

Analysis of Carat Gold

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Introduction

The analysis of gold jewellery alloys has two objectives: first the fineness of gold must be determined with high accuracy and precision. In addition, the remaining main constituents, principally silver, palladium, copper, nickel and zinc, and the elements present in trace amounts must also be known. Such analysis applies to the starting raw materials, the process control of the precious metal alloying, the gold jewellery alloy intermediates and fabricated materials as much as the finished articles of gold jewellery. This wide range of tasks requires the strategically favourable use of classical methods such as cupellation, but also the introduction of modern spectrometric methods such as X-ray fluorescence, glow discharge lamp and ICP emission spectrometry, and atomic absorption spectroscopy.

Internationally over a number of years, the fineness determination of precious metal jewellery alloys has focused particularly on gold. Apart from the fact that gold has served as the pacemaker for the development of modern methods for all other precious metals jewellery alloys, the cupellation of gold by fire assay remains predominant as before for fineness determination having the utmost precision. This was the reason why the ISO Standards Committee TC 174 first set the cupellation method as the internationally known standard ISO 11426 (1). On the other hand it is now clear that, especially with the solution ICP spectrometric method, all precious metals can be determined with a precision that comes close to that of the cupellation of gold (2).

The analytical quality assurance of gold jewellery has several requirements:

- the fastest possible determination of all components of gold jewellery alloys including the content of trace elements; this is required for in-house quality control purposes only.
- the non-destructive determination of the composition of gold jewellery and, where possible, at least the almost non-destructive fineness determination by microcupellation or Micro ICP.

This paper does not claim to provide conclusive answers for all questions of detail in relation to the analysis of gold jewellery. As an example, the wide field of work on surface treatment and, for example, detection of soldering areas can at best be touched upon. With regard to hallmarking by the assay offices, the determination of gold fineness still involves mainly the cupellation of a representative sample of a lot of jewellery articles, i.e. with its destruction.

Determination of gold content in jewellery alloys

In the following section a number of analytical methods are presented that have been tested in long-term practice in the quality assurance of gold jewellery alloys. Some of these methods have been sanctioned as ISO Standards or are on the way to being included as standards in the working group of the ISO Committee TC 174. Other spectrometric methods are dealt with as they are customarily in industrial laboratories.

(a) Cupellation for the determination of fineness (Fire Assay)

According to ISO Standard 9202:1991 "Jewellery Fineness of Precious Metal Alloys", including their planned extension for gold jewellery with gold quality up to 999‰ gold, strictly speaking only cupellation is adequate for analysis with the required repeatability of

< 1‰ gold¹. On the other hand, it has been proved that, under the present practical conditions and those described later, a series of additional methods must be employed for the production of gold jewellery. The cupellation method described in ISO 11426:1993 (1) "Determination of Gold in Gold Jewellery Alloys - Cupellation Method (Fire Assay)" depends on two weighings, the weighing of the sample - 125 to 250 mg - and the weighing of the separated gold after the analytical process, i.e. the accuracy of the analytical result is directly predetermined by the precision of the analytical balance. In this way, under ideal conditions for pure gold and also the Au-Ag-Cu system, a standard deviation of 0.1‰ Au can be expected, a property of cupellation which is shaped by the behaviour of gold during its separation at about 1000°C, Figure 1. This state of affairs is confirmed impressively in Table 1 (3,4).

The prediction of the accuracy of the cupellation, dependent on the precision of the weighing, is reflected well by a guaranteed standard deviation between 0.1 and 0.2‰ gold. Nevertheless, it is known that alloy components such as nickel make cupellation, Figure 2, more difficult so that before the actual cupellation of gold, scorification must be instigated to remove the nickel as slag. A scorification in the presence of quartation silver is generally to be recommended for many interfering elements of this type. In the case of nickel white gold alloys, the measured analysis time of about 2h for Au-Ag-Cu coloured gold alloys is extended by about 30 min by the necessary scorification. With

¹ Footnote: 1‰ = 1 per thousand (10⁻³)

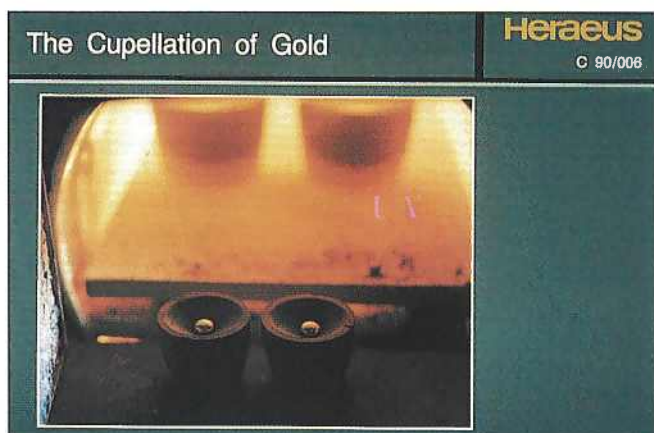


Figure 1 - The Process of Cupellation and the Gross Beads obtained thereby

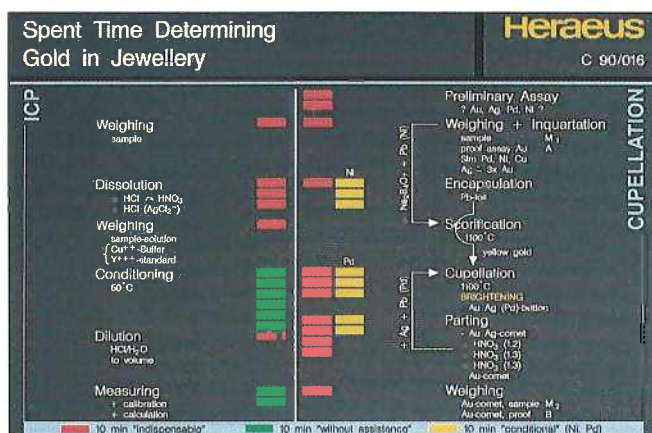


Figure 2 - Cupellation - Schematic, Compared with ICP

Table 1. 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

white gold alloys containing palladium, the repeated procedure of “inquartation, cupellation and parting” requires an additional time of about 50 min (4,5).

