods, although in some instances very sensitive, are quite complicated and very expensive. On the other hand, gold determination by potentiometry has enjoyed wide acceptance among analytical chemists, due to its simplicity and rapidity. Results obtained by potentiometric methods are also reliable and usually comparable to those obtained by other chemical methods.(Juvonen & Vanen 1993),(ASTM Standards 1979),(Bucknam & Hausen 1986),(Erickson ‘et al.’1966),(Gott & McCarthy1966).

1.4.4.2 Methods of determination by instrumental analysis

(A) Atomic Absorption (AAS)

The atomic absorption spectrometry uses absorption of light of intrinsic wavelengths by atoms.

Direct atomic absorption is the most common means for determining gold in rocks,ores and other geological materials. This choice is dictated by its relatively low cost for single element determinations, short analysis time and reasonable accuracy.

Genrally use background correction (continuum source, Smith-Hieftje, or Zeeman) for all determinations. Double beam optics are preferred. Graphite furnace atomization is only used for samples which require lower detection limits. Organic concentration or inorganic concentration is sometimes used to enhance sensitivity or accuracy for flame atomic absorption,the methods for atomic absorption consist of general operating parameters, a list of various blank/standard matrix solutions and a composite of operating.(Shimadzu corporation2015), (Parks, A. and Mtirry Smith, R.1979)

(B) Atomic Emission (AES)

Emission equipment is relatively expensive to operate, but it is particularly cost-effective for multi-element analysis. A radio frequency generator (ICP) or a direct current (DCP) generates a plasma to stimulate atomic emission for analysis. Chromium (Cr), iron (Fe),
manganese (Mn) and vanadium (V) are listed as potential emission interference elements. The ICP method programs the interference patterns out. The DCP method dilutes samples until interference is insignificant. As in the atomic absorption method, exact operation instructions are left to the manufacturers' operating manual. (Siepak, J. (1992).

(C) Atomic Fluorescence - (AFS X-Ray)

X-Ray fluorescence does not currently have accurate direct sensitivity equivalent to AAS or AES, but field or benchtop instruments, which will continue to function under treatment hostile to AAS or AES equipment, have been attractive for some mine operations. A sealed radioisotope capsule or an X-ray tube is used as a source of high energy x-rays to excite inner shell electrons. An x-ray sensitive detector (scintillator, gas-proportional counter, solid state detector, etc.) is used to count the characteristic fluorescent x-rays which are emitted by the excited gold. Spectra are simple, but some corrections for spectral overlap (mercury, thallium, etc.) or background effects must be made. This is done with dispersing crystals in high resolution sophisticated instruments or Ross filters in benchtop models. Sample preparation is not normally required,

Note: A Ross filter consists of two filters that transmit interfering x-rays equally while one limits analytical line transmission. The transmission difference is used to calculate "true" analyte fluorescence. (Beamish & Vanon.1977),(Parks & Mtirry Smith 1979)

1.4.4.3. Hazards And Precautions (General)

- The necessity, for both safety and sample preservation, of keeping the pH of cyanide solutions well into the alkaline range (10.5 to 14) by adding sodium hydroxide or calcium hydroxide.
- The release of cyanide gas, a highly lethal poison, from any admixture of cyanide and acid (or, to a lesser extent, non-alkalinized water) -- cyanide to be mixed only under fume hoods The release of toxic cyanogen chloride from any admixture of cyanide and chlorine, hypochlorite, or aqua regia.
- The necessity of following strict hygiene practices when handling cyanide.
- An up-to-date cyanide safety program that includes a rescue contingency plan.
- Poisoning by fumes from solvents (MIBK, Aliquat 336), acids (nitric, hydrochloric, aqua regia, sulfuric), and lead (during cupellation, fluxing, fusion).
- Poisoning by ingestion or inhalation of lead (lead oxide dust in flux, lead acetate crystals) or of other chemicals.

