Studies on the determination of gold in geological samples without separation by ICP-OES

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ABSTRACT

Fire assay is the most common technique for the determination of gold and other precious metals in rocks and ore samples, it is generally an accurate technique. However, with the development of modern laboratory techniques such as Inductively Coupled Plasma – Optical Emission Spectrometry (ICP – OES) and Inductively Coupled Plasma – Mass Spectrometry (ICP – MS), ICP's methods have become available which are rapid methods for the determination of small concentrations of gold in rocks and ore samples. A simple analytical method for the determination of gold in ore samples using ICP – OES is reported, the interference effect of the other elements have been studied on two wavelengths of gold 242.795 nm. and 267.595 nm. with detection limits 10 ppb and 5 ppb respectively. The results show that this method can be successfully applied with an error about 7.6% in ore sample. This method is fast, consumes small amount of sample compared with fire assay.

Key words*:* Determination, Gold, Geological samples, ICP-OES
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INTRODUCTION

Gold has an inestimable effect on human history; it has been crafted, mined, worshipped, blundered, fought over and traded for thousands of years. Its initial attraction is its color which is directly related to its purity, an eye-catching and characteristic bright yellow with a soft metallic glint. Gold can be hammered into very thin sheets, drawn into wires, cast, carved, polished, heated without tarnishing and easily combined with other metals to make alloys.

Gold is very stable over a wide range of conditions, so it is very widespread in the earth's crust. While its overall concentration is very low (about 5 mg / ton of rocks), rich concentration of gold, forming ore deposited are known world wide.

Accurate analysis and ore reserves are two of the most important functions of professional geologists in gold mine development. Fire assay [1] and [2] remains the most common technique for the determination of precious metals in rock and ore samples. The accuracy of the fire assay technique is satisfactory for the analysis of the vast majority of precious metal-bearing ores.

However, there are problems associated with the fire assay method which are complex and not very well understood. The examples of high recovery rates in some cases of apparently more than 100% and the results obtained in micro-analytical studies both indicate that there can be inaccurate.

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Inductively coupled plasma optical emission spectrometry (ICP-OES) is a powerful and time-saving method with multi-element capabilities [3].

Geology of gold

Natural gold has cooled from a molten state. In fact, gold is transported through the earthˈs crust dissolved in warm to hot salty water. These fluids are generated in huge volumes deep in the earthˈs crust as water-bearing minerals dehydrated during metamorphism. Any gold present in the rocks being heated and squeezed is sweated out and goes into solution as complex ions. In this form, dissolved gold along with other elements such as silicon, iron and sulpher migrates wherever fractures in the rocksˌ allow the fluids to pass. This direction is generally upwards to cooler regions at lower pressures near the earthˈs surface. Under these conditions, the gold eventually becomes insoluble and begins to crystallize, most often enveloped by masses of white silicon dioxide, known as quartz. This association of gold and quartz forms one of the most common types of "primary gold deposits".

Veins and reefs of gold-bearing quartz can occur in many types of rock, for example around granites, in volcanic rocks or in regions of black slate, but in most cases these host rocks are not the immediate source of the gold. For such an apparently simple element, the mineralogy of gold is quite complex, gold can occur in a wide variety of forms. In massive quartz reefs, gold occurs as disseminated, irregular grains, scales, plates and vein lets with microscopic dimensions and as larger compact, reticulated, spongy or hackly masses or slugs.

Other important metal-bearing minerals can also be found in the quartz reefs with the gold, the presence or absence of these minerals can be used to help classify the type of gold field. The most common and widespread are pyrite and arsenopyrite. Sulphides of lead, zinc, silver, bismuth and antimony also occur and may be locally abundant in some gold fields.

This study is based on representative sample selected from Mahd Ad Dahab, Mahd Ad Dahab is situated in the western region of the Kingdom of Saudi Arabian (KSA) known as Hejaz in the Al Medinah Province (figure 1) [4] Mining is carried out by underground methods with a total tunnel development in excess of 60km and a metallurgical plant.

