

Assaying of gold jewellery – Choice of technique

DR CHRISTOPHER W. CORTI
World Gold Council, London, England

Introduction

Ancient man first learnt the craft of metalworking several thousand years ago, making jewellery and other decorative artefacts from native gold and copper, well before the Bronze and Iron Ages. This native gold contained silver and other metals as impurities, but it did not take long for man to deliberately alloy gold with copper to improve properties during the second millennium BC. All this naturally led to the early use of gold and silver as coinage around the 7th Century BC.

Forgery of coinage

It was not long, however, before the appearance of debased or plated coins. Andrew Oddy (1) notes that coin forgery was commonplace in the ancient world, a fact which is demonstrated by the number of surviving counterfeits made of silver-or gold-plated base metal. Forgers exist for virtually all the precious metal coinages struck in antiquity. Gilding of silver and base metal (i.e. coating the object with a gold-rich surface layer) was a technique well known to ancient man (1-3). It is not surprising, therefore, that governments of antiquity were very concerned that their coinage was not debased or counterfeited and many enacted laws to protect it, with severe penalties for those convicted of forgery.

To detect forgery, coins needed to be tested. There was little indication in these early laws of how testing of coins was to be carried out. Cutting of coins was one method used and many examples of coins with cuts are known, made to ensure that the coins were not plated. Acoustic 'ringing' of coins by dropping them onto a hard surface was also practised, as was melting of the coin and its subsequent solidification. A plated

coin, when melted, results in the gold plating alloying with the underlying base metal with a consequent colour change.

However, as well as these rough and ready methods of testing precious metals, the ancient Greeks knew of 3 quantitative methods for assaying gold and silver and all 3 are still in use today: the touchstone, fire assay and density methods. We will examine each of these techniques later in terms of their relevance in today's world.

Definition of 'assaying'

At this point, it is appropriate to define the term 'Assaying'. Assaying is the technical chemical term used for the quantitative chemical analysis of a material, or object, for one specific metal or chemical element of particular interest. It is often associated with the analysis of ores and metals; in the context of gold jewellery, assaying means the determination of the gold content of the item.

Assaying of gold jewellery

Why assay?

Why do we need to assay gold jewellery in modern times? Why? – Because gold jewellery is sold on the basis of its gold content. We describe jewellery in terms of its Fineness, in parts per thousand gold, or Caratage, where 24 carat represents pure gold. In many countries, there are laws that govern the actual caratages of jewellery that can be sold and the allowable tolerances on the gold content. In many countries, the law insists that each piece of jewellery is tested – or assayed – and marked with the gold content. This is commonly known as Hallmarking when done by an independent assay laboratory. Rushforth (4) has discussed this aspect in some detail. Since the price you pay is primarily governed by the gold content, undercarating, whether by accident or by intention, is tantamount to fraud, particularly where there is hallmarking legislation giving consumer protection. As has been remarked previously (5),

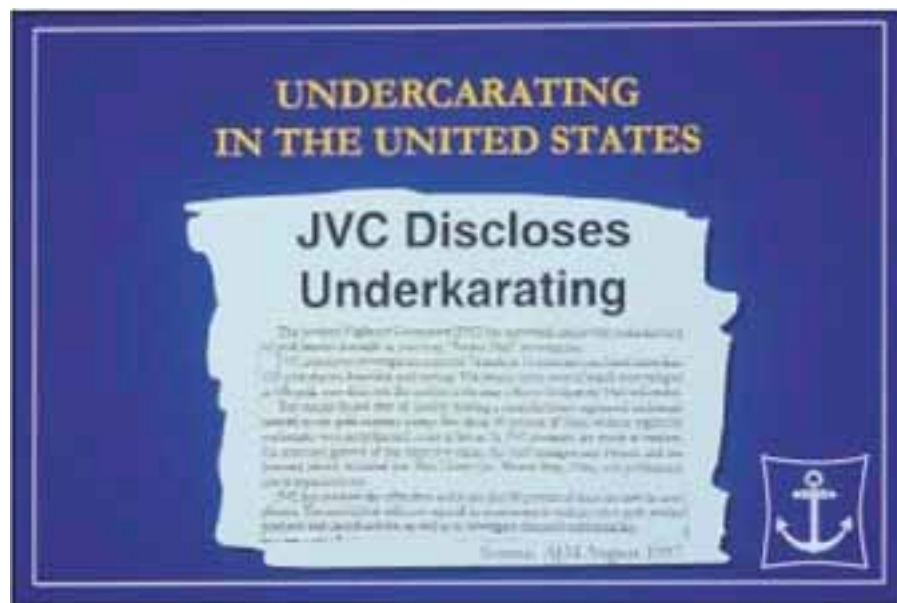


Figure 1 - Undercarating of gold jewellery in the USA (AJM Magazine, 1997)

undercarating is a major problem in some countries. Even the USA is not exempt from the problem, Figure 11

The important point is that knowledge of the gold assay is essential to the jewellery manufacturer, the retailer and the customer. That jewellery is not undercarated or debased can only be determined by testing – by assaying the item. Assaying ensures that the gold content meets legislative requirements, protecting the consumer and allowing manufacturers and retailers to operate their business on a level playing field. For manufacturers, there is also a need to assay jewellery, work-in-progress and recycled scrap during manufacture for quality control purposes. Sometimes, there is a need simply to distinguish different caratages of component parts. For buyers of scrap jewellery, there is a need to determine its caratage to enable a fair price to be paid without excessive risk.