  Tissue destruction from acids (above) and alkalies (sodium and calcium hydroxide)

  - Burns from furnaces, ovens, hot plates, tools, and from flame, torch, or electric-arc instruments.
  - Cuts from glassware.
  - Explosions (e.g., acetylene for atomic absorption instruments).
  - Hazards related to improper housekeeping and hygiene.
  - Offsite hazards due to improper protective clothing or personal hygiene. (e.g. organic solvents, particularly chlorinated hydrocarbons, which are carried home on an employee's clothing or body are associated with a higher incidence of childhood leukemia within an employee's family). (Gilbert,Smith,& Anderson 1987),(SAMA 1970)

1.5 Objectives

The geneal objectives of this research is to compare three different analytical methods used in Sudan based on the atomic absorption determination of gold (1) Lead fire assay followed by determination of gold by flame atomic absorption spectrometry (AAS). (2) Aqua regia leach followed by MIBK and determination of gold by flame atomic absorption spectrometry (AAS). (3) Sodium cyanide leach followed by determination of gold by (AAS.) in six ore samples collected from north of Sudan in Abouhmd area and Umtrambesh area with the reference samples .

Specific objectives are:

- To determine whether there is a difference in the gold content of the splits of a large sample after crushing
- To determine the optimum sample size in order to obtain reproducible analytical results for gold of various types of ores
- To determine whether grinding to a finer grain size improve the results
- To compare the analytical methods based on either aqua regia(AR) leach or NaCN leach with that of the classical widely accepted lead fire assay in the determination of gold content in ore samples

Chapter two

2.1 Materials

2.1.1 Chemicals and Reagents

Reagents: Unless otherwise noted, all chemicals are analytical reagent grade.

Lithage PbO, sodium carbonate Na_2CO_3, Borax $Na_2B_4O_7$, potassium carbonate K_2CO_3, potassium bitartate $KHC_4H_4O_6$, Ag as silver nitrate $AgNO_3$, sodium nitrate $NaNO_3$, Nitric acid HNO_3 (65% v/v), hydrochloric acid HCl (37% v/v),silica SiO_2, ,distilled water, methyl isobutyl ketone (MIBK), trialkyl ammonium chloride(Aliquat 336), gold Primary Standard solution 1000 ppm (available from Shimadzu corporation),gold Secondary Standard solution Prepared as needed, Reference Standard Material of gold (RSM), sodium cyanide NaCN solid reagent, calcium hydroxide $Ca(OH)_2$, sodium hydroxide NaOH, 4.0,7.0 and 10.0 pH buffer solution.

2.1.2 Apparatus

The following equipment were used : safety Equipment Chemical-resistant lab aprons and gloves, safety glasses and chemical mask, emergency cyanide-poisoning first aid station, emergency eye-ash and shower,self-contained breathing apparatus and rescue contingency plan.

Glassware; (burette, pipettes,funnel, beakers) Class A, sized as needed, borosilicate, calibrated volumetric flasks Class A, sized as needed, glass stirring rods, auto-diluters assorted reagent dispensers, graduated test tube, volumetric cylinder sized as needed.

Spatula, porcelain crucible sized as needed, Teflon beaker 250ml, magnesite cupel,Plastic ware; eyedroppers, disposable teaspoon.

2.1.3 Instrumentation

Atomic absorption spectrophotometer (SHIMADZU 6800 Japan) was used with background correction (flame atomization), (Wavelength: 242.8 nm, Burner:

Straight (no angle), Flame: Lean, blue @ maximum absorbance, Integration: 1.0 Second, Slit: 0.7 nm, Autosampler, Standard balance (readability 0.0001g OHAUS, Model AS60s ,USA.),

Equipment; Fire Assay Furnace equipped to fuse samples at 1065°C and cupel at 1065°C, Hot Plate (up to 300°C), Annealing and parting trays, Cupel tongs, horizontal shaker,oven, Muffle furnace, pH meter, bottle roller, Centrifuge, fume hood, magentic stirrer.