According to ISO 11426, the gold portion of the jewellery sample is given by:-

$$(1) W_{Au} = \frac{m_2 + \Delta T}{m_1} \times 1000 (\% \text{ Au})$$

m_1 = Mass of the sample (mg)
 m_2 = Mass of the gold cornet (mg)
 ΔT = Mean of the weighed masses of the gold proof assay minus the mean of the masses of the gold cornets of the proof assay (after cupellation) [mg]
 ΔT can lie between 0.1 and 1‰ and be positive or negative depending on the composition of the gold jewellery alloy and the temperature of the cupellation. For this reason the proof assay must be similar in its composition to the actual sample.

In order to test the resilience of this excellent aspect of cupellation method ISO 11426, many tests were carried out using nickel white

gold alloys. These results are presented in Table 2. The cupellation was also carried out with 12 synthetically prepared 750-Ni-white gold samples without the proof assay. (6)

It should be noted that the gold content has been determined correctly and precisely in spite of the additional procedural step of scorification. In the case of nickel white gold alloys the standard method indicates a repeatability, $r = 1\text{‰ Au}$.

In general, better precision is observed for the coloured Au-Ag-Cu alloys and a repeatability, $r = 0.5\text{‰ Au}$, as mentioned in the standard ISO 11426, is appropriate.

The efficiency of cupellation can therefore be described as excellent and its performance enables it to be employed routinely in assay offices for hallmarking where up to 1000 gold jewellery samples per day are analysed in this manner (7). With a large number of samples of the same type of alloy, 100 samples can be cupelled at the same time in appropriate cupellation ovens. Quartz thimbles with a dissolution basket consisting of Pt/Ir or Pt/Rh are very suitable for the dissolution stage for this considerable sample throughput. When carried out in this manner, cupellation has no competitors with regard to cost.

Cupellation can be carried out for jewellery alloys with the aforementioned precision if the conditions mentioned by ISO 11426 are observed also with regard to the elements Ag, Cu, Zn, Pd and Ni, named in the 'scope' of the standards. This does not mean that gold cannot be determined by cupellation in possibly unknown metallic matrices, or possibly by inquartation with much less silver than 2.5 times the amount of gold. Understandably, such special cases cannot be dealt

Table 2. Cupellation results of gold in white gold containing nickel after scorification

Type	Au ‰		Ni ‰	Cu ‰	Zn ‰
	found $N=12$	$S_{N=12}$			
335 ₊₁	336.11	0.20	130	455	80
590 ₊₁	590.72	0.14	160	250	100
750 ₊₁	750.77	0.23	150	60	40
synthetic - without proof assay					
750 ₊₀	749.77	0.23	60	60	40

with within the scope of this article. Of course, some hints and peripheral examples are useful for the application of cupellation:

- At the working temperature of cupellation (about 1000°C), 99% of the lead oxide (PbO) formed with atmospheric oxygen and the lead present is absorbed in the porous cupel made from magnesium oxide (MgO), 1% goes over to the vapour phase and must be drawn off. Expert waste disposal of these lead containing residues is therefore necessary.
- If cupellation is used for matrices with "too broad" a composition, unexpected events may occur. Even tiny amounts of platinum group metals (PGM) such as Pt, Rh, Ir, Ru and Os are evident when carefully observed by an analyst on the surface of the gold-containing metal beads and by their irregular behaviour at the end of the process. In principle these properties can be traced back to the poor solubility of these PGM metals even at very low concentrations in silver and gold. Although these PGMs may be found in gold jewellery alloys only rarely, nevertheless, their affect should be considered, as the cupellation of recycling material with PGMs, e.g. from dental alloys, can certainly arise²

Platinum manifests itself even at 0.4% in the beads by their characteristically matt surfaces. At higher concentrations, platinum is responsible for a retention of lead in the beads which adhere firmly to the cupel mass.

Even in the fluid phase, **iridium** separates out in the form of dark spots; these occur especially during rolling out of the beads for the nitric acid separation. The embrittlement of the beads occurs even at 0.01% iridium which also prevents the brightening of the beads.

In the presence of **rhodium** above 0.1%, a sputter of silver rich beads is unavoidable and the surface of the bead takes on a blue-grey colouring.

Ruthenium produces, even at 0.004%, blue-black precipitates on the underside of the beads with a dendritic toothed surface structure.

Osmium has less effect in this connection because of its volatilisation as the tetroxide (OsO₄); there is also no basis for its presence in gold jewellery alloys.

It is clear that the cupellation of gold jewellery alloys is sensitive to other element variations, i.e. that because of arbitrary material composition, the quality of the determination of the gold can be affected (8). For material recycling, rigorous determination of all precious metals are necessary, particularly considering the value of gold and platinum. Cupellation alone can no

² Footnote: for a further description of possible contaminants in gold and scrap and their influence on Fire Assay, the reader is referred to the Assaying and Refining Booklet (8), published by World Gold Council and described later in this issue.

longer keep pace with the current and future requirements of analysis. Consequently, spectrometric methods are usefully employed, which, apart from precision, exhibit significantly greater element selectivity in comparison with gravimetric methods and cupellation. Methods such as ICP spectrometry, glow discharge lamp emission spectrometry and X-ray fluorescence are indispensable for the quality control of gold jewellery alloys.

(b) *Determination of the fineness of gold by ICP solution spectrometry*

With the emergence of ICP solution spectrometry, gravimetric elemental analysis and cupellation can be largely replaced (5, 9-12), although the latter method still shows advantages in precision when applied to Au-Ag-Cu coloured gold alloys. However, in the presence of palladium and nickel in white gold alloys, there are advantages with ICP, especially because of the greater element selectivity.

The use of ICP for the fineness determination of precious metals in aqueous solutions have been introduced worldwide into many analytical precious metal laboratories.

Nevertheless, it should be pointed out that the equipment needed to achieve this is critical and some comments should be made (4, 5).

The spectrometer configuration - using the simultaneous measurement of the yttrium line 371.03 nm in the sequential spectrometer - has allowed so much confidence to be gained today with the method, that exclusively simultaneous spectro-meters can be equipped with effective element lines for the purpose of precision measurement as well as the remaining analytical tasks,



Figure 3 - Light detector in a multichannel ICP-vacuum spectrometer, Thermo-Jarrell-Ash Corp. (13)

namely trace determination. Such a spectrometer configuration with a single plasma source, but two adjacent spectrometers with 58 lines in each case, is presented in Table 3 with reference to the precious metal lines present and, in each case, some yttrium internal standard channels (13), Figure 3.