In 2007, Mahd Ad Dahab mined and processed approximately 183,425 tones of ore at a grade of around 11.1 g/t of gold from underground operations, resulting in gold production of approximately 58,256 ounces. In addition, the mine also processes reclaimed tailings and produces copper and zinc concentrates for third party toll smelting. Figure 2 show the image of the sample.

Figure (1): Location map of Mahd El Dahab, Kingdom Of Saudi Arabia

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Figure (2): Images of gold sample, Mahd Ad Dahab, Kingdom of Saudi Arabia

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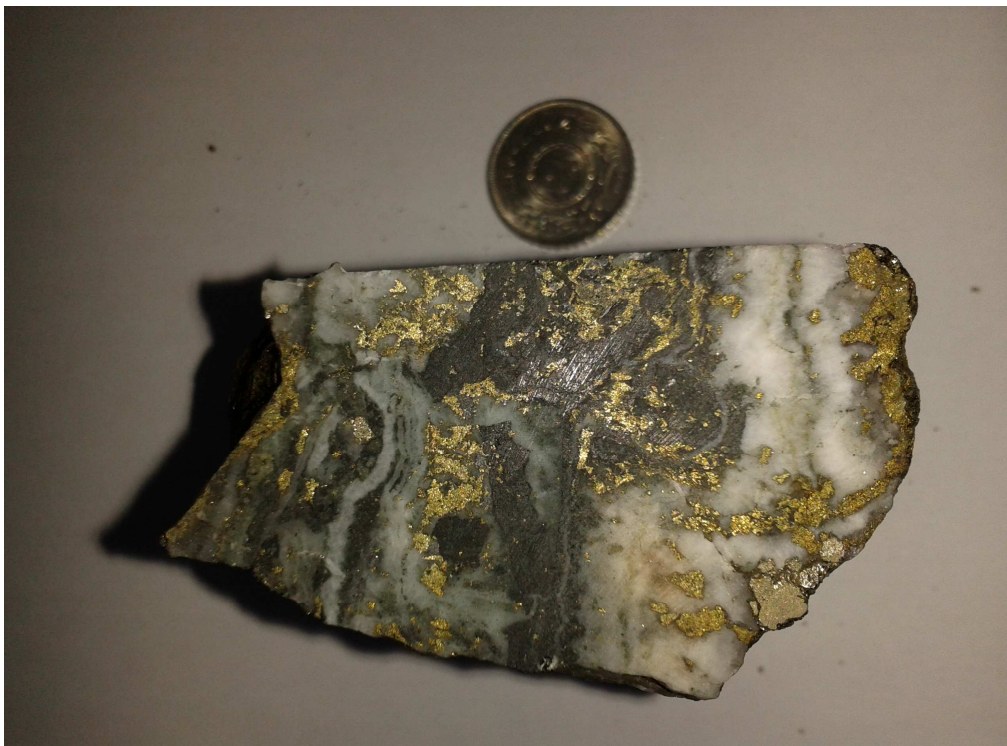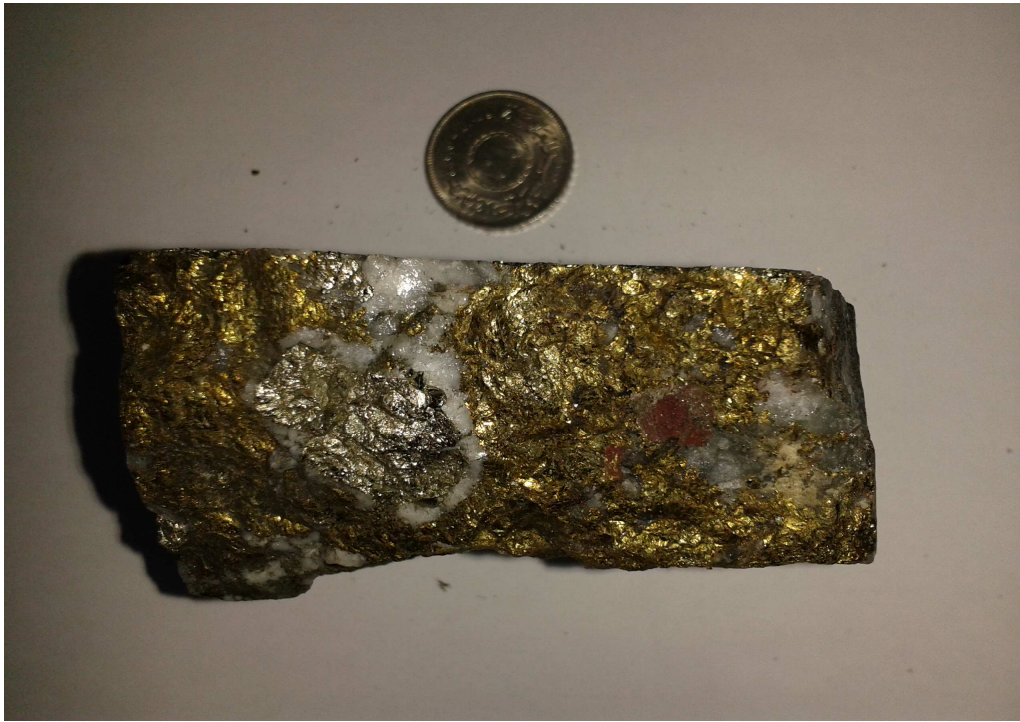
MATERIALS AND METHODS