2.2 Samples and sample preparation

In fact the study samples were taken as composite sample(a mixture of samples collected from more than one sampling location, or at the same location more than once), these should be specified in a sampling protocol. (Fig. 4) (a) Normal sampling.

2.2.1. Description of the six Au ores

In choosing the ore samples for the study an attempt was made to select a variety of ore types.[1] and [2] were refractory ores disseminating sulfides, mainly pyrite and arsenopyrite, gold correlated with arsenopyrite,[2] and [4] contained native gold and Te minerals ,gold in variable associations, native gold as inclusions in potassium feldspar and between silicate grains intergrown with tellurides and with pyrite grains ,[5] and [6] were known to contain free-milling native gold of fairly large grain size.

2.2.2. Sample pretreatment

The 20-kg samples were crushed with a jaw crusher (Retsch BB3) in two steps: first, a crude crushing and then a finer crushing, after which 80– 90% of the sample was reduced to a particle size of less than 3 mm.

The crushed sample was split with a Jones splitter into three parts of about 5–7 kg each. One part was saved for further studies and two parts, splits A and B, were further split into two. The two splits, of about 3 kg each, were ground with a swing mill (Labtechnics LM 5), to two grain sizes. The first split was ground using the routine grinding time of 6 min and the other split was ground using

12–18 min. Grain size determinations of the ground samples were made with a laser diffraction instrument (Sympatec Helos). At least 75% of the sample particles were of the grain size presented in Table 3 or smaller. With the exception of the [2] sample, the grain size was substantially reduced with prolonged grinding time. The [4] and [6] samples were ground for 18 min because the 12 min grinding time for these samples gave particle sizes of 0.06 mm for [6] and 0.04 mm for [4].

Table [3] Grain sizes of the ore samples after grinding.

Sample	Particle size, mm 6 min grind	Particle size, mm 12–18 min grind
[1]	0.06	0.02
[2]	0.02	0.02
[3]	0.04	0.02
[4]	0.04	0.03
[5]	0.05	0.03
[6]	0.07	0.03

2.3. Analytical methods

In nature, gold occurs as native or refractory type Refractory gold ores are not free milling and cannot be leached without some form of physical, chemical or pyro metallurgical pretreatment. Refractory gold is found in association with sulphides (pyrite, arsenopyrite and chalcopyrite), whereas native gold is associated with tellurides, bismuthides, silver, antimony and copper. In general, fire-assay (FA), cyanide leach, (open) aqua regia hot blate and microwave (closed) are some of the important extraction methods. (Hoffman 1998).

The following routine analytical methods were used: (1) Lead fire assay followed by determination of Au by flame atomic absorption spectrometry (AAS). (2) Aqua regia leach followed by MIBK and determination of Au by flame atomic absorption spectrometry (AAS). (3) Sodium cyanide leach followed by determination of Au by flame AAS.

2.3.1. Lead fire assay

The 20-g sample was mixed in a plastic bag with 50 g PbO and about 200 g of the flux containing 32 g Na_2CO_3, 44 g $Na_2B_4O_7$, 52 g K_2CO_3, 52 g $KHC_4H_4O_6$ and 20 g quartz. After mixing, the bag with its contents was put into a fire-clay crucible, and Ag was added as $AgNO_3$ solution. The crucible was transferred into a preheated furnace and fused at 1100°C for 1 h. The contents of the crucible were poured into an iron mold to cool. After cooling, the Pb regulus was hammered and brushed clean, after which it was cupelled in a magnesite cupel at 940°C. The Ag bead remaining after the cupellation was flattened with hammer and anvil, and was transferred into a graduated test tube and dissolved by adding 0.5 ml HNO_3 (65% v/v) and 1.5 ml HCl (37% v/v). To avoid overboiling, the test tubes were allowed to stand at room temperature overnight before heated on an electric block heater. When the bead was dissolved, the volume was made to 10 ml with 6 M HCl. The solution was read by AAS to measure gold using a shemadzu AA 6800 instrument with an air–acetylene flame with continuum (D2) background correction.(Beamish&Vanon.1977),(Parks&MtirrySmith1979).

