Malaysian Journal of Science **21A**: 27-30 (2002)

Development of a non-destructive quantitative procedure for the analysis of gold in jewellery

Meor Yusoff M.S., Hairunazifah Maarop, Muhd Noorul Ehsan and **Hishamuddin Harun**

Malaysian Institute for Nuclear Technology Research (MINT), Bangi, 43000 Kajang, Selangor, Malaysia.

ABSTRACT Malaysian standard on determining the purity of gold is based on the fire assay method. But this technique has several disadvantages such as it is destructive, long analysis time and can only determine a single element. Energy-dispersive X-ray Flourescence (EDXRF) is an analytical technique offering a fast and simple elemental analysis. The technique is able to do analysis on a range of sample types from solids to liquids, powders, granules and films. Measurements can be done on the concentration range of parts per million (ppm) to 100%. One of the main benefits of EDXRF analysis is its ease of sample preparation. Precious metal analysis such as gold can be done by directly measured the sample on to the sample station. Every element present will be identified and also quantified for their concentrations.

(Gold, EDXRF, Non-destructive, Fire assay)

INTRODUCTION

Energy dispersive X-ray fluorescence (EDXRF) is a modern technique developed for fast and non-destructive analysis. It has its beginnings in 1913 when H.G.J. Mosley showed the possibility of using X-ray as an analytical tool. The technique is based on the measurement of characteristics X-rays produced from the absorption process. Elements are identified based on their characteristics energies and the quantity of element present is measured from the amount of counts produced. EDXRF had its breakthrough with the development of lithium drifted silicon detector and computer in the 1970s. In determining the purity of precious metals, EDXRF has its advantages of analyzing gold, silver, platinum and their associated metals simultaneously (1). A repeat analysis can also be done without any further loss on the precious metal.

The EDXRF laboratory at MINT started in 1994 with the purchase of a Baird EX-3000. Its major component comprises of a 50 kV X-ray tube and a Si(Li) detector. Elemental analysis can be performed from sodium (atomic no.11) to uranium (atomic no.92) with their minimum detection limits varies from ppm to 100%. In EDXRF analysis, the minimum detection limit of an element depends on the atomic number of the element as well as the environment of the sample chamber. Light elements such as sodium, magnesium and aluminium can be detected in percentage level under normal atmosphere but under vacuum, a more sensitive detection level can be achieved. In 1999 the EDXRF Laboratory purchased a transportable Jordan Valley EX-310 model to complements the need for on-site analysis as well as for demonstration and training purposes. The differences between these two equipments are explained in the Table 1.

Table 1: Differences between Baird EX-3000 and Jordan Valley EX-310

Specifications	Baird EX-3000	Jordan Valley EX-310
Detector	Silicon Lithium	Peltiered-cool Silicon
Resolution	140 eV	220 eV
Minimum detection limit for silver	3 ppm	20 ppm
Cooling system	Liquid nitrogen	Electricity
Transportability	Difficult	Easy
Application	Bench top	Bench top / Fieldworks / On-line
Cost	RM 350,000	RM 200,000

Touchstone technique is the common method used by most goldsmiths. It involves the rubbing of gold articles onto the stone. Gold dust form from the procedure will then be dissolved by acid. The different gold purity is measured by visual inspection on the leached solution colour. Even though the technique is fast but it lacks reliability and accuracy especially for article with small differences in gold content. Fire assay technique had been applied since the 16 century and the method basically involved the differences between original gold weight and after the dissolution of its associated metals. This traditional technique is the benchmark method for gold assay due to its accuracy in measurement. But the technique had its disadvantages such as it is destructive and requires a long analysis time. The destructiveness of the technique is also a drawback for those who want to assay their jewellery articles.