Instrumentation
Prism ICP high dispersion, Teledyne Leeman Labs. (U.S.A.) in Nuclear Materials Authority (NMA), Egypt was used to study the method of gold analysis.

Reagents and standards
High-purity water with a resistivity >18MΩ was obtained from Human lab Instrument Co. and fed with deionized water (Aquatron). Nitric acid (5%) was prepared from high-purity concentrated HNO_3 (Burdick& Jackson, Germany). The standards used for calibration and overview of the physical operating parameters were ICP-AES & ICP-MS and ICP-OES standard solutions 1000 ppm spikes in 4% HNO_3 manufactured in Canada.
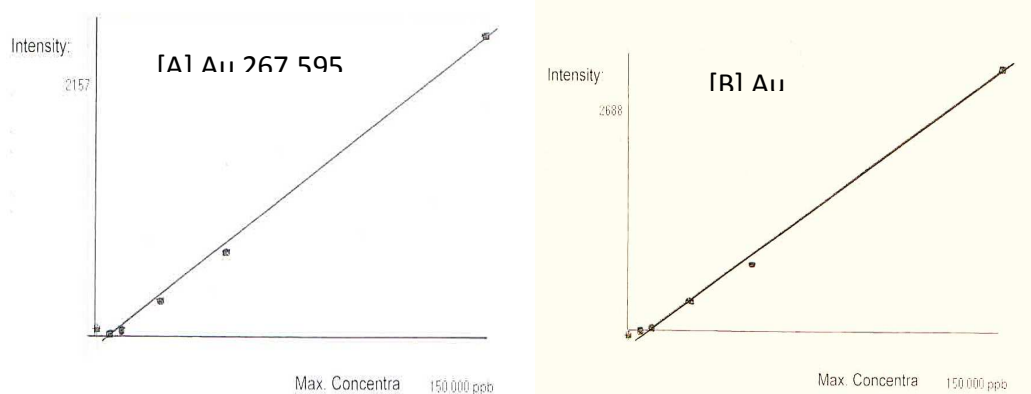
Measurements
The calibration curves of gold were performed using the gold emission lines at 242.795 nm and 267.595 nm by using standard solutions of 25, 50, 100, 250, 500 and 1000 ppb gold. Figure (3) shows the calibration curves of gold.

Experiments were carried out using 100 ppb gold to optimize the instrumental parameters. The optimum instrumental parameters selected for this study are listed in Table (1).