2.3.2. Aqua regia leach

The method of gold determination based on AR leach and MIBK has been developed at the Geological Survey of Finland (GSF) .

The sample was first roasted in a porcelain crucible at 600°C in order to oxidise organic material, graphite and sulfides. The sample (20 g) was transferred into a 250-ml Teflon beaker.30 ml of conc HCl and 10 ml of conc HNO_3 were added and the mixure was digested by heating on a"hot plate" at 230°C for 2 h,after that 25ml of 5% HCl was added and digested at 80°C -85°C for 15 minutes to dissolve the gold salts .The mixure was allowed to stand at room temperature ,and then transfered into 100-ml volumetric flask by 5% HCl and 10 ml of (MIBK) were added to extract gold into methyl isobutyl ketone (MIBK) containing chelating agent (1% Aliquat 336).Finally the mixure was shaked vigorously for 15 minutes on a horizontal shaker which shakes them automatically . The flask was filled to the mark with 5% HCl and the absorbance was read by a Shemadzu AA 6800 instrument with continues (D2) background correction and an air–acetylene flame at a wavelength of 242.8 nm ,a standard calibration curve of absorption against gold concentrations of the standard solution expressed as parts per million in the organic phase was plotted.(Erickson ‘et al.’1966)**.**

2.3.3. Sodium cyanide leach

A basic cyanide solution is known to leach Au from rock samples upon the oxidation of Au and the formation of the easily soluble $[Au(CN)_2]$ complex. Leaching with a basic solution of NaCN has been used widely in Au production since the turn of the century. Quantitative determination of Au can also be based on the cyanide leach. The method has been used, for example, in the analysis of siliceous limestone ores and in geochemical exploration for Au. The NaCN leach was introduced as an analytical method for Au at the Geological Survey of Finland (GSF) in 1995, to enable the use of a large sample size, 250–1000 g. (Collis et al., 1991).

The sample (20 g) was weighed into a bottle and 40 ml of water were added. The pH was adjusted to 11 by adding 0.1 g of NaOH sodium hydroxide. The solution was made 0.3% with respect to NaCN by adding 0.12 g of the solid reagent. The open bottle was laid on its side on a bottle roller and allowed to roll for 24 h. The bottle with its contents was weighed before and after the cyanide leach to estimate the amount of evaporation. After the replacing the evaporated water, solution were transferred into a test tube and centrifuged. A 5-ml aliquot of the solution was pipetted into a test tube and 5 ml of HCl (37% v/v) were added. After evaporate of the HCN gas in the fume hood, the Au content of the solution was determined by AAS(using a shemadzu AA 6800 instrument with continuum (D2) background correction and air–acetylene flame), Sample-to-water ratio and the concentration of the NaCN solution were kept constant regardless of sample size.(Erickson ‘et al.’1966).

Chapter Three

3.1. Results and discussion

The four subsamples of each ore were analysed for Au using the three analytical methods described above. Each determination was performed five times, and the sample weight used in all of the determintions was 20 g. The fire assay method was used as the reference method. Reference sample results as the reference method. Reference sample results, which have been collected over several years using the FA and the AR methods, are presented in Table 4. The effect of sample size on the variance was studied by comparing the results obtained for subsamples of 1 g for the AR leach and subsamples of 250 g for the NaCN leach with the 20-g subsample results. Mean recoveries for Au using the AR and the NaCN methods were given in Table 5.

Table(4) Results for reference samples using the aqua regia leach method and the lead fire assay method (sample size is 5 g in each determination)

Method	Reference sample	Result of Au(ppm)	RSD(%)	Number of determinations	Reference value Au (ppm) [a]
Aqua regia leach (AR)	GXR-1	3.10±0.20	6.5	5	3.10±0.20
	GXR-4	0.42 ±0.01	2.4	3	0.44±0.16
	SARM 7	0.36 ±0.066	18.3	6	0.31±0.02
Fire assay (FA)	MA-1a	19.91 ± 1.2	6.0	3	21.4±0.4
	MA-3	7.4 ± 0.3	4.1	9	7.49±0.19

GXR-1 jasperoid and GXR-4 copper-mill head, United States Geological Survey; SARM 7 platinum ore, Council for Mineral Technology, South Africa; MA-1a and MA-3 gold ore, Canada Centre for Mineral and Energy Technology.