EXPERIMENTAL

Baird Ex-3000 EDXRF equipment at MINT was used for the analysis. It consists of a 50 watt X-ray tube that acts as the source for X-ray beam to initiate the absorption process of atoms. Characteristics X-ray produced by this process will then be channeled to the peltiered-cool silicon detector. The presence of a multi-channel analyzer card in the computer enables the identification of the elements present through their energy spectrum. Gold standards comprise of a set of gold alloy with different concentrations of gold, copper and silver were used for the quantitative analysis and the elemental composition of these standards is as shown in Table 2. These standards are produced by RM Assay (M) Sdn Bhd, an ISO 25 accredited gold analysis laboratory. The techniques used for determining gold are by fire assay while copper and silver are determined by atomic absorption spectrometry.

Table 2: Content of gold standards

Reference Standards	Elemental Content (%)		
	Gold	Silver	Copper
Gold 999	99.99	0.00	0.00
Gold 950	94.93	2.10	2.54
Gold 916	91.53	3.90	4.25
Gold 875	87.36	6.40	6.40
Gold 835	83.33	10.36	6.17
Gold 750	74.84	12.40	12.40

RESULTS AND DISCUSSION

Gold used in the making of local jewellery is an alloy comprising of the metal mixed with copper and silver. The value of fineness of gold in an article is essentially the amount of gold content in the alloy. Thus a 916 gold article means that it contains 91.6% of gold. An EDXRF spectrum of the said gold article is as that shown in Figure 1. In the spectrum, copper is identified through its K_α peak, while the dominant gold has two peaks L_α and L_β. The K_α peaks of gold were not seen in the spectrum as its energies are beyond the 40 KeV range. Silver is also identified through its K_α peak (4). When an electron from the inner K shell lost its electron as a result of x-ray bombardment, electrons from the L or M shells will try to replace this vacancy. K_α refers to replacement of electron from the L shell to the K while K_β involves the replacement of M shell electron.

Quantitative analysis was carried out by measuring the amount of counts under each identified elemental peaks. Figure 1 also shows that the K_α peak for gold and silver is very much resolved and also had less spectral interference compared to that of copper. Thus a net counting method was used for gold and silver. This technique enables the background reduction to be carried out. For the copper peak, a digital filter technique was chosen as this will help to minimize the spectral interference effect on this peak.

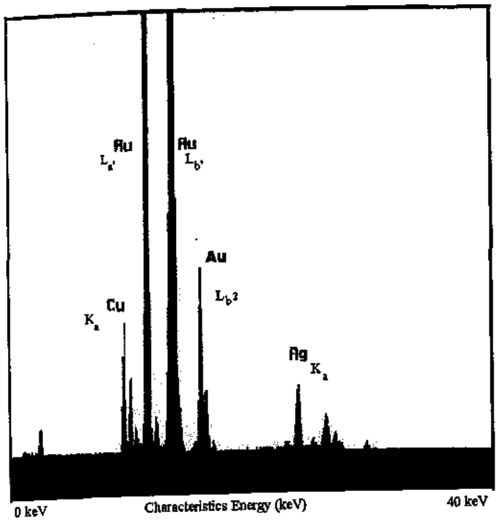

Figure 1. EDXRF spectrum for gold alloy

Characteristics X-rays are not only produced as a result of absorption process from the source but it can also be generated from other atoms present in the sample. This will eventually result in the enhancement of intensity. Nevertheless atoms are also known to absorb these energies and thus it will reduce the overall intensity. This effect is known as matrix effect and is common in XRF analysis. In gold jewellery, the different alloying elements can effect each other X-ray transmission to varying degree. A different mathematical model had to be incorporated into the quantitative determination to minimize the matrix effect (5, 6).

Concentration of analyte, $C_i = A_o + A_i I_i + \Sigma(A_{ij} * C_j)$

Where: C = concentration (%)
I = intensity (counts per second)
A = regression coefficient
i = analyte and matrix element
j = matrix element

The accuracy of this technique was then established by comparing the results of gold reference standards obtained with and without the matrix effect correction (Table 3).