Table 3. The precious metal line channels installed in the Dual ICP Multichannel Spectrometer and their optical parameters (grating 1510 lines/mm)

Element	Emission Line (nm)	Order	Resolution (nm)	Spectr.
Au	Au 197.8	2	0.024	1
	Au 242.7	2	0.024	1
	Au 267.5	2	0.024	1
	Au 267.5	2	0.048	2
Ag	Ag 328.0	1	0.048	1
	Ag 338.2	1	0.048	1
Pd	Pd 340.4	2	0.024	1
	Pd 360.9	1	0.048	1
	Pd 363.4	2	0.024	1
Pt	Pt 214.4	2	0.024	1
	Pt 265.9	2	0.024	1
	Pt 299.7	2	0.024	1
	Pt 306.4	2	0.024	2
	Pt 265.9	3	0.016	2
Rh	Rh 252.0	2	0.024	1
	Rh 343.4	2	0.024	1
	Rh 369.2	1	0.048	1
Ir	Ir 212.6	2	0.024	1
	Ir 215.7	3	0.016	1
	Ir 224.2	2	0.024	1
	Ir 292.4	2	0.024	1
Ru	Ru 240.2	2	0.024	1
	Ru 349.8	1	0.048	1
	Ru 372.8	2	0.024	1
Os	Os 189.8	2	0.024	1
	Os 225.5	3	0.016	1
	Os 290.9	2	0.048	1
Y	Y371.0	2	0.024	1
	Y371.0	2	0.024	2

With the aid of these types of spectrometers, with a Paschen-Runge arrangement equipped with photomultipliers for light measurement, ICP has achieved international recognition for gold fineness determination in jewellery alloys in comparison with cupellation, as summarised in Table 4 (10-13).

Sample and standard solutions prepared according to ISO Draft N71 can now be measured in a convenient sampling mode, even automatically when the laboratory is unoccupied, and the results, including Nalimov's outlier test, calculated in a few minutes.

The rapid development in the area of ICP spectrometers are resulting in a displacement of classical Paschen-Runge systems with photomultipliers in favour of echelle spectrometer arrangements with charge transfer detectors.

As seen in Figure 4, the observation of the ICP plasma of the spectrometer systems employed above occurs in a radial manner. Today, the axial observation of the ICP plasma has proved successful.

In this way, at least a 10-fold increase in signal/background ratio

is obtained which indicates that this technique stands in good stead for the precision of gold fineness determination. This has been proved with the CCD (Charge Coupled Device) detection method of the echelle configuration.

Detailed evaluation of ICP equipment and knowledge of the necessary performance characteristics are indispensable for the fineness determination as well as for the analysis of the remaining components and traces in gold jewellery alloys; the suitability of the ICP equipment should be checked carefully

Table 4. International 'round robin' analysis for the determination of the fineness of gold in gold jewellery alloys - comparison of cupellation ISO 11426 and ICP ISO/N71

Test Sample		Cupellation Italy U		ICP Switzerland A		ICP Japan I		ICP Germany D	
		% Au	s(n) % Au	% Au	s(n) % Au	% Au	s(n) % Au	% Au	s(n) % Au
2409	Pd WG	752.83	0.06 (8)	752.90	0.28 (6)	751.84	0.81 (6)	752.38	0.36 (6)
2410	Ni WG	335.85	0.29 (6)	335.60	0.15 (6)	377.51	0.69 (6)	335.94	0.28 (6)
2411	CG	586.11	0.14 (8)	586.90	0.41 (6)	583.41	0.52 (6)	586.28	0.26 (6)
2412	Ni WG	753.49	0.13 (8)	752.60	0.42 (6)	753.37	0.69 (6)	733.05	0.21 (6)
2413	CG	333.07	0.16 (8)	332.50	0.15 (6)	332.83	0.29 (6)	332.80	0.28 (6)
2414	CG	750.28	0.13 (8)	751.80	0.41 (6)	750.48	0.92 (6)	750.06	0.33 (6)
9 ct.	CG	376.81	0.22 (8)	375.90	0.47 (6)	377.25	0.42 (6)	-	-
9 ct.	Ni WG	377.80	0.04 (8)	377.60	0.26 (6)	378.72	0.48 (6)	-	-
22 ct.	CG	917.05	0.21 (8)	916.60	0.29 (6)	916.82	0.73 (6)	-	-

Test Sample		Cupellation Germany W		ICP(In) Germany G		ICP Germany H		ICP Germany W	
		% Au	s(n) % Au	% Au	s(n) % Au	% Au	s(n) % Au	% Au	s(n) % Au
2409	Pd WG	753.40	0.17 (5)	752.90	1.5 (6)	752.59	0.8 (5)	754.20	0.14 (5)
2410	Ni WG	336.00	0.10 (5)	335.40	1.1 (6)	336.15	0.4 (5)	335.70	0.25 (5)
2411	CG	585.80	0.12 (5)	587.10	0.3 (6)	586.10	0.5 (5)	586.05	0.43 (5)
2412	Ni WG	753.60	0.05 (5)	752.80	1.1 (6)	752.20	0.5 (5)	754.00	0.60 (5)
2413	CG	332.70	0.02 (5)	333.10	1.1(6)	332.70	0.5 (5)	333.10	0.11 (5)
2414	CG	750.40	0.14 (5)	751.70	1.0 (6)	750.90	0.4 (5)	751.27	0.13 (5)
9 ct.	CG	376.60	0.06 (5)	-	-	376.81	0.1 (5)	375.80	0.10 (5)
9 ct.	Ni WG	376.70	0.26 (5)	-	-	377.07	0.2 (5)	376.20	0.18 (5)
22 ct.	CG	917.70	0.21 (5)	-	-	917.23	0.8(5)	916.20	1.07 (5)

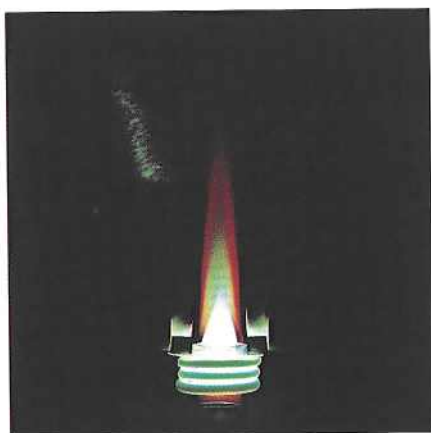


Figure 4 - Radial ICP Plasma Observation and the 2 Light Intakes of the Dual Spectrometer

before purchase due to rapid advances in development in the fields of excitation, optics, electronic light measurement, computation, etc.