Table (1): Instrumental parameters for ICP-OES

RF current	1200 Watt
Coolant gas	18 L/min.
Neublizer gas pressure	36 L/min.
Replicate	3

Figure (3): The calibration curves of gold

Interference Study
The analytical protocol for the determination of gold ore was established with synthetically prepared solutions of gold, so the interference study was very important for accurate measurements, for this purpose a series of 19 interfering elements were prepared by concentration from 5 ppm to 100 ppm (10 elements) and from 1 ppm to 20 ppm (9 other elements) to make binary solutions with 100 ppb gold. These binary solutions were measured at the gold lines (242.795 nm and 267.595nm) to ensure the interfering elements of gold.

Each of these 19 elements is pure and single standard elements, Table (2) showed those elements under study and their concentration ranges.

From this study, only nine elements (U, Th, Cu, Cr, Co, Ca, Ni, Mn and Zr) caused interference during the determination of gold.

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Table (2): The interfering elements for this study

Element	Conc. Range (ppm)	Au at 242.795 nm.	Au at 267.595 nm.
Single Au	100 ppb	98.45	98.56
Al	5 – 100	101.01	102.01
Ca	5 – 100	15.2	9.91
Cr	5 – 100	54.07	39.07
Cu	5 – 100	39.31	36.38
Ni	5 – 100	2.91	4.64
Fe	5 – 100	98.91	99.08
Mg	5 – 100	99.31	99.91
Mn	5 – 100	96.18	n.d.
U	5 – 100	34.3	764.89
Th	5 – 100	491.78	18.18
Pb	1 – 20	99.45	99
Zn	1 – 20	85.91	90.39
Zr	1 – 20	78.1	69.9
Ag	1 – 20	99.74	98.97
As	1 - 20	98.9	101.1
Cd	1 – 20	98.96	100.2
Co	1 – 20	73.59	131.48
Ga	1 – 20	99.7	99.65
Mo	1 – 20	101.4	100.2

RESULTS AND DISCUSSION

The spectral interference from these nine accompanying concomitants (U, Th, Co, Cu, Cr, Ni, Ca, Mn, Zr) on gold concentration was investigated, where each element was measured as a single element on gold emission line then, binary solutions of gold with 100 ppb concentration and each of these interfering elements were prepared for this purpose and measured on the same gold emission lines. The concentration of gold was recorded in each solution at wavelengths 242.796 nm and 267.5 nm, a mixture of 100 ppb Au and different concentrations of the interfering elements were prepared and measured on the same lines of gold. (Table 3).

Table 3: Apparent gold concentration in the presence of the interfering elements

Element	Conc. (ppm)	Measured gold conc. (ppb) at 242.7 nm	Measured gold conc. (ppb) at 267.5 nm
Ni	10	52.94	49.83
Cu	5	67.14	72.34
Th	50	487.5	Zero
U	50	Zero	710.42
Ca	100	78.83	77.7
Mn	50	377.99	6.86
Zr	10	67.76	69.24
Cr	5	72.25	49.78
Co	5	Zero	74.86
Mixture		573.96	697.54

Conc. = Concentration

From Table (3) it can be seen that, those interfering elements affect on the accurate determination of gold. A software program is developed to calculate the gold equivalents for each of the concomitants. We used a simple mathematical model for the interference study originally proposed by Thompson et al. [5] and Pszonicki [6, 7] to overcome the interference effect.

All analytical methods are based on the relation between an analytical signal and the concentration of the component to be determined (analyte). The concept of the analytical signal is universal. This signal would be the intensity of the radiation, absorbance, and values of various electrochemical or electrical parameters.

If the method is not totally specific, then the measured signal (R) is a function of the concentration not only of the analyte (C_d) but also of other components of the sample (C_b) that interfere in the determination.

$$R = F (C_d, C_b, \ldots\ldots, C_{bn}) \quad \rightarrow \quad (1)$$

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This is the calibration function of the method. Usually the value of this function is unknown and participation of an individual component in the emission of the measured signal can not be simply calculated on the basis of its concentration. After the transformation of this function into Taylor's series, it may be approximated locally as a surface of the first order in an n- dimensional space (over a small range of concentration). For a larger concentration range, comparable with that found in real analytical samples, approximation as a surface of the second order gives better results. The function then has the form:

$$R = K_o + K_d\, C_d + K_{b1}\, C_{b1} + ... + K_{ad}\, C^2_d + ... + K_{an}\, C^2_{bn} \quad \rightarrow \quad (2)$$

Where K_o etc. are the proportionality coefficients.