Table 3: Comparison analysis on gold in reference standards with and without matrix effect correction

Reference Standards	Certified Value (ppt)	Gold content in standard (ppt)	
		Without matrix effect correction	With matrix effect correction
Gold 950	949.3	966.7 ± 0.6	948.8 ± 0.4
Gold 916	915.3	887.2 ± 2.2	915.8 ± 0.7

The result shows that when analyzed initially without any matrix effect correction, the differences between certified and EDXRF results for Gold 950 reference standard is 1.84%. This value is then reduced to only 0.4% when matrix effect correction is applied. In the Gold 916 reference standard a more drastic change can be seen where a 3.07% error registered for analysis without matrix effect correction was able to reduce to 0.1% with the application of matrix effect correction.

The precision of the technique was also determined by the repeatability test. In this case a Gold 916 standard was analyzed repeatedly for 10 times. The standard deviation (σ) was obtained and compared with results obtained from previous study (Table 4).

Table 4: Comparison of standard deviation obtained with that of other studies

Analytical Technique	References	Standard deviation (σ)
EDXRF	Seiko SEA2001, 1990 (7)	0.08
EDXRF	De Hui Yang et al, 1994 (5)	0.06
WDXRF	A. Marucco et al., 1998 (8)	0.01
EDXRF	MINT	0.07

The results show that the standard deviation value is in comparison with similar runs by other EDXRF equipments although works done by A. Marucco et al (9) using WDXRF was shown to have smaller standard deviation value. Comparing this result with that obtained from fire assay (σ = 0.1), it shows that EDXRF has better precision than the conventional technique.

This may be due to the large number of stages involved in the latter technique.

Analysis was also carried out on a series of gold jewellery which had been analyzed by the fire assay technique. The results obtained are shown in Table 5.

Table 5: Comparison of results between EDXRF and fire assay for gold articles

Jewellery Articles	Gold/silver content (ppt)		Difference in value
	Fire Assay	EDXRF	
Gold ring 1	920.1	919.2	0.9
Gold ring 2	918.6	918.4	0.2
Gold necklace 1	917.6	917.3	0.3
Gold necklace	918.8	922.2	3.4
Gold Bracelet 1	920.4	921.6	1.2

Table 5 shows that the EDXRF result is very close with that of fire assay for most of the gold. Differences in value between these two techniques ranges from 0.2 to 3.4 ppt or 0.02 to 0.3%. These values are also in agreeable with the accuracy required by the American National Gold and Silver Marking Act (8).

CONCLUSION

The EDXRF technique proves to be very useful in the determining the purity of precious metals especially for gold jewellery articles. Results from this study show that the technique is comparable to the fire assay technique.

REFERENCES

1. Yokhin B. and Tisdale R.C., (1993), High-sensitivity energy-dispersive XRF technology Part 1: Overview of XRF technique, Am. Lab., July 1993.
2. Ministry of Domestic Trade and Consumer Affairs Malaysia and RM Assay (Malaysia) Sdn. Bhd., (1994), A guide to buying gold, silver and platinum, NBS Advertising, Kuala Lumpur
3. M. Ismail M. Yunus, (1999), Implementation of Trade Description Act 1994 (Articles made from precious metals), Presented at Seminar on Gold and Precious Metals Assay, Bangi, May 1999
4. C. Yuanpan et al, (1998), Analysis of major and minor elements in gold jewellery by XRF Modified Proportion Method, Presented at Denver X-Ray Conference, 3 August 1998, Denver, USA.
5. De Hui Yang et al., (1994), EDXRF analysis of gold, unpublished report.
6. Seiko Instrument Technical Brief, (1990), Gold karat and Precious Metal Assay, Seiko Instrument, Japan.
7. Baird Technical Report, (1994), The application of X-Ray Flourescence for karat gold analysis, Baird Corporation, USA.
8. A. Marucco et al, (1998), Development of an XRF spectrometry analytical method for gold determination in gold jewellery alloy, Gold Technology, **24**, September 1998, p.14-22.