From a practical point of view, some observations are necessary for the ICP emission analysis of gold jewellery alloys for gold fineness determination which should contribute to avoiding errors.

Weighed samples of alloys with high silver content - turnings or pressed thin strips are optimal - must be etched with nitric acid, as foreseen by ISO Method N71, in order to depassivate the surface of the turnings prior to adding the hydrochloric acid. If silver chloride precipitates out, the gold determination is not impaired as long as AgCl particles do not hinder the nebulisation of the solution. The cross flow nebulizer normally employed is not sensitive to this effect; also, about 50 mg/l of silver complex can be held in solution in the solution mixture.

It is important that, with the high accuracy requirements, sample solutions and standard solutions are quickly prepared from the appropriate stock solutions (by weighing) with simultaneous weighing of the yttrium internal standard into the solution in order to compensate for a weight loss of stock solutions by evaporation. The longer storage of stock solutions - samples and standards - results in a certain loss of stability because of the influence of derivatives of nitric acid on the strongly oxidising gold ion. In order to limit this effect, ISO Method N71 provides for the high hydrochloric acid concentration of the solution medium, in order to limit the reducing effect by

formation of the NO^+ (nitrosyl) cation. A possible measure, to counteract this instability effect of the gold solution, is the addition of sulfamic acid or urea, to what extent such a variation in the ISO method becomes established will be determined by future conferences of the Standards Committee.

At present, the ICP method is, compared with cupellation, the more meaningful technique for the analytical determination of the gold content. The higher sensitivity of ICP emission spectrometry makes the non-destructive analysis of gold jewellery articles on the basis of samples of about 10 mg possible; (likewise so-called microcupellation with similar sample weights has been proposed). Including the touchstone test, what follows below will deal with the performance of those types of micro detection processes for the fineness determination of gold in gold jewellery alloys or articles.

Gold and its purity control

The determination of gold fineness and the measurement of the concentration of trace elements for certification of the purity of gold merge together. ISO Standard 11426 offers for the future the possibility of analysing

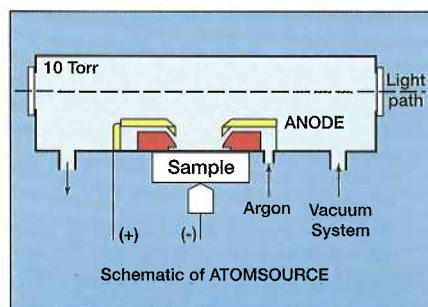


Figure 5 - Diagram of the Atomic Source of the solid AA Spectrometer

gold up to a purity of Au 99.9% by cupellation. Higher finenesses should be restricted to measuring the gold content by difference after determining the concentrations of all impurities.

Fundamentally, optical emission spectrometry is capable, on the basis of its detection performance for the trace elements of interest in fine gold (and Ag, Pd and Pt), of fulfilling the purity criteria; here ICP, spark emission spectrometry, GDL (Glow Discharge Lamp), and solid sample AAS should be considered, Figures 5 and 6.

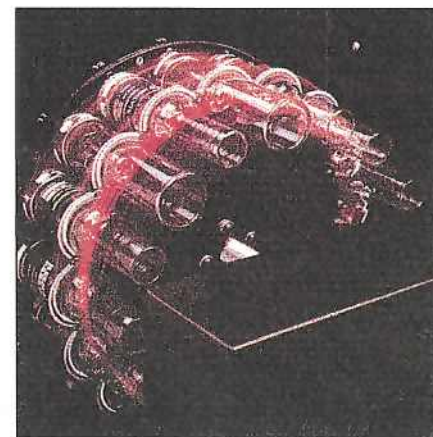


Figure 6 - The HCL turret

The determination of gold, alloying elements and trace contents in gold jewellery alloys using multielement spectrometers

The required depth of analytical information can vary greatly. In the following, however, it should be assumed that self-sufficiency of process-oriented quality control is kept in mind so that multielement analysis can be carried out with minimal expenditure on equipment and above all favourable throughout speeds. Apart from the optimum equipment for this - X-ray fluorescence and GDL emission - several additional methods - ICP, AAS, solid AAS - are dealt with which are just as suitable for element analysis even if they require more time.

The problem with the multielement methods discussed is that they, not being especially representative, do not achieve the exact gold content measurement at the high accuracy required for gold fineness and so cupellation of gold by fire assay must always be considered.

(a) Determination of the composition of gold jewellery alloys by X-ray fluorescence spectrometry

When considering X-ray fluorescence, one generally decides in favour of the **wavelength dispersive (WD)** spectrometer (over energy dispersive spectrometer) which, with regard to gold jewellery alloys, produces a surprising performance in the determination of alloy contents even, for example, trace levels. As this breadth of performance is optimised by the sequential spectrometer by specific selection of X-ray lines, crystals, the scintillation counter and the gas flow counter, what follows should represent the present performance of WD X-ray spectrometers. WD multichannel X-ray spectrometers with their material specific design, mostly equipped with gas-filled proportional counters for elements of interest, should not be forgotten in this context.

Because of the limited dynamic range of scintillation and gas flow counters, problems with impulse counting and therefore with the accuracy of the analysis occur with high element concentrations due to the "dead time".

The X-ray fluorescence spectrometer is, among spectrometric equipment, the most stable instrument over a long period of time. The great consistency of the excitation parameter for the X-ray tube ensures that the X-ray quantum yield is very stable. The impulse rates of element lines with discrete energies emitted from the sample excited in this way are approximately constant, e.g. 9.17 keV for Au L α radiation, for the same gold jewellery alloy. The impulses collected in this measurement time allow the estimation of precision of the gold

determination.

A jewellery alloy with 750‰ Au produces an impulse rate of about 100,000 (Imp/sec) in the Au L α channel; it is possible to obtain 10⁶ impulses in 10 seconds and therefore a precision of 0.75‰ gold; with a measurement time of 100 sec, a gold signal is obtained which exhibits approximately the precision of cupellation. X-ray fluorescence with this prerequisite puts great demands on the sample surface; the emergence of Au L α radiation (9.17 keV) amounts to 10-50 μ m. This means that calibration, recalibration and measurement of the actual samples must take place on smooth surfaces with the minimum uniform roughness. A wet polish under water with SiC abrasive paper of 400 grain size proves its worth for the final surface preparation. Under these conditions polishing sludge containing gold can be recovered relatively simply.