Accuracy of assaying

Thus, there are several reasons why determination of gold content is important. The accuracy of measurement required, however, varies according to need. For Hallmarking purposes, gold content is defined in parts per thousand, so the measurement technique used must be capable of measuring to 1 part per thousand or less, i.e. in parts per ten thousand. On the other hand, to distinguish between, say, 14 carat and 18 carat components in a mass manufacturing line requires a lower accuracy, say only 1-2 wt. %.

At this point, it is worth noting that the accuracy of the assay is not only determined by the accuracy of the assaying technique, but also by the representativeness of the sample on which the measurement is taken. The only truly accurate assay value of a piece of jewellery is obtained by testing the whole piece destructively. This is obviously not a practical proposition and so some compromise has to be made. The sample size required to assure representativity is almost a science in itself (6,7).

Choice of technique

The methods of assaying are also of interest for other reasons. Apart from

cost and accuracy, factors such as speed of measurement, consistency of measurement, whether it is destructive or non-destructive, size of sample, etc also play a part in selecting the appropriate technique. The need for an accurate, quick technique, using cheap equipment and a low skill base to operate is a continuing requirement in the industry.

Today, there are a number of modern instrumental analysis techniques available as well as the 3 ancient techniques mentioned earlier. Are these old techniques still relevant in today's world? Unfortunately, for most jewellers, it is difficult to make an informed comparison of techniques. Whilst there are articles in the literature on some techniques, there have been few attempts to provide an overall review. The Assaying and Refining booklet (8) published by World Gold Council was a recent attempt and this review seeks to update that publication in a way useful for jewellers so that they can make an informed choice.

The techniques of assaying

Table 1 lists the more common techniques available for assaying of gold jewellery, each of which we shall discuss in turn. In some of the modern instrumental techniques, not only can the gold content be measured, but the other alloying metals and impurities can also be analysed simultaneously. This is of some importance in a manufacturing situation and is an additional advantage.

In several of the techniques, the accuracy of the method depends on the use of reference alloy standards, either to calibrate the equipment or run against the test sample. Optimum accuracy in some techniques requires a large number of reference alloy standards.

For hallmarking purposes, we should also note that the allowable techniques and procedures are defined in various ISO Standards

Table 1. Assaying techniques for gold jewellery

	Technique	Destructive	Comment
Ancient	Fire Assay	Yes – sample taken	Weighing
	Touchstone	Yes, rubbing taken	Colour comparison
	Density	No	Archimedes method
	Parting	Yes – sample taken	Weighing
Modern	Electronic Gold Pen	No – surface only	Capacitance decay
	X-ray Fluorescence Spectrometry (XRF)	No – surface only	Measures emitted X-rays
	Atomic Absorption Spectroscopy (AAS)	Yes – sample in solution or as solid cathode	Atomic absorption lines measured
	Inductively Coupled Plasma Spectrometry (ICP)	Yes – sample in solution	Atomic emission lines measured

1. Fire Assay (Cupellation)

This ancient technique is first referenced by the Egyptians in a Cuneiform tablet dating back to around 1360 BC, Figure 2, and is based on a gold refining technique. In its present form, it remains the most accurate technique for gold assay and serves as the standard technique against which all others are compared. It is covered by ISO standard ISO 11426:1993 and is the reference technique used by all the Assay Offices worldwide.

The technique depends upon two weighings, so analytical accuracy is related to the ability to weigh to high accuracies, i.e. the precision of the analytical balance.

The principle is based on the removal of all base metals from a small weighed sample by oxidation in the cupellation stage to leave a pure gold-silver alloy, followed by removal of the silver by dissolution in nitric acid – the parting stage – to leave a residue of pure gold which is then weighed to allow calculation of the gold content.