[a] Values of reference sample from certificates.

Table(5) Mean recoveries for Au using aqua regia leach and NaCN leach for different sample sizes of the six Au ores; the fire assay recovery for the 20-g sample was assumed to be 100%

Ore	Mode of occurrence of Au	Recovery (%)			
		AR leach		NaCN leach	
		1 g	20g	20g	250 g
[1]	Au associated with arsenopyrite, pyrite and in silicate inclusions	93.7	86.8	73.1	n.d.
[2]		98.5	95.7	85.6	88.9
[3]	metallic Au and Au tellurides	104	98.9	94.9	105
[4]		105	102	99.3	103
[5]	coarse-grained metallic Au	76.4	95.7	97.5	111
[6]		121	102	92.2	110

n.d. : not determined.

3.1. Evaluation of homogeneity of the samples after crushing and splitting

For both split A and split B of each of the six Au ore samples, two subsamples of different grain size were prepared. Because each subsample was analysed five times, there were ten Au results for samples of both splits. Even distribution of Au in splitting was tested by applying the t-test on all ten Au results obtained for splits A and B regardless of grain size.

The results of the t-test are presented in Table 6. None of the t-test values for the six ore samples was above the critical value, indicating that there were no significant differences in the Au contents of the splits A and B.

Table (6) The t-test for Au determinations of splits A and B

Ore	Split	Mean ± SD Au (ppm)	Value t-test
[1]	A	10.68 ± 0.14	1.56
	B	10.49 ± 0.36	
[2]	A	12.03 ± 0.97	0.21
	B	11.93 ± 0.92	
[3]	A	322.61 ± 9.34	1.02
	B	312.75 ±29.23	
[4]	A	136.18 ± 4.52	0.64
	B	134.79 ± 4.49	
[5]	A	37.86 ± 16.72	0.49
	B	45.17 ± 43.64	
[6]	A	15.62 ± 1.58	0.12
	B	15.50 ± 2.90	

For 18 degrees of freedom ($n_1 + n_2 - 2 = 18$, where $n_1 = 10$ samples of split A and $n_2 = 10$ of split B) the critical value of the t-test is 2.1. Gold is determined using the fire assay pre-concentration and AAS determination.

3.2. Effect of sample grain size on the Au results

The effect of sample grain size on the Au results was studied by applying the F-test on the standard deviations of the ten results of the finer grain size of splits A and B and the ten results of the larger grain size of splits A and B. A value above the critical value in this test indicated that the difference between the variances of the tested sets of values was statistically significant. The results are presented in Table 7. From these results, it can would be seen that grinding to a finer particle size did not improve the variance of the results, except in the case of the [5] sample. According to the F-test, statistically significant differences in variances of different grain size fractions were also found for the [3] and [4]samples. However, in these cases, the standard deviation values were higher for the subsamples of finer grain size.

Table (7) The F-test for the two different grain size fractions of the six Au ore samples

Ore	Grain size	Mean ± SD Au (ppm) n = 10	RSD) (%)	Value f-test
[1]	0.06 mm ^{a}	10.43 ± 0.27	2.6	1.61
	0.02 mm ^{b}	10.74 ± 0.21	2.0	
[2]	0.02 mm ^{a}	12.76 ± 0.49	3.8	1.28
	0.02 mm ^{b}	11.20 ± 0.44	3.9	
[3]	0.04 mm ^{a}	332.3 ± 10.1	3.0	4.16
	0.02 mm ^{b}	303.1 ±20.6	6.8	
[4]	0.04 mm ^{a}	132.1 ± 1.92	1.5	3.57
	0.03 mm ^{c}	138.8 ±3.63	2.6	
[5]	0.05 mm ^{a}	52.29 ±44.0	84.1	77.4
	0.03 mm ^{b}	30.91 ± 5.00	16.2	
[6]	0.07 mm ^{a}	14.61 ± 1.70	11.6	2.09
	0.03 mm ^{c}	16.51 ± 2.46	14.9	

The critical value for the F-test is 3.18 (degrees freedom are 9 and 9) at a = 5%. Values above the critical value were underlined. Grinding time: ^{a} 6 min, ^{b} 12 min, ^{c} 18 min.