The measured impulse rates are well defined for a single sample of one composition with homogeneously distributed alloy element constituents. This is a peculiarity of X-ray fluorescence spectrometry. For the final determination of concentrations, e.g. of Au, Ag and Cu, many standards are, of course, required in order to determine, with a so-called empirical multivariable regression, intensity sensitivity factors as well as the mutual element influencing factors (alphas) characteristic of X-ray fluorescence spectrometry. These are characteristic of the element X-ray radiation of concern.

The analysis technique of X-ray fluorescence permits non-destructive measurement and fully automatic interpretation of the method including recalibration and

type standardisation. In this way and on the basis of its high precision, which, particularly for gold, approaches that of cupellation, X-ray fluorescence is the preferred method for quality control of gold jewellery alloys. Using the sequential spectrometer, a full analysis is available in a few minutes.

On the basis of its flexibility with regard to detectors, collimators, crystals, etc., the optimum performance for X-ray fluorescence is obtained today by the sequential spectrometer. The full goniometer range of $2\theta = 155^\circ$ can be covered in 2.5 sec so that, in comparison with multichannel spectrometers, the time factor no longer has such a large influence.

On the grounds of cost, wavelength dispersive (WD) XRF can, in many cases, be replaced by the more cost favourable **energy dispersive (ED) XRF**. An essential difference of the two systems is based on the different detection of X-ray radiation. With ED systems, the measurement time must be increased compared with WD systems. The fundamental relationships are shown in Table 5.

In Tables 6 and 7, the excellent performance of the ED-XRF spectrometer with a Si(Li) semiconductor detector is highlighted for gold jewellery alloys compared with the cupellation of gold and the ICP spectrometry of all components of interest (14).

In connection with rapid methods of investigation, a further Mini-ED-XRF system is described later which represents, from the perspective of the cost/use relationship, the most surprising new development in the sector of analysis instruments for gold jewellery alloys.

Table 5. Operating conditions and the optimum impulse rates of detector systems of three XRF spectrometer systems

Spectrometer X-ray tube excitation	Counter	Maximum Impulse Rate (counts sec ⁻¹)
WD 50kV/50mA	scintillation	7×10^5
WD 50 kV/50mA	flow Ar/10% CH ₄	10^6
ED 33kV/1 mA constant	proportional Xe-filled 512 energy channels	30,000
ED 50kV/1 mA maximum	Si(Li)-semiconductor liquid N ₂ cooled 4096 energy channels	25,000 50,000*

* in future with digital pulse processor

Table 6. X-Ray Fluorescence vs. Fire Assay. Result comparison - assorted 14 carat pin dips (rolled/sanded)

Pin Dip Sample #	X-Ray Data	Fire Assay Data	Difference
1	Au 58.194% Ag 6.831% Zn 5.832% Cu 29.143%	Au 58.018%	0.176%
2	Au 58.173% Ag 5.831% Zn 5.830 % Cu 29.167%	Au 58.140%	0.032%
3	Au 58.063 % Ag 6.733% Zn 5.895% Cu 29.309%	Au 58.081%	0.018%
4	Au 58.038% Ag 7.246% Zn 5.766% Cu 28.951%	Au 58.001%	0.037%

Table 7. X-Ray Fluorescence vs. Fire Assay and ICP. Result comparison. Melted homogeneous jewellery scrap

Sample/Method	Element (%)							
	Au	Cu	Ag	Zn	Ni	Fe	Pd	Cd
49692 XRF FA-ICP	59.45	25.47	9.05	4.25	0.89	0.12	0.70	0.07
	59.11	25.7		4.1	0.91	0.07	0.99	0.09
49796 XRF FA-ICP	56.43	28.66	9.59	4.19	0.70	0.11	0.27	0.06
	56.36	28.7		4.2	0.68	0.04	0.31	0.06
49362 XRF FA-ICP	60.85	24.51	9.50	4.06	0.66	0.09	0.26	0.07
	60.71	24.8		3.8	0.68	0.05	0.35	0.10
49829 XRF FA-ICP	53.77	32.08	8.26	4.65	0.84	0.12	0.24	0.05
	53.73	32.2		4.5	0.78	0.08	0.35	0.09
49646 XRF FA-ICP	56.39	27.11	11.63	4.05	0.42	0.10	0.22	0.08
	56.39	27.3		4.0	0.39	0.05	0.24	0.03
49751 XRF FA-ICP	57.07	25.48	12.11	4.48	0.50	0.11	0.11	0.13
	57.06	25.7		4.3	0.49	0.04	0.06	0.16
49751 XRF FA-ICP	56.54	29.40	8.12	4.77	0.83	0.13	0.14	0.08
	56.76	29.3		4.7	0.80	0.05	0.15	0.09

Table 8. Determination of Gold in High Carat Gold Jewellery Alloys using GDL Spectrometry

Jewellery Alloy							
Carat	Sample No.	Element	GDL: type standard		GDL: batch sample		XRF: batch sample
			(%)	v%	(%)	v%	
23	10058	Au	96.01	0.02	95.98	0.05	96.01
		Ag	3.00	0.9	2.97	1.0	2.99
		Cu	1.00	1.4	1.04	1.3	1.00
22	10056	Au	91.69	0.05	91.74	0.06	91.74
		Ag	4.00	0.8	4.04	1.1	3.98
		Cu	4.30	0.7	4.26	0.8	4.28
20	10057	Au	83.32	0.12	83.38	0.14	83.36
		Ag	11.00	0.7	10.93	0.6	10.96
		Cu	5.30	0.8	5.34	0.7	5.28
		Zn	0.40	1.7	0.38	1.6	0.40

Al, Si, Fe, Ni, Pb, Sb, Si, Te, Zn each < 0.001 %

b) Determination of the composition of gold jewellery alloys by glow discharge lamp emission spectrometry

The glow discharge lamp (GDL) as a light emission source for metallic samples has the greatest universality with respect to the analysis of main components and trace elements and this is also the case for gold jewellery alloys (15-17). This emission method is employed effectively in combination with X-ray fluorescence in order to make measurements of trace levels down to less than 10 ppm possible. On the other hand, GDL spectrometry is capable of determining high concentrations, e.g. of gold, with a precision almost equal to that of XRF. Unfortunately, the GDL method is not capable of automation; however, the simultaneous measurement of all elements of interest is possible in minutes with the vacuum multichannel spectrometer and, above all, also the trace contents of lighter elements (Si, Al, B) which cause problems with XRF.