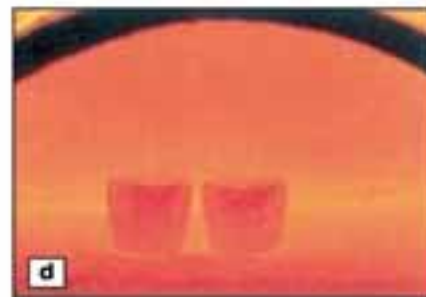


Figure 3 - Fire Assay

- (a) Sampling a gold ring by scraping
- (b) Weighing sample on an analytical balance
- (c) Wrapping gold sample and silver addition in lead foil
- (d) Samples in refractory cupel placed in furnace
- (e) Cupels after removal from furnace showing gold-silver beads
- (f) Rolling the flattened gold-silver bead
- (g) Dissolution of the silver from the 'cornet' in nitric acid



Figure 2 - Cuneiform tablet of King Burraburiash of Babylon (1385-1361 BC), recording assaying of a consignment of gold from Egypt (from reference 1).

In practice, a sample of the jewellery is taken, usually by scraping, Figure 3a, and weighed, Figure 3b. Some additional silver is added before wrapping it in a pure lead foil, Figure 3c, and placing it in a special porous crucible called a cupel. This is placed into a furnace at around 1100°C (2012°F), Figure 3d. The silver is added to dilute the gold content to 25% or less (known as Inquartation). The lead melts and alloys with the sample and added silver and then all base metals are oxidised to form a liquid slag. This slag is absorbed into the cupel to

leave a small gold-silver alloy bead, Figure 3e, which will also contain any platinum group metals present in the sample. A reference gold sample of known gold content is normally run in parallel with the sample to eliminate experimental errors.

On cooling, this bead is hammered flat and rolled to a thin strip to increase its surface area, Figure 3f. It is coiled loosely into a 'cornet' and the silver dissolved out in 2 stages in nitric acid, Figure 3g. This is why silver is added to the original sample. For successful parting of the silver, it is necessary for the gold content to be

Table 2. Fineness of gold in gold jewellery alloys obtained by cupellation (ISO 11426)

Test Alloy	Alloy Type	Cupellation Italy U [%] (s)(a)	Cupellation Germany A [%] (s)(a)
333/932	CG	333.05 ±0.16 (8)	332.96 ±0.15 (5)
376/904	CG	375.86 ±0.13 (8)	375.77 ±0.10 (5)
585.1403	CG	585.32 ±0.13 (7)	585.27 ±0.10 (5)
585/1430	CG	584.88 ±0.21 (8)	585.00 ±0.35 (5)
585/1451	CG	587.74 ±0.12 (8)	588.19 ±0.23 (5)
751/1802	CG	750.98 ±0.07 (7)	750.70 ±0.16 (5)
751/1810	CG	750.08 ±0.36 (7)	749.68 ±0.32 (5)
755/1885	CG	753.27 ±0.12 (8)	753.43 ±0.12 (5)
750/1851	CG	751.90 ±0.14 (8)	751.90 ±0.15 (3)
750/1853	CG	747.00 ±0.08 (8)	747.44 ±0.07 (5)
585 Pd WG	WG	584.88 ±0.08 (8)	585.00 ±0.00 (2)
590 Ni WG	WG	590.30 ±0.14 (7)	590.60 ±0.35 (2)
750 Pd WG	WG	750.92 ±0.13 (8)	750.50 ±0.00 (2)
760 Ni WG	WG	759.83 ±0.12 (8)	758.90 ±0.14 (2)
22/Gold G	CG	917.18 ±0.11 (7)	917.30 ±0.57 (2)
Au99/T11	CG	988.57 ±0.14 (8)	988.60 ±0.00 (2)
Standard deviation of all single determinations of Au (%)		s (123) = 0,134	s (48) = 0.215

a maximum of 25%. Otherwise the gold atoms will surround some of the silver atoms and prevent access by the nitric acid. In practice the gold content can be higher than 25%, up to 34% (9). The remaining gold cornet is pure and can be washed, dried and weighed.

If insoluble platinum group metals such as iridium and ruthenium are present in the jewellery, these remain in the gold and so will lead to high values of gold being recorded unless further steps are taken to remove them. Their presence can often be observed on the gold-silver bead after cupellation (8). Nickel and soluble platinum metals such as palladium are more difficult to remove and modified procedures to ensure their removal must be taken (8). Thus, if this method is not done properly, there will be a tendency to overstate the gold content. It helps to know the approximate gold content of the sample so that the correct amount of silver can be added. This can be determined roughly and quickly by touchstone or X-ray fluorescence, as we shall see later.

A typical Fire Assay takes about 2 hours but many samples (up to 100 at a time) can be assayed simultaneously. Where nickel or palladium are present, processing time is extended by 30 and 50 min.

respectively. Sample size is typically about 250 mg, although microcupellation techniques allow for much smaller samples of about 10mg with consequent shorter processing time (10). At such small sample sizes, ensuring that it is representative of the bulk alloy becomes more difficult.

Typically, Fire Assay can achieve an accuracy of about 2 parts per ten thousand, as demonstrated from the standard deviation values in Table 2, which is taken from Brill's detailed review (10). Brill notes that the efficiency of fire assay can be described as excellent and its performance enables it to be employed routinely in assay offices for hallmarking where up to 1000 samples per day are analysed. He also remarks that, at such outputs, fire assay (cupellation) has no competitors with regard to cost. Not bad for an ancient technique!