3.3. Statistical comparison of results obtained with the three analytical methods

Results for the median, mean and standard deviation of all twenty analyses obtained for each of the six Au ore samples using lead fire assay, AR leach and NaCN leach are presented in Table 8. The t-test was used to test for statistically significant differences between the results for the AR leach method and -

Table(8) Median, mean, standard deviation (SD) and relative standard deviation (RSD) of the gold determinations results using the fire assay and AR leach and NaCN leach

Statistical parameters of results of the ore samples	Au (ppm)		
	Fire assay	AR leach	NaCN leach
[1], n = 20, median	10.53	9.19	7.80
Mean	10.58	9.18	7.73
SD	0.28	0.21	0.44
RSD (%)	2.7	2.3	5.7
[2], n = 20, median	12.04	11.38	10.19
Mean	11.98	11.47	10.26
SD	0.92	0.82	0.57
RSD (%)	7.7	7.2	5.6
[3], n = 20, median	323.8	312.2	308.0
Mean	317.7	314.1	301.5
SD	21.72	8.65	16.41
RSD (%)	6.8	2.8	5.4
[4], n = 20, median	133.8	138.5	133.0
Mean	135.5	138.3	134.6
SD	4.45	5.44	6.9
RSD (%)	3.3	3.9	5.1
[5], n = 10, median	29.04	27.46	28.68
Mean	30.91	29.57	30.14
SD	5.00	6.96	9.31
RSD (%)	16.2	23.5	30.9
[6], n = 20, median	15.50	15.18	13.74
Mean	15.56	15.84	14.34
SD	2.28	2.77	1.76
RSD (%)	14.6	17.5	12.3

-NaCN leach method as compared with the fire assay method. Differences in variance of the results were evaluated with the F-test. According to the t-test (Table 9), significant differences between the results of the AR leach and the fire assay method were found only in the results for the [1] sample. The slightly lower recovery with the AR leach method for this sample than that of the others could be explained by its mineralogical composition.Au was been found as inclusions in the silicate minerals which wre not attacked by AR . The standard deviation of the results for [3] with the AR leach method was significantly lower than that of the fire assay method. This could be explained by the high Au content of the sample unlike that case of samples of low Au concentration, variable and detectable amounts of Au remain in the slag after fire assaying causing variation in the results. The first three values of the t-test using the fire assay method in comparison with those useing the NaCN leach(Table 9) were above the critical value, indicating that the lower recoveries obtained using the cyanide leach method were statistically significant. Gold was found as inclusions in pyrite and silicates in these ores. For samples in which Au was present as metallic Au or Au tellurides, good recoveries with the cyanide leach were obtained. In comparing the NaCN leach with the fire assay method, a significant difference in the variance of the results was found in all samples except the [3]and [6] samples. In three cases, the standard deviation of the fire assay results was lower than of that of NaCN leach, and in one, the reverse was true.

Table (9)Comparsion of the result of fire assay method with both those of aqua regia leach(AR) and of sodium cyanide leach methods

Ore samples	Fire assay vs AR		Fire assay vs NaCN	
	t-test value	F-test value	t-test value	F-test value
[1]	17.7	1.82	24.3	2.40
[2]	1.85	1.26	7.11	2.60
[3]	0.69	6.31	2.66	1.75
[4]	1.78	1.50	0.50	2.41
[5]	0.57	1.94	0.27	3.46
[6]	0.35	1.47	1.90	1.67

Values for the t-test and the F-test were calculated using the means and the standard deviations given in Table 7 for the 20 determinations of each sample using the three analytical methods (10 determinations of the [5] sample). The critical value for the t-test is 2.03 (2.1 for the [5] sample) at 5% significance level, and the critical value for the F-test is 2.2 (2.9 for [5] sample). Values above the critical value were underlined.