If the GDL spectrometer has a simultaneous-sequential design, then this equipment is almost self-sufficient for metal spectrometry in the field of precious metals. In addition, the calibration and the computation are very clear, and further, a significantly smaller number of precious metal standards are required compared with spark spectrometry.

The flexibility of the method with regard to the analysis of precious metal alloys and pure precious metals has been known for some time and the GDL vacuum emission spectrometer in its simultaneous-sequential version can also be seen as the basic equipment for the quality control of gold jewellery alloys.

In Table 8, gold determination of high carat gold jewellery alloys are cited for the GDL technique in comparison with x-ray fluorescence values.

It is interesting to note that, with GDL, trace limits under 10 ppm can be detected easily. Crucial for this investigation is the fact that with GDL, gold values can be obtained which approach the precision of those of cupellation.

c) Determination of the composition of gold jewellery alloys by solid atomic absorption

This spectrometer seems to be

capable of being used for the multielement analysis of gold jewellery alloys, whereby high concentrations of Au, Ag, Cu, etc., and trace concentrations can be determined at the same time (18). In comparison with the GDL technique, the sample is sputtered as the cathode and the atomic vapour in the absorption cell measured by the atomic absorption technique with irradiation of the specific element light of the particular hollow cathode lamp at the resonance of the atomic lines. The specific element signal must be optimised in view of its detection with regard to the sputter rate and the setting of the optical parameters. At the moment there is a certain amount of empirical latitude with regard to multielement analysis of dental alloys, which points to the fact that gold jewellery alloys can also be determined with a similar quality.

d) Determination of the composition of gold jewellery alloys by solution ICP spectrometry

Multielement analysis with ICP multichannel spectrometers, also those with charge transfer detectors (CID, CCD), can be employed for gold jewellery alloys. Moreover, a measurement strategy can be recommended such as that which the Japanese standard ISO/CD 14138.2 proposes for the measurement of platinum alloys. Here platinum is used as an internal standard which results in high precision after numerical analysis (RSD < 0.1%). The element measurement lines permit measurement with a high dynamic range (10^5), serving to register trace contents as well as alloy concentrations. With regard to process control, solution methods such as ICP and AAS are significantly more time consuming - see below, for comparison, with the XRF and GDL methods which measure the metal directly. However, the ICP solution spectrometer can be employed very flexibly in the field of precious metal chemistry if rapid analysis throughput is not important.

e) Determination of the composition of gold jewellery alloys by solution AAS spectrometry

Atomic absorption spectrometers, which are generally less costly than ICP spectrometers, are of interest for the analysis of gold jewellery alloys. Regarding the FAAS detection limits of some elements which can be present in gold jewellery alloys, namely those measured with a compressed air-acetylene flame from aqueous mineral acid solution, it is worth considering the determination of the fineness of gold, Table 9.

The high quality demanded for fineness determination with an



Figure 7 - AAS Spectrometer

Table 9. Analysis of main components of gold jewellery alloys by AAS Spectrometry

Total Analysis by AAS Spectrometer (%)					
Sample	Au	Cu	Zn	Ag	Total
3488	68.75	12.90	0.50	17.80	99.95
3489	72.67	7.96	0.02	19.44	100.09
5953	58.88	18.48	1.25	21.91	100.52
X	59.81	19.26		20.68	99.75

Gold Content of Jewellery Found by Two Methods			
Sample	AA	SO ₂	AA-SO ₂
3603	76.63	76.20	+0.43
5582	74.77	74.85	-0.08
5583	74.25	74.77	-0.52
3488	68.75	68.58	+0.17
5953	58.89	58.87	+0.02
5952	58.57	58.68	-0.11
5531	48.60	48.52	+0.08
5496	37.77	37.73	+0.04
5429	56.15	56.33	-0.18
95% CL of the Mean	± 0.322	± 0.572	

accuracy better than 1‰ Au is a challenge for atomic absorption. Nevertheless, this limiting performance has been attempted. The optimal gold signal is attained with 12 mg/l gold with an absorbance of about 0.4 and a minimal measurement error.

It is well known that gold standards consisting of solutions of gold in aqua regia are not stable long-term; therefore they should be stored in the dark.

As Table 9 shows, AAS spectrometry is capable of carrying out a full analysis for dissolved samples of gold jewellery alloys (19). One should also compare the accuracy with respect to the gravimetric analysis of gold by SO₂ precipitation. Because of the limited dynamic range at the atomic resonance lines, an economical multielement analysis, such as that with ICP, cannot be carried out at present.

Rapid and economical investigation methods for the identification of gold jewellery articles

The high value of gold jewellery alloy semis, initial products or the finished gold jewellery itself generally requires a careful and, if possible, a non-destructive method of examination. This aim was not especially to the forefront in the analytical methods discussed previously but the following do have this aim - the touchstone test, microcupellation, micro ICP, micro AAS and non-destructive testing with an X-ray fluorescence jewellery tester. The touchstone test, though only approximate, has been widely applied. Because it is inexpensive to implement, it would be misplaced to disregard its current importance. However, there is no doubt that in the course of time the XRF jewellery tester will replace the touchstone test more and more.

a) The Touchstone Test

A shiny metallic streak is produced by rubbing the article of gold jewellery to be tested on a smooth touchstone, usually a smooth black quartz slate plate; about 0.5 mg of a metal layer is applied. Using so-called touch needle standards having carat specifications similar to the article under test, streaks are applied parallel to the test streak on the touchstone. The streaks are washed transversely with various strong acid mixtures (HNO₃, HCl, CuCl₂, H₂O). That touch needle

streak which shows analogous stability with respect to the test acids as the test streak indicates its carat specification.

With the widespread use of the touchstone test for the non-destructive identification of jewellery - also used frequently in assay offices - the question arises as to how precise this procedure really is. In Table 10, results are compared with cupellation. From this, a precision of about 5-10 ‰ Au is attainable with the touchstone test (20).

b) Microcupellation

Microcupellation has become established in recent years, within the context of the cupellation of gold according to ISO 11426; with only about 10 mg of material taken from concealed places of a jewellery article by scraping, microcupellation can be carried out in a short time as clearly described in Table 11.