The form of this equation is too complicated for use in practical analysis but it can be simplified if the following assumptions are made:

1- The analytical signal is equal to zero when the concentration of the analyte and interferents are equal to zero, then $K_o = 0$.

2- The analytical signal is a linear function of the concentration of analyte and of every individual interferent.

3- The effect of individual interferents is independent of the ratio of their concentrations.

The total analytical signal (R) consists of the signal (R_d) emitted by the analyte, and the interfering signal (R_b). The analyte signal is a linear function of the analyte concentration.

$$R_d = K_d\, C_d \quad \rightarrow \quad (3)$$

It is necessary to note that the term " interfering signal " means the difference between the value of the total signal emitted by the sample and the value of the signal emitted by the analyte. Defined in this way, the interfering signal contains not only the real signal (R'_b) emitted by the interferent (s), but also the influence (R''_b) of the interferent on the analyte signal.

$$R'_b = K_p\, C_b \quad \rightarrow \quad (4)$$

$$R''_b = K_a\, C_d\, C_b \quad \rightarrow \quad (5)$$

Where K_p and K_a are

The relative error of the analytical result when interference is present is given by:

$$B_{Re\,l} = \frac{R - R_d}{R_d} \quad \rightarrow (6)$$

Taking into account (4), (5) and (6) we get

$$B_{Re\,l} = \frac{k_p\, C_b + k_a\, C_b\, C_d}{k_d\, C_d} \quad \rightarrow (7)$$

This equation contains three constants which are K_p, K_a and K_d. Putting

$$K_P = \frac{k_p}{k_d} \quad \rightarrow (8)$$

And

$$K_A = \frac{k_a}{k_d} \quad \rightarrow (9)$$

From (7), (8) and (9) we get

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$$B_{\mathrm{Re}l} = \mathrm{K_P} \sum_{i=1}^{N} \frac{C_{bi}}{C_d} + \mathrm{K_A C_b}$$

ANALYTICAL APPLICATION

To verify the applicability of the proposed method (model), a synthetic mixture of gold and inherent elements (U, Th, Co, Cu, Cr, Ni, Ca, Mn and Zr) were prepared. The concentration of gold present in the synthetic mixture was estimated using the calibration curves which are made earlier.

The measured concentration of gold obtained from pure gold calibration curve was subjected to the mathematical correction for interference (table 4).

Table (4): Analysis of synthetic solutions of gold in the presence of interfering elements

Conc. of interfering elements (ppm)									Conc. Of Au (ppb)			Error%
Co	Cu	Cr	Ni	Zr	U	Th	Mn	Ca	Added	Meas.	After corr.	
5	5	5	10	10	50	50	50	100	50	73.9	50.01	+0.02 %
5	5	5	10	10	50	50	50	100	150	168.0	141.0	- 6 %

The sample from mahd ad dahab was analyzed by fire assay in the central Laboratory of the Egyptian mineral resources Authority, Ministry of Petroleum, Cairo, Egypt. Table (5) shows the concentration of the sample by fire assay and by ICP-OES.

Table (5): The conc. Of gold by fire assay and ICP-OES

Conc. Of gold By fire assay	Conc. Of gold By ICP-OES	Error %
9.2 ppm	8.5 ppm	- 7.6%

CONCLUSION

For the determination of gold in geological samples, fire assay technique is the most accurate method. However, with the development of instrumental techniques like ICP-OES, alternative methods have became available which may offer the advantage of rapid determination of gold and also the advantage of the analysis of a several number of samples.

The results for the gold analysis from the present method are in good agreement with the results obtained by fire assay. This means that, the recommended method is verified in the determination of gold in ores.

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