POLISHING COMPOUND RESIDUES IN GOLD JEWELLERY ALLOYS

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The assaying of gold jewellery before hallmarking is generally carried out on samples scraped from the surface. But the assay result may not necessarily be representative of the bulk composition. Analyses reported here have shown the presence of polishing compound residues on, and just below, the surface of some of the jewellery tested.

Introduction

All precious metal ornaments intended for sale in the U.K. are required to meet certain legally designated standards of alloy content. The gold articles meeting these standards contain 375, 585, 750 and 916 parts per thousand (ppt) of pure gold (by weight) and are commonly referred to as 9, 14, 18 and 22 carat alloys. For silver items, the 'Sterling' and 'Britannia' standards indicate silver contents of 925 and 958.4 ppt. It is the responsibility of the four U.K. Assay Offices to maintain constant control over the composition of items marketed and apply their 'hallmark' to those that prove to satisfy such requirements. Details of the sampling and testing procedures employed have been published [1].

The sampling and testing of precious metal artefacts is carried out by hand but the throughput is very high. For example, the London Assay Office (which is controlled by the Goldsmiths' Company) received approximately ten million samples for hallmarking in 1986 alone. It is not surprising, therefore, that the Goldsmiths' Company should have an interest in minimizing any factors that may result in a reduction in throughput. One such factor is the relatively large number of items that have to be re-sampled because the first assay (obtained by removing a minimum of material) suggested that the

alloy is sub-standard. Generally, such samples are found to be above the required minimum standard when repeat samples are taken from below the surface; however, this is both expensive and time consuming. It is perhaps significant that a majority of the problems are to be found with samples submitted in the polished, ready-for-sale condition. By comparison, since samples from articles in the unpolished condition are usually taken after removal of any surface contamination, the need for repeat sampling is less common. This apparent correlation between polishing and assay problems forms the basis for the investigation reported in this paper.

The surface contamination of polished jewellery has been investigated using X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and laser microprobe mass spectroscopy (LAMMS). The combination of SEM and EDS is a powerful technique which is particularly useful in the present investigation. This is because the depth to which material is removed by scraping (to provide the assay sample) is between 0.5 and 10 μm , while the excitation depth from which X-rays are generated in EDS is approximately 0.5 to 2 μm , depending on the material and instrumental parameters (2). Therefore, EDS is capable of providing information about a comparable depth of sample to that analysed during assay.

It should be emphasized, however, that results obtained by EDS do not provide information about elements with atomic numbers less than 10. Therefore, sample constituents such as oxygen and nitrogen (which

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may comprise a significant proportion of, for instance, the polishing compounds) will not be included in these analyses. In addition, data obtained for all other elements are presented normalized to 100 per cent and should not be interpreted as absolute concentrations.

The LAMMS technique complements EDS analysis well because it provides qualitative information on the low-atomic-number constituents undetectable by EDS. Also, it gives information about elemental changes in the sample with depth. This is achieved by progressively eroding the sample surface using a high-energy laser and carrying out an ion mass analysis at 0.1 μm intervals in depth. A review of the technique and its extensive applications is given in [3].

Experimental

Samples of 375 and 750 gold were supplied jointly by the Goldsmiths' Company and selected goldsmiths from the U.K. and Europe (see Table I). Examples of materials used to polish the gold were also submitted for elemental and structural analysis.

Samples of polishes were structurally characterized by X-ray diffraction using a Philips vertical diffractometer in both continuous and step-scan modes. A copper target producing $\text{CuK}\alpha$ radiation and a standard 1° collimating slit were used.

SEM and EDS analyses were performed using an ISI 100A instrument with an integrated Link microcomputer system. Specimens were mounted on one-inch stubs using conducting glue and orientated at a 45° tilt. Surface features of interest were photographed using a built-in camera and elemental analysis was carried out on many areas of the surface. An unpolished 750 gold reference was also examined in detail for comparison with polished samples.