2. Touchstone

This technique is known to date back to the Greeks in the 6th century BC, although there is some belief that it originated in Egypt in the 12th century BC (1). An ancient touchstone found in France is shown in Figure 4. It dates back to the late Bronze Age, about 8-7th century BC (11), showing that the use of

touchstones was quite widespread in prehistoric times.

It is arguable that this ancient method is essentially non-destructive. It is based on rubbing the jewellery article on the surface of a smooth, slightly abrasive hard stone – or touchstone – to leave a metallic streak of the item on the stone. Rubbings of known standard reference alloys (touch needles) are placed beside it, Figure 5a; all are then treated with some drops of special touch acids, which are based on nitric acid, Figure 5b. This reacts with the base metals and silver to leave a coloured mark which, after drying, is compared to the colour of the reference alloy rubbings, Figure 5c. A darker colour means more chemical attack that, in turn, means less gold. It is a subjective test, in which the colour of the sample after attack is compared to that of the reference alloy rubbing.



Figure 4 - Touchstone from Choisy-au-Bac, France (from reference 11)

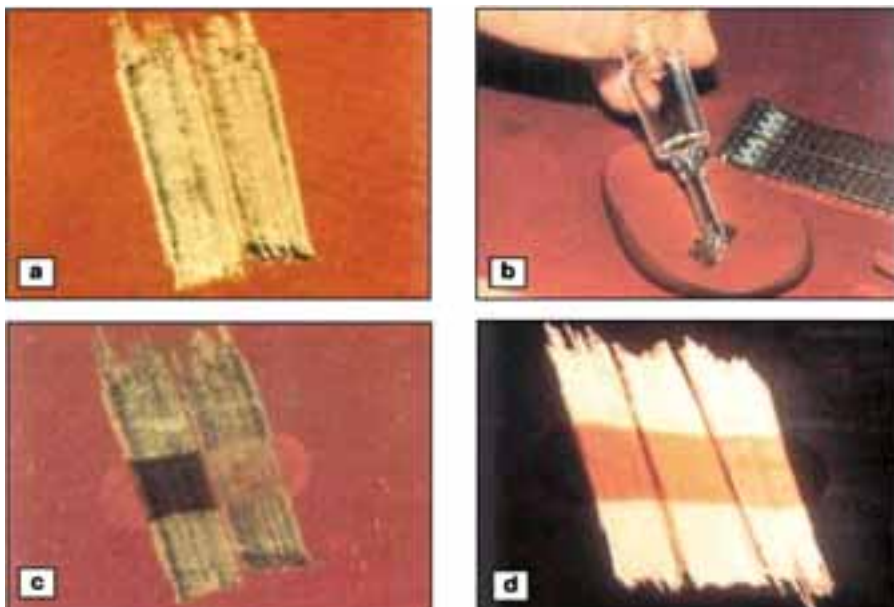


Figure 5 - Touchstone testing (from reference 12)

- (a) Rubbings from test piece (left) and touch needle
- (b) Applying touch acids to rubbings
- (c) Visual observation of rubbings
- (d) Rubbings of alloys containing (from left) 700, 720 and 750 parts per thousand gold



Figure 6 - Equipment for touchstone testing (from reference 12)

The accuracy of the method depends, in part, on knowing the silver : copper ratio. Oddy claims an accuracy of 1-2 wt % at best from historical reports. This accords well with the modern estimates of distinguishing between alloys of slightly different gold contents, if done by skilled hands, Figure 5d. Clearly, it is not nearly accurate enough for determination of a definitive assay value for hallmarking purposes but it is a quick test and useful as a sorting test and as a preliminary test prior to fire assay. It is still used in Assay Offices for this latter purpose. It is not so good for the soft high carat golds and the white golds (12).

The equipment is simple and cheap, as seen in Figure 6. Full details of testing by this method, including details of the touch acids, are given in the paper by Walchli & Vuilleumier in *Gold Technology* no. 3(12).

3. Density Method

Gold is one of the heaviest metals with a density of 19.32 g/cm^3 , whilst the alloying metals in carat golds are much lighter. Silver has a density of only 10.5 g/cm^3 and copper is even lighter at 8.9 g/cm^3 . Therefore, as caratage is lowered, the alloy density – or specific gravity – reduces. Thus

ancient man realised that measurement of density could be used as an indication of debasement of the gold.

The philosopher, Archimedes, who lived about 287 – 212 BC, discovered the principle known by all schoolboys that when a solid is immersed in a liquid, its mass is reduced by an amount equal to the mass of liquid displaced. This allows calculation of density by weighing the solid in air and then again when immersed in a liquid. It is reported (1) that Archimedes himself used the technique to check whether the craftsman who made a crown for King Hiero had added any base metals to the gold.