As shown in Table 12, very accurate gold fineness are obtained by microcupellation. Of course, a microbalance is essential for the weighing procedure; otherwise the

Table 10. The gold content of ten jewellery gold samples determined by cupellation and by five analysts using the Touchstone method

Gold content %					
Cupellation	Analyst No.				
	1	2	3	4	5
57.3	56.0	58.5	58.5	57.0	58.0
58.0	57.5	58.5	57.5	57.5	57.5
58.7	58.5	57.5	57.5	59.0	58.0
59.0	56.0	57.0	57.0	59.5	58.0
59.4	59.0	59.0	58.5	59.0	58.5
72.5	72.5	74.0	74.0	73.5	73.5
73.7	73.5	75.0	74.5	75.0	74.5
74.5	75.0	74.0	74.0	74.0	75.0
75.0	75.0	75.0	75.0	75.0	75.0
75.5	74.5	75.5	74.5	74.0	74.0

usual equipment specified in ISO Standard 11426 can be employed.

c) Micro ICP

The micro ICP method is a well-validated method for the fineness determination of gold with weighings of about 10mg (22). Table 13 shows an impressive comparison between micro ICP and cupellation for gold fineness determination.

Table 11. Microcupellation and its implementation - method of the Dublin Assay Office (21)

Proposal ISO 11426 amended for small test portions	
As for ISO 11426 but with the following amendments:	
Test portion 9 mg to 10,5 mg weighed to $\pm 0,001$ mg.	
For samples containing approx. 999% gold, add 0.8 mg of copper to test portions of c.10mg.	
Lead foil 2g.	
Furnace temperature approx. 1065°C.	
Duration in furnace 8.5 to 9 minutes.	
Omit brushing precious metal buttons.	
It is optional to anneal beads after flattening them on anvil.	
It is optional to roll them but, if omitted, aim to achieve strip thickness of 0.12 mm to 0.15 mm by hammering and follow by annealing.	
Omit rolling strips into cornets if too small to do so.	
Duration of samples in acid bath (density 1.2 g/cm ³) in minutes	
Duration of samples in acid bath (density 1.3g/cm ³) in minutes	
Where platinum basket used, finally place the basket with the gold samples contained in silica thimbles for about 2 to 3 minutes in a muffle furnace heated to approx. 900°C.	

Table 12. The determination of the fineness of gold in 9 ct and 18 ct gold jewellery alloys by microcupellation

Proof Assay 0.000, 0.002, 0.004				Proof Assay -0.003, 0.001, 0.000			
Mean Proof Assay 0.002				Mean Proof Assay -0.006			
First Wt mg	Final Wt mg	Gold ppt		First Wt mg	Final Wt mg	Gold ppt	
9.696	3.648	376.4	(1)	10.480	7.870	750.9	(1)
10.156	3.819	376.2	(2)	10.344	7.761	750.2	(2)
9.429	3.550	376.7	(3)	10.441	7.839	750.7	(3)
9.793	3.683	376.3	(4)	9.765	7.330	750.6	(4)
9.337	3.512	376.3	(5)	9.549	7.168	750.6	(5)
9.030	3.394	376.1	(6)	9.262	6.955	750.8	(6)
9.612	3.617	376.5	(7)	10.434	7.832	750.6	(7)
10.178	3.829	376.3	(8)	10.188	7.647	750.5	(8)
10.493	3.955	377.1	(9)	10.224	7.677	750.8	(9)
9.480	3.567	377.1	(10)	9.393	7.051	750.6	(10)
10.180	3.828	376.2	(11)	10.303	7.737	750.9	(11)
9.352	3.516	376.2	(12)	9.333	7.001	750.1	(12)
10.256	3.853	375.9	(13)	9.272	6.955	750.0	(13)
9.347	3.515	376.3	(14)	9.477	7.112	750.4	(14)
10.507	3.956	376.7	(15)	8.927	6.700	750.5	(15)
9.518	3.581	376.4	(16)	9.932	7.454	750.4	(16)
Mean ppt 376.4 Stand Dev. 0.28				Mean ppt 750.5 Stand Dev. 0.27			

Table 13. The results of ICP-Micro AES and cupellation analysis of finished gold articles - Method of the Dutch Assay Office [m ‰]

ICP-AES (A) ‰		Cupellation (B) ‰		mean values (A)- (B)
595.9		596.3	596.4	-0.4
642.8	645.7	642.6	642.7	1.6
721.5	723.3	724.0	723.9	-1.6
713.5		709.5	709.8	3.9
663.0	655.1	661.9	662.5	1.8
659.4		658.8	658.7	0.6
700.7		700.0	699.8	0.8
672.2		671.8	672.0	-0.7
682.2		682.0	681.9	0.3
589.0		588.6	588.1	0.6
591.6		588.8	588.1	3.1
589.4		587.9	588.0	1.4
578.3	578.0	576.6	577.0	1.4
577.5	577.3	577.3	577.3	0.1
590.3	590.8	590.0	592.1	-0.5
577.6	578.6	577.4	577.2	0.8
576.1	578.6	577.3	577.5	0.0
577.4		579.9	580.2	-2.6
577.1		577.1	576.9	0.1
548.5		554.2	581.1	-9.2
560.8		559.1	558.6	1.9
579.4	576.8	578.9	578.6	0.7
581.8	581.1	581.1	580.7	0.5
736.8	737.1	737.1	736.5	0.2
582.4	581.1	581.5	581.4	0.3
580.0		580.0	580.4	-0.2
579.8	579.8	579.8	580.4	-0.3
581.8		580.1	579.6	2.0
582.0		581.0	581.2	0.9
			mean	0.2

Table 14. The analysis of jewellery articles with the XRF minispectrometer - new merchandise (%)

Designation	Nominal ‰ Au	Au	Ag	Cu	Zn	Pd
Necklace						
Yellow ball link	750	75.4	15.6	8.6	0.4	
Red ball link	750	77.1	3.0	25.7	0.1	
Yellow clasp	750	75.0	15.0	9.7	0.4	
Red gold ring	585	59.7	0.0	40.8	0.5	
Ear stud (cultured pearl)						
Clip	585	63.6	21.9	14.6	0.0	
Ring						
Yellow part	750	75.3	16.9	7.8	0.0	
Red part	750	80.5	3.5	23.8	0.8	
Bracelet						
Yellow link	750	75.2	13.7	10.0	1.1	
White link	750	79.8	18.7	0.3	1.2	
Bracelet						
White link	750	74.4	11.0	0.1	0.0	12.3
Yellow link	750	74.8	12.6	12.1	0.4	
Yellow clasp	750	74.9	14.9	10.3	0.1	
White clasp	750	74.5	11.7	0.0	0.1	11.6

d) Micro AAS

If the accuracy and precision of micro AAS, carried out with 10 mg sample gold jewellery weighings, are compared with the values of micro ICP then the question arises whether the possibilities of AAS have indeed been exhausted. A comparison of values with cupellation are not encouraging.

e) The X-ray test jewellery tester

An essential discovery from the previous micromethods described is that gold jewellery alloys generally possess a high homogeneity. From this is derived the application of a non-destructive instrument without direct contact based on X-ray fluorescence which has been extensively investigated with regard to its analytical performance in the gold jewellery sector.