3.4. The effect of sample weight on the analytical results of Au

The NaCN leach was carried out on 250-g subsamples and the AR leach on 1-g subsamples. The results of these determinations together with the results for the previously presented 20-g subsamples by both methods are presented in Table 10. The NaCN leach was not performed on the 250-g [1] sample because preliminary tests showed that not more than 10% of the Au would be leached with NaCN unless the sample had been roasted prior to leaching. Roasting of the 250-g subsamples was not undertaken. The results with the higher sample weight had a general tendency to be higher. This could clearly be seen in the NaCN leach results. Increasing sample size to 250 g significantly lowered only the SD of the [5] sample. Variance of the [4] results increased with increase in sample size.In comparison with the results obtained when the AR leach was uesed for 1-g and 20-g samples, gave higher SD values,but gave significantly higher variance values in only half of the number of the samples.

Table (10)Effect of sample size on the results of Au determinations of the six Au ore samples

Statistical parameters of results of the ore samples	Au (ppm) NaCN leach		F-test value	Au (ppm) AR leach		F-test value
	20 g	250g		20g	1g	
[1], n = 20, median	7.80[a]	n.d.		9.19	9.87	2.18
Mean	7.73[a]			9.18	9.91	
SD	0.44			0.21	0.31	
RSD (%)	5.7			2.3	3.1	
[2], n = 20, median	10.19	10.54	1.07	11.38	11.13	12.08
Mean	10.26	10.56		11.47	11.8	
SD	0.57	0.55		0.82	2.85	
RSD (%)	5.6	5.2		7.2	24.1	
[3], n = 20, median	308.0	334.1	1.65	312.2	325.9	18.50
Mean	301.5	334.3		314.1	330.1	
SD	16.41	21.1		8.65	37.2	
RSD (%)	5.4	6.32		2.8	10.6	
[4], n = 20, median	133.0	143.6	4.16	138.5	135.2	2.02
Mean	134.6	139.6		138.3	142.4	
SD	6.9	14.08		5.44	7.74	
RSD (%)	5.1	10.1		3.9	5.4	
[5], n = 10, median	28.68	33.13	4.11	27.46	22.60	1.30
Mean	30.14	34.36		29.57	23.60	
SD	9.31	4.59		6.96	7.94	
RSD (%)	30.9	13.35		23.54	33.6	
[6], n = 20, median	13.74	17.24	1.31	15.18	11.42	27.51
Mean	14.34	17.13		15.84	18.87	
SD	1.76	1.54		2.77	14.53	
RSD (%)	12.3	9.0		17.5	77.0	

n.d. : not determined.

Critical value for the F-test is 2.2 (2.9 for [5]). Values above the critical value are were underlined

3.5. Evaluation of the results on the basis type of ores

3.5.1. [1] ore

A diagnostic leach procedure according to the method of Lorenzen (1995), involving alternating leaches with acids and NaCN solution, was used to identify minerals with which Au is associated in this sample. It was found that the highest concentration of Au was liberated after digestion of the sample with nitric acid, which attacks the sulfides. The silicate phase of the sample was also found to contain appreciable amounts of total Au (20–30%). According to thet-test, a significantly higher result was obtained with the lead fire assay than with either the AR or NaCN leach for this ore. Roasting of the sample prior to the cyanide leach was found necessary. Without roasting, the recovery of Au was only about 6% of the fire assay recovery.