However, the use of the density method as a quantitative assaying technique is not recorded until much later in the 6th century AD, followed by several later manuscripts dating from 10th - 13th century AD, one of which refers to assaying of gold-silver alloys. Figure 7 shows its use in London in the 17th century.

With modern analytical balances, it is possible to weigh very accurately so, in theory, determination of density can be made to a high accuracy. The technique measures the whole piece of jewellery and is non-destructive. There are no sampling errors in this method!

In practice, however, there are a number of problems in using this method. Firstly, how do we relate the



Figure 7 - Density measurement (foreground) in London, 17th century. Fire assay can be seen behind (from reference 1)

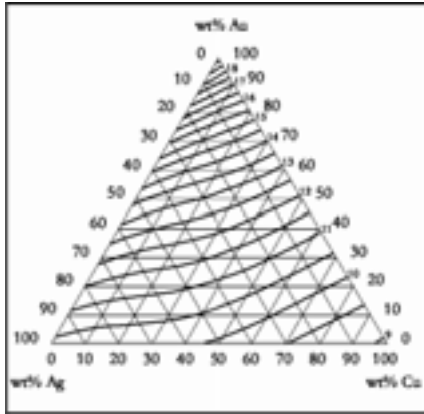


Figure 8 - Alloy densities in gold-silver-copper alloy system (from reference 13)

measured density to gold content? For binary alloys such as gold-silver or gold-copper, this is straightforward. Real jewellery alloys are rarely simple binary alloys but contain 3 or even more metals – gold-silver-copper with, perhaps, additions of zinc, nickel, palladium, grain refiners and deoxidisers. Thus, for a given gold content, the actual density of the alloy will depend on the relative amounts of the alloying metals. For 18 carat golds, typical densities range from 15.15 for red golds to 16.1 for white golds. It must be remarked that a density figure for one alloy may be identical to that of another with a differing gold content. This is clearly shown for ternary gold-silver-copper alloys in Figure 8, taken from the work of Kraut and Stern (13).

The second practical problem is that of measuring density accurately. If the jewellery contains porosity or inclusions, the measured apparent density will be lowered. It is also difficult to ensure that no air bubbles are trapped when weighing the item in a liquid. Lastly, a piece of real jewellery will also contain solders of different compositions (and hence densities) which will complicate things further. Thus, the density method is a simple, cheap and quick non-destructive method but it cannot give an accurate assay. At best, it can only give a semi-quantitative indication of caratage, unless the item is a known binary alloy without any solders. Hence its continued use in examining old coins. A full description of the method and some

of its limitations is given by Nordt et al (14).

4. Parting (False Fire Assay)

I include this assaying technique to illustrate some of the ignorance still found today in the industry around the world. Not infrequently, I have found manufacturers and so-called assayers claiming to do fire assay when all that they do is to place the sample of the gold alloy in nitric acid – the parting stage of the fire assay procedure. The assumption is that nitric acid will dissolve all base metals and silver and leave pure gold untouched. This is not true. For a start, not all the silver will be dissolved away as some will be masked by the gold, unless the gold content is 25% or less. There is also no guarantee that all other base metals will be removed completely. Certainly, any non-metallic inclusions, oxides, etc are unlikely to be removed. Thus, this method will always give false high results, so that a gold item that is actually undercarated can appear to be over the minimum gold content and within caratage. A method not to be recommended!

5. Electronic Gold 'Pen'

It is possible to buy cheap portable electronic instruments for measuring gold content, Figure 9. A probe or 'pen' is placed on the surface of the jewellery in contact with a conductive gel and the gold content read off a meter attached to it. This type of instrument usually works on the capacitance decay principle of the surface and relating it to gold content. Whilst quick and non-destructive, it is dependent on surface composition. It measures



Figure 9 - Electronic Pen

only to the nearest 1-2 carats (4-8 wt.%). It is not consistent and nowhere near accurate (15) and so should only be used as a quick sorting test to differentiate caratages.

6. X-ray Fluorescence Spectroscopy ('XRF')

Commonly known as 'XRF', this is an increasingly popular technique, finding service in both jewellery manufacturing and in assaying laboratories. In this technique, the surface of the jewellery is bombarded with radiation, usually from an X-ray tube source. This radiation impacts the atoms and causes electrons to move levels (orbital shells) with the

emission of X-rays, Figure 10, hence the term 'fluorescence'. These are collected and measured in a spectrometer. The important point is that the X-rays excited and emitted from the surface will have a defined energy with a wavelength characteristic of the atom from which it is generated. Thus, different metals emit X-rays of different wavelengths. The amount of energy emitted will depend on the relative number of atoms of that metal present. If we count that energy, we can determine the amount of that metal present. Figure 11 shows a typical spectrum from a 14 carat gold.