Figure 8 shows this instrument in action with the collimator measurement probe (0.5 mm Ø) investigating the composition of the main alloy components in both alternating yellow and red gold ball links.

The analytical results of this examination are recorded in Table 14. This shows that by the measurement of the original jewellery surfaces, deviations from

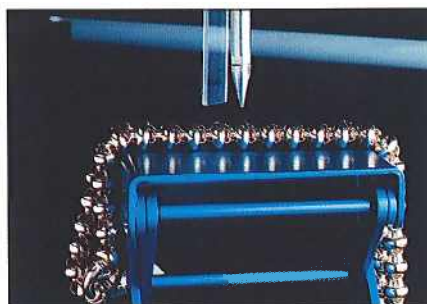


Figure 8 - Analysis of Ball Links of a Coloured Gold Chain with the X-Tester

the nominal content can occur because of their method of manufacture. On the other hand this analysis is, considering the total analysis of the main components very meaningful and superior to that of the touchstone test (23).

Nevertheless, the accuracy of the analysis of gold jewellery alloys is guaranteed with the X-tester. Here, even the quality of the gold fineness determination can be thoroughly checked with an accuracy of 0.2 to 0.3% gold, with a measurement time of only 3 minutes.

The operation of this energy dispersive X-ray fluorescence instrument is not distinguishable in principle from spectrometers of larger design. What is decisive, however, is the difference in that it possesses a low power X-ray tube and consequently is operational in a household electrical power socket. Instruments with a comparable measurement principle, although with different ways of working, are on the market.

It can be assumed that the jewellery X-tester is capable of recording the most rapid information about the composition of gold jewellery alloys with a high precision for the main components. It can be predicted that this instrument will find further utilisation in the jewellery trade and in future will replace the touchstone test. The instrument with its probe is also capable of testing the composition of filigreed areas of the jewellery.

Evaluation of the methods for analysing gold jewellery alloys with reference to their advantages and limitations

The analytical methods applicable for the determination of precious metal contents must be of high quality, i.e.

the concentration value of the precious metal in the sample must be very accurate. Apart from the quality built into the method, the care of the operator is a crucial prerequisite for reproducing this quality.

From the standpoint of obtainable quality, *cupellation is unequalled*, leaving aside the determination of high purity gold. The strongest competition for cupellation is ICP emission spectrometry which, because of its sensitivity, is well suited for the determination of trace metals in the gold.

As alloy components apart from gold can be determined by spectrometric methods, it can further be shown that XRF and GDL techniques have a great importance for the process control of precious metal alloy production, especially as the full analysis of gold jewellery alloys can be obtained in a few minutes with both these types of spectrometer. Here, X-ray fluorescence shows the greatest degree of automation of all the methods.

The X-tester should, because of its proven performance and flexibility with regard to the determination of other alloy components, really be able to *totally replace the touchstone test*, especially as this equipment can be operated on the shop counter of the jeweller without background knowledge. Besides, different areas of a piece of jewellery can be analysed individually with the probe technique so that variations in composition can be measured.

Whether, for example, GDL emission can compete with XRF analysis for alloy process control leads necessarily to the costs of these types of equipment, to the strategy of their employment, the maintenance of expensive precious metal standards as well as the required know-how of the manpower.

If one considers a comparison of the operating costs of the XRF spectrometers applicable for the analysis of gold jewellery alloys and a further comparison of their analytical performance, then it becomes clear that one should think about the necessary combination of instruments adequate for the required analysis, naturally including the consideration of the required manpower.

Table 15. Equipment for a precious metal analytical laboratory for gold jewellery alloys

Equipment	Purchase price [DM]	Operating costs per year [DM]
Cupellation according to ISO 11426 equipment	150 000	30 000
ICP spectrometer	250 000	50 000
GDL spectrometer	350 000	20 000
WD XRF	250 000	50 000
ED XRF Si(Li) detector	150 000	1 000
ED XRF X-test	50 000	500
Calibration standards	200 000	40 000
Sample preparation	200 000	10 000

A convenient equipment decision can be obtained from Table 15, enabling hundreds of samples per day to be analysed. With a corresponding supply of calibration standards and a developed stock of methods, it can be assumed that this equipment can be operated by semi-skilled personnel with the necessary resident stored analytical programs called up by the computer terminals of the spectrometers. With this equipment, starting metals, new alloys and also recycled material can be determined with the optimum degree of automation.

Conclusions and prospects for the future

Although cupellation represents the optimum technique for fineness determination of gold for the classical Au-Ag-Cu coloured gold alloys, it cannot continue as the only method for the determination of composition of the materials to be examined. The question arises as to whether it can be replaced, especially because of its limited utility. Everything points towards the non-destructive measurement by X-ray fluorescence (24). Nevertheless, it would be presumptuous to favour a method of determination in general without reservations.

Serially manufactured jewellery articles can today be hallmarked extremely economically by the laser technique so that a hallmark is "branded" secure from forgery. As the laser irradiation applies a high thermal energy to the surface of the gold jewellery alloy and vaporised metal is excited to atomic emission, analysis of the alloy could be carried out simultaneously in future with a reasonably priced emission spectrometer. Such investigations show the possibility in principle of an effective analytical identification of the main components, with, of course, at present less precision (RSD ~ 10%).

With regard to the variation of jewellery articles, the integration of certified quality systems is desirable to validate production steps such as analytical laboratory methods of investigation. In this regard, no compromise is permissible for the application of analytical methods, a point of view unanimously supported by the international ISO Standards Committee.

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