One sample (No. 9), of particular interest because it was supplied as an example of a genuine assay failure, was further analysed by LAMMS using a LIMA model 2A (Cambridge Mass Spectrometry Ltd) in the depth-profiling mode. This was achieved by progressively eroding the sample surface using a high-energy pulsed Nd:YAG laser at depths of 0.1, 0.2, 0.3, 0.5 and 2.0 μm .

Table I

Gold Samples Analysed and the Polishing Procedures Employed in their Preparation

No.	Alloy	Item	Polishing Sequence	Origin
1	375 Y	link	pR	U.K.
2	375 Y	link	L	U.K.
3	375 Y	coupon	pR, L	U.K.
4	375 Y	coupon	gR, pR, xC	U.K.
5	375 Y	coupon	gR, D, xC	U.K.
6	375 W	coupon	L, gR, pR, xC	U.K.
7	750 Y	ring	Rb, Az	Germany
8	750 W	ring	Rb, Az	Germany
9	750 Y	earring		France
10	750 Y	earring	pR, xC	France
11	750 Y	coupon	pR	U.K.
12	750 Y	coupon	L	U.K.
13	750 Y	coupon	pR, L	U.K.
14	750 Y	coupon	C	U.K.
15	750 Y	coupon	pR	U.K.
16	750 Y	coupon	L, pR	U.K.

Table II

Results of EDS Analyses of Polish Materials (wt.%)

	pR	gR	D	Rb	Az	L
Si	3.0	2.2	2.6	2.8	3.1	92.8
Mg	0.5	0.2	1.1	1.0	1.0	0.1
Al	1.6	2.4	94.9	94.4	94.2	5.8
Fe	94.1	4.6	0.4	0.9	0.8	1.1
Cr	0.1	0.3	0.3	0.2	0.7	—
Ti	0.1	—	0.2	0.1	0.2	—
Ca	—	—	0.1	0.4	—	0.3
K	0.2	—	0.4	0.1	—	—
Mn	0.4	0.3	—	0.2	—	—

Results are for elements with atomic numbers greater than 10 and have been normalized to 100%

Key to Tables I and II

pR	pure rouge	Rb	Rubisel (German origin)
gR	greasy rouge	Az	Azuran (German origin)
L	Lustre	C	Crocus
xC	no final cleaning stage	Y	yellow gold
D	Diamantene	W	white gold

Table III
EDS Results for the U.K.
375 Gold Samples (wt.%)

No.	Au	Ag	Cu	Zn	Al	Si	Fe	Cr	Mg
1*	33.5	11.6	42.9	7.5	2.0	0.8	0.4	0.2	1.1
1	34.9	12.0	43.8	6.7	0.6	0.9	0.2	—	1.0
1**	24.9	13.9	39.7	7.0	3.3	1.9	0.3	0.5	9.3
2*	35.5	10.9	42.2	7.3	2.5	0.8	—	—	0.8
2	38.1	10.5	42.2	7.1	0.7	0.8	0.1	—	0.6
3	35.0	10.5	43.1	7.4	0.7	0.6	0.2	—	0.8
3	36.4	10.6	42.6	8.1	0.8	0.7	0.1	—	0.7
4	35.2	11.3	44.6	6.9	0.1	0.6	0.1	—	1.1
5	36.8	11.3	44.3	5.2	0.3	0.7	0.2	—	1.1
6***	35.6	56.3	4.9	0.7	1.0	0.8	—	—	0.1

* featureless region

** region with a high density of inclusions

*** also contains 0.4% Ni

Data have been normalized to 100%

Results

Analysis of Polishes

X-ray diffraction analysis was used to characterize the polishes into broadly similar structural types. Scanning between 10° and 120° 2θ revealed strong similarities between Diamantene, Rubisel and Azuran. Not surprisingly, pure and greasy jeweller's rouge were found to be strongly similar but Lustre differed substantially from both rouge and Diamantene. Results obtained by EDS are presented in Table II and reflect the similarities indicated by diffraction analysis.