This technique is non-destructive but it only measures a small sample at the surface of the jewellery, typically a layer of 10 - 50 microns thick, depending on alloy composition and the metal being measured. Thus, ensuring the sample is typical of the bulk alloy is critical. Electroplating or chemical treatments, such as bombing and acid pickling which change the surface composition, will distort the analysis. Measurements can be made on a single spot, on an average of several spots or line or an area by rastering the beam over the surface. In the latter mode, an elemental distribution map can be produced.

For optimum measurement, the surface should be clean, flat and polished and at least 3mm diameter. Curved surfaces reduce accuracy as the emitted X-rays are scattered. Typically, measurements take about 2 - 3 min. with the instrument computing the results automatically. Accuracy improves with increasing measuring time.

The physics of the technique are complex and it is not appropriate to go into much detail here, as Kloos has recently reviewed this topic (16). Suffice to say that there are matrix interaction effects between metals and so the raw data collected must be corrected to yield an accurate analysis. As you will note in Figure 11, there can be overlap of adjacent wavelengths and these must be mathematically deconvoluted to separate the individual metals. Cheaper instruments may not be able to *quantitatively* separate metals with overlapping curves due to their poorer resolution. Zinc is a typical

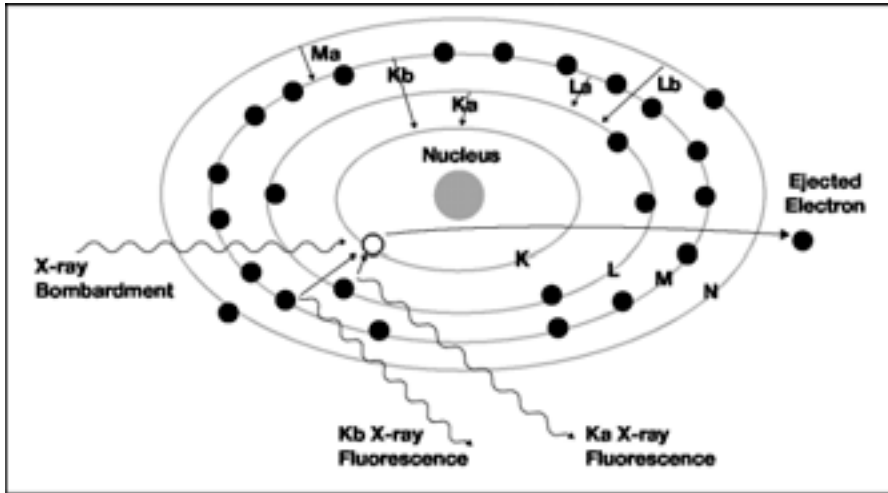


Figure 10 - X-ray Fluorescence: the photoelectric effect (from reference 16)

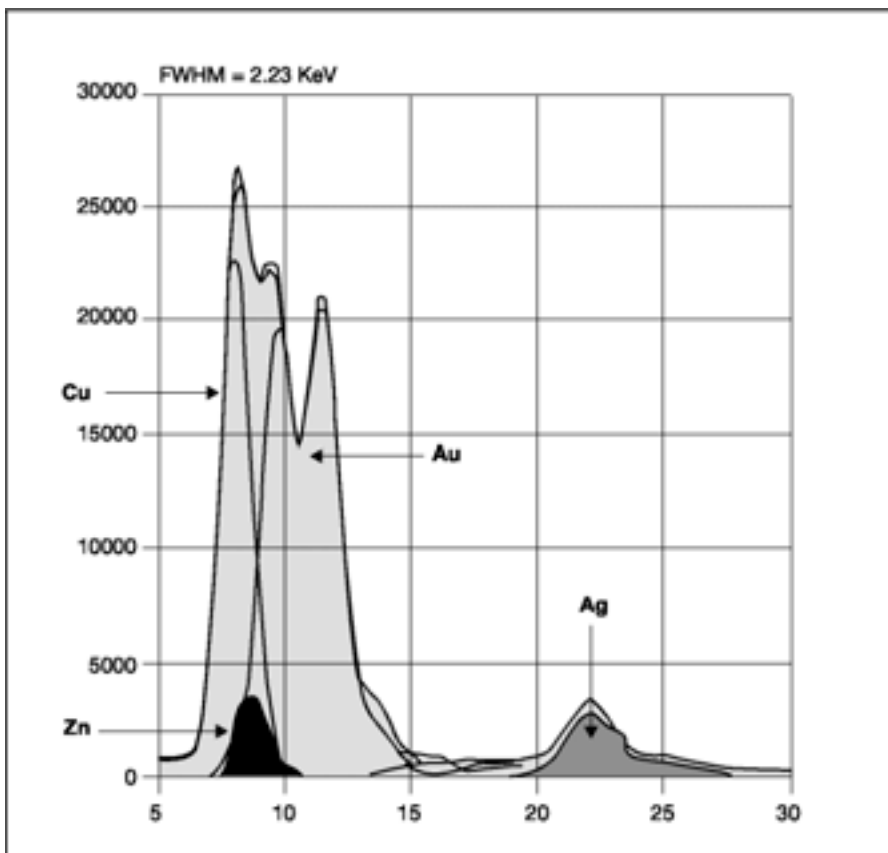


Figure 11 - X-ray spectrum from a 14 carat yellow gold (from reference 16)