3.5.2. [2] ore

The arsenic content of the sample was high, 6.61%. The highest recovery was obtained with the fire assay method, where the Au contained within the crystal lattices of the arsenopyrite and silicate minerals was released upon fusion of the minerals. Leaching with NaCN does not liberate all the Au. According to the t-test, the difference in favour of the fire assay method was statistically significant for the NaCN leach, but not for the AR leach. Table 3 shows that, the grain size did not become smaller by increasing the grinding time and, consequently, the grinding time did not have any effect on the repeatability of the Au results (Table 7).

3.5.3. [3] ore

Grinding of the sample to a finer grain size cause the standard deviation of the Au results to increase. According to the F-test result (Table 7), the difference was statistically significant. However, the RSDs of the results were very low compared to the RSDs of the certified reference samples presented in Table 4, making it questionable to draw the conclusion that Au nuggets might be joining together and the sample becoming more hetrogeneous owing prolonged grinding. What can be stated is that increased grinding time and smaller grain size did not give better repeatability. The highest Au values were obtained with the cyanide leach on a 250-g sample and the lowest SD with the AR leach on a 20-g sample. This is in agreement with the fact that Au was present as visible Au. The slightly lower results obtained with the Pb fire assay might be due to the extremely high Au concentration of this sample. Upon refusing the slag, it was found that about 5% of the Au remained in the slag.

3.5.4. [4] ore

The sulfide content of these sample was low, at 0.03% S. Table 8 shows that all methods gave equivalent results, with the NaCN leach method giving a higher standard deviation value than the other two methods. Increasing the sample size from 20 g to 250 g gave higher results (Table 10). A t-test value of 6.4 was obtained, indicating a significant difference in the results. This may be due to the large size of the sample which increased the probability of having more of the larger nuggets in the sample. The smaller grain size of the sample again gave inferior repeatability, similars that of [3] sample.

3.5.5. [5] ore

The Ba content of this sample was high at 18%, indicating the presence of the quartz–barite lenses. Increasing the grinding time to produce a sample of smaller grain size lowered the variance of the analytical results for this sample significantly (Table 7). For this reason, only the finer grain size fractions of splits A and B are considered in Tables 8–10. Nevertheless, the RSDs of the results of the 20-g subsamples obtained in the three methods were quite high, between 16 and 31%, indicating that Au was hetrogeneous distributed in the sample. The highest results and the lowest RSD were obtained in the NaCN leach determination method of 250-g subsamples.

3.5.6. [6] ore

According to the results of the 20-g subsamples presented in Tables 8 and 9, the three analytical methods gave equivalent results for this sample. The variance of its results was higher than the other samples, but not significantly higher, for the finer particle size sample. The highest Au value and the lowest SD values were obtained by the NaCN leach determination method of the 250-g sample. The high SD value shown in Table 10 of the results by the AR leach determination method 1-g samples indicated the presence of Au nuggets.

3.6. Conclusion and recommendations

The crushing and splitting procedures produced subsamples of equivalent Au content. Further comminution of the sample, after the routine grinding, improved the subsample representativity in only one case: the [5] sample. For three of the ore samples ([1], [4]and [5]) increasing the sample size from 1 g to 20 g did not change the variance of the results significantly. Increasing the sample size from 20 g to 250 g did not give a significantly lower SD except for the [5] sample.

A sample weight higher than 250 g was needed for ([4],[5] and [6]) samples in order to obtain RSDs equivalent to those obtained by the laboratory reference samples. A significant difference between the results of the fire assay and the AR leach method was found only for the refractory ore of [1]. A significantly higher variance for results of [3] sample was obtained by fire assay method than that obtained by AR leach method. This is due to the fact that sample had unusually high Au content of the sample and fire assay method gave low recovery results. For the three ore samples ([1],[2] and [3]) the NaCN leach results were significantly lower than fire assay results. For the other three ore samples ([4],[5] and [6]) the results did not differ significantly. A study of the type of the analytical method chosen and the size of the sample was taken of a particular gold ore could be important in term of amount to financial savings. The present study showed that both the AR and NaCN leach methods gave good recoveries for Au in various types of Au ores and thus they could be applied as alternatives for the fire assay method.

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