Analyses of U.K. 375 Gold Samples

SEM analysis of the 375 gold samples revealed broadly featureless surfaces with some randomly distributed inclusions of approximately 1-5 µm in diameter. EDS analyses of the samples are given below in Table III.

The corresponding analyses for the U.K. 750 gold samples are given in Table IV.

Analysis of 750 Gold Rings of German Origin

Table V gives the EDS results for the yellow and white 750 gold rings manufactured in Germany. The specimen numbers relate to those listed in Table I. The lower case letters (a to f) refer to the different areas of

the sample on which the analysis was conducted.

Analyses 7a and 7b were taken at a magnification of approximately x200 at random locations on flat areas of the ring. Analyses 7c and 7d were taken at the base of the ring claws. A photomicrograph of the area analysed in 7c is shown in Figure 1. The figure reveals that the surface has been scored by abrasive particles, two of which are seen in the centre of the micrograph (their glowing appearance is due to charging caused by prolonged exposure to the electron beam). Analysis 7c indicates a correspondingly high impurity level. For comparison, analysis 7d was taken on an adjacent area containing no visible particles.

Analyses 8a and 8f are of the white gold ring; 8a, 8b and 8c are those taken on flat areas of the ring; while 8d, 8e and 8f were carried out on the ring claws. The photomicrograph in Figure 2 illustrates that the region between claws is rough and may represent a potential area for particle entrapment. In Figure 3, embedded particles can be seen trapped in the gold surface. While this is not typical of an area that would be chosen to obtain scrapings for an assay test, it can be envisaged that any complex-shaped artefact may retain foreign bodies more readily than would a smooth flat surface.

Analysis of 750 Gold Earrings of French Origin

The final set of analyses by EDS is given in Table VI. These were carried out on samples 9 and 10, which are 750 yellow gold earrings of French origin. The earrings are hollow and moon shaped with a scalloped design on their surface. As a result, they contain a variety of surface features ranging from deep grooves to smooth flat areas. Analysis 10a was taken on a relatively flat

Table IV
EDS Results for the U.K.
750 Gold Samples (wt.%)

No.	Au	Ag	Cu	Al	Si	Fe	Cr	Mg
11	74.7	15.0	8.4	—	1.1	0.3	—	0.5
12	74.5	15.7	8.2	—	1.2	0.1	—	0.2
13	75.0	15.4	8.0	0.2	1.2	0.1	—	0.3
14	74.7	14.7	9.0	—	1.1	0.2	0.1	0.3
15	73.7	16.2	8.5	—	1.1	0.3	—	0.1
16	75.5	15.4	7.9	—	1.1	—	—	0.1
Standard	80.0	11.3	8.6	—	—	—	—	—

Data have been normalized to 100%

region of a sample that had been polished with rouge and not cleaned. Analysis 10b was taken from an adjacent area where polishing debris had accumulated around a groove.

Analyses of earring number 9 were carried out on several surface regions a-h. Analyses 9a, 9b, 9e and 9h were taken on flat areas of the sample. 9f and 9g relate to analyses taken on raised, scalloped areas. Analysis 9d was taken near the punched maker's name mark and 9c was taken in a region containing 1-10 μm 'blisters'.

LAMMS Analysis

The surface of earring No. 9 was randomly analysed by LAMMS and it was found that the relative proportions of gold, silver and copper varied considerably over the surface. The blistered appearance of some surface regions observed by SEM was also observed during LAMMS analysis. Depth-profiling was carried out close to the site of EDS analysis (9f) and the results are shown in Figure 4 (a-e) on page 46. The surface was irradiated 20 times on the same spot to a depth of approximately 2 μm . The results showed that at depths of more than 0.3 μm , the alloy consisted of gold, silver and copper only. Interestingly, although this indicated that contamination was contained within the top 0.3 μm , the highest impurity levels were found to be at a depth of 0.2 - 0.3 μm . The analysis supported EDS results, but also revealed the presence of sodium, potassium and carbon at the surface.