example of this problem in gold alloys

The accuracy of the technique depends, therefore, on the correction models used in the software as well as the physical conditions of measurement. Therefore, the instrument needs to know what metals are present and to measure them all, if accurate values for gold are to be obtained. The spectrometer commonly used is the energy dispersive type, which collects and measures the whole spectrum of X-radiation simultaneously, which allows all metals present to be analysed. A more accurate type is the wavelength dispersive spectrometer, which measures only one metal at a time but it is more expensive.

Accuracy is significantly improved by calibrating the XRF using standard alloys of known composition and close to that of the unknown sample. In some instruments, such calibration is done by the XRF manufacturer and stored in the instrument, so that it can be used without the need for further calibration during use. According to Brill (10), XRF can measure gold to 0.75‰ (parts per thousand) under optimum conditions but for microXRF, typical of many gold assaying instruments, an accuracy of 0.2 – 0.3% can be achieved with a measurement time of 3 min. Marrucco and Stankiewicz (17) demonstrated an accuracy of 0.12% was attainable in their research studies of the technique.

Thus, XRF is not quite accurate enough for Hallmarking purposes, but is close and improving every year. It finds considerable application in Assaying Offices as an alternative to touchstone for preliminary testing of jewellery. It can be used to examine jewellery by scanning

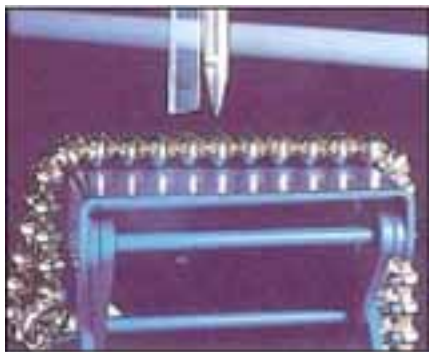


Figure 12 - XRF analysis of ball links in a coloured gold chain (from reference 10)



Figure 13 - Typical XRF instruments (a) Spectro Analytical Inc (b) X-Tester installed in retail shop in India

different areas to determine if undercarated solders or components have been used, for example, Figure 12, or if the item has been gold plated or the solders contain cadmium. This can help to select which areas of jewellery are sampled for fire assay. It is a quick and very flexible technique and can analyse for all metals present in the jewellery.

It also finds increasing application in jewellery manufacturing as a quality control tool, not only for gold content but for complete analysis of jewellery alloys and scraps. In India, one major upmarket jewellery chain has installed XRF machines in each of its shops, Figure 13b, so that customers can check that their new jewellery is on caratage. A certificate is printed out as a guarantee within 3 minutes.

There are many manufacturers of XRF instruments on the market, many with models tailored for assaying of gold alloys and jewellery. Two examples are shown in Figure 13. The price and performance of these varies. For example, cheaper models may be fitted with a proportional counter which only has a resolution of 0.5%, whereas more expensive models are fitted with solid state counters with a higher resolution of 50 ppm. However, these latter cost a factor of around 6 times more. A typical cost of suitable instruments is US\$20,000 – \$35,000, depending on performance and additional features fitted.

7. Atomic Absorption Spectrometry

Atomic absorption spectroscopy (AAS) using a multi-element spectrometer, Figure 14, is another possible technique for assaying of gold jewellery, using either solid

samples or samples in solution. The solid sample is sputtered as the cathode and the resulting vapour measured by the atomic absorption technique. Solution AAS, using samples dissolved in aqua regia, is another approach but solutions of gold standards are not stable, according to Brill (10) who concludes that AAS is not as economical as ICP spectrometry.

MicroAAS uses only a 10 mg sample but Brill claims that the results are not as good as ICP spectrometry. On this basis, AAS will not be discussed further here. Accuracy of the technique is about 0.1% at best, making it unsuitable as a routine test for fineness measurement for hallmarking.



Figure 14 - Atomic Absorption Spectrometer (from reference 10)

8. Inductively Coupled Plasma Spectroscopy ('ICP')

Inductively coupled plasma solution spectrometry (ICP) is a serious contender to fire assay for assaying of carat golds and it is finding considerable use in many precious metal analytical laboratories. For white golds containing nickel or palladium, ICP has an advantage due to its greater element selectivity (10). The technique allows for a full analysis of the gold sample, which is an added advantage over fire assay. The use of ICP for gold determination in jewellery has been discussed by Brill (18) in some detail.

In this technique, a weighed buffered aqueous solution of the gold sample is nebulised and injected into a plasma flame, Figure 15, and the spectral emission analysed in multi-element spectrometers, with simultaneous measurement of Yttrium as an internal standard. The intensity of the emission is related to the amount of metal present. Calibration against solutions of alloy standards is required. Micro-ICP allows use of samples of about 10 – 20 mg. Accuracy is 1 part per thousand for gold.



Figure 15 - Plasma flame in ICP Spectrometry (from reference 10)



Figure 16 - Inductively Coupled Plasma Spectroscopy machine (from reference 18)

ICP has a number of advantages over fire assay:

- Speed of assaying is similar to fire assay
 - Speed is faster than fire assay for nickel- and palladium-white golds
 - Smaller sample weights are required
 - There is no interference due to platinum, rhodium and iridium
 - All alloying additions analysed simultaneously, including trace elements
 - There are no emissions of toxic lead fumes as in fire assay
 - The process can be automated
- (19) The major disadvantage of ICP is its cost, typically about \$150,000. Thus, it finds use only in the laboratories of the major Assay Offices and large precious metal and jewellery companies, Figure 16.

Comparison of techniques

As stated earlier, Fire Assay (Cupellation) is the standard reference technique against which all other techniques may be compared. Despite its age, it remains the most accurate technique. In his review, Brill (10) gives much data on such comparisons in the assaying of gold in jewellery alloys. This clearly demonstrates the superiority of fire assay over all others.

The question of which technique is selected for assaying of gold jewellery turns on the specific needs:

1. Fineness determination for Hallmarking purposes.

Fire assay has the best accuracy. ICP Spectrometry is close and has a number of advantages, including an ability to provide a complete analysis. Its major disadvantage is its cost. XRF is not quite good enough, although improving, in accuracy terms but has an advantage in being non-destructive. Its major shortcoming is

that it measures only a thin surface layer that may not be typical of the bulk alloy composition.

For a rough preliminary assessment, touchstone or XRF may be used. XRF has advantages in being able to quickly scan items to determine any potential problem areas and to assist in selecting where samples are taken.

2. Quality control in production

Fire assay remains a preferred technique for accurate gold assaying, but XRF is finding increased application, with a sufficient accuracy for most purposes. A fast technique that allows a complete analysis of the alloying metals.

3. As a quick sorting test to determine approximate caratage

Touchstone remains useful for this purpose; it is quick and cheap and portable. XRF is just as quick and more accurate, but more costly. Both are non-destructible. The Electronic pen is also applicable to this sector but it does not give consistent results.

Summary

A summary of the techniques is given in Table 3. The equipment costs are only indicative. The cost of fire assay will depend on the number of samples tested per day. Where this is low, capital costs will be lower than those quoted. Brill also gives an indication of annual operating costs in his review (10), based on carrying out hundreds of assays per day.

Future developments

As we have seen, the most ancient technique of fire assay continues to dominate today. It has a number of advantages including accuracy, although it can only measure gold content. The continuing improvements to the XRF technique have already been mentioned and it is reasonable to consider that it may yet become a technique accurate enough for fineness determination. This will depend on improved detectors and software. Progress in solid state detectors is being made steadily. Wider use of ICP spectrometry remains unlikely unless the capital cost of the instruments is reduced substantially.

Table 3. Comparison of Assaying Techniques

Technique	Versatility	Sample size	Accuracy	Limitations	Equipment Cost
Fire Assay	Only gold	~ 250 mg	0.02%	Modifications for Ni and Pd	Moderate \$50,000
ICP	Complete analysis	~20 mg	0.1%	–	High \$150,000
XRF	Complete analysis	Non-destructive	0.1 – 0.5%	Surface layer, flat samples	Moderate \$25,000+
Touchstone	Only gold	Almost non-destructive	1-2%	Unsuitable for high carat and white golds	Low \$100
Electronic Pen	Only gold	Non-destructive	4-8%	Not consistent	Low \$200
Density	Only gold	Non-destructive	Poor	Only for binary alloys	Low \$500

The use of lasers to put hallmarks on jewellery is a recent development (20, 21). It is possible to envisage that the metal vapour generated from the laser engraving could be fed into an atomic emission spectrometer for direct analysis, as Brill has suggested (10) in his review. If this should materialise, then it is possible to conceive that the ancient methods for gold assaying will finally be replaced with the modern ones.

Conclusions

This review has shown that whilst the modern instrumental techniques for assaying gold jewellery have much to offer, the ancient techniques of Fire Assay and Touchstone continue to play a major role because of their advantageous characteristics, with accuracy and cost being of significance in the case of fire assay. However, XRF continues to progress and is finding increasing application.

The assaying technique selected will depend on the particular need and cost of the equipment. For the latter reason, ICP Spectrometry will only find limited application.

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