Table V
EDS Results for the 750 Gold Rings
of German Origin

No.	Au	Ag	Cu	Al	Si	Fe	Cr	Mg
7a	74.8	12.9	10.9	—	1.1	0.1	—	0.2
7b	75.8	12.3	10.2	—	1.2	—	0.1	0.5
7c	43.4	31.7	10.5	4.2	4.6	—	0.2	5.4
7d	75.3	12.9	10.3	—	1.2	—	0.2	0.1
						Zn	Ni	
8a	73.6	16.0	16.0	—	1.2	5.1	4.1	0.1
8b	73.8	15.6	15.6	—	1.1	4.7	4.5	0.4
8c	72.8	16.3	16.3	—	1.1	4.5	—	0.2
8d	75.5	14.7	14.7	—	0.9	4.5	3.4	0.5
8e	73.9	15.8	15.8	—	1.1	4.2	4.7	0.4
8f	73.2	16.4	16.4	—	1.0	4.5	4.6	0.3

Wt.% element $\pm 0.1\%$ (normalized to 100%)

Table VI
EDS Results for the 750 Gold Earrings
of French Origin

No.	Au	Ag	Cu	Zn	Fe	Cr	Si	Mg	Ca
9a	80.6	7.9	10.2	0.2	0.3	0.1	0.5	0.2	—
9b	75.9	10.7	12.1	—	—	—	0.9	0.4	—
9c	75.8	10.9	11.8	—	—	0.1	1.2	0.2	—
9d	73.4	11.5	12.8	—	0.4	0.2	1.1	0.5	—
9e	75.6	10.0	12.5	0.2	0.1	0.2	1.0	0.3	0.2
9f	76.7	8.6	13.0	0.3	0.1	0.3	0.8	0.1	0.3
9g	77.3	8.9	12.5	—	0.1	—	0.9	0.2	0.2
9h	75.1	10.6	12.6	—	—	0.2	1.0	0.4	—
10a	73.6	11.2	13.3	0.3	0.1	—	1.0	0.4	—
10b	46.6	11.6	13.5	1.9	24.0	—	1.9	—	0.4

Wt.% element $\pm 0.1\%$ (normalized to 100%)

Discussion

Polishing compounds used in the jewellery trade have extremely complex structures. They may generally be described as materials that consist of abrasive particles bound together in a soft medium. The analyses of polishes by X-ray diffraction and EDS (Table II) did not attempt to resolve the detailed and precise structure of each material. Nevertheless, the combined data correlate well to reveal clear similarities between certain of the polishes listed in the key under Table II.

The EDS analysis of sample 1 shown in Table III indicates that there is a difference between regions exhibiting a high density of inclusions, and relatively featureless areas. Each analysis was carried out on an area of approximately 0.1 mm^2 . Inclusions were frequently angular, about 5 μm in longest dimension and randomly distributed over the surface. Sample 1 was polished with pure rouge only. The high iron content of rouge is due to haematite (Fe_2O_3) but it appears that it is the siliceous material in the binder rather than the abrasive oxide that has remained in the surface. This observation also applies to samples 2-6, which were prepared by different polishing regimes. Generally, the impurities identified in the alloy do not reflect the major constituents of the polishes as shown in Table II.

The data quoted for samples 4, 5 and 6 in Table III are mean values. However, it was found during analysis that the relative concentrations of the four constituent

Fig. 1 SEM micrograph of the surface of a German ring (sample No. 7)

Fig. 2 SEM micrograph of the area between claws on the German ring in Figure 1

elements of the alloy (Au, Ag, Cu and Zn) varied by up to 4 per cent over the surface. This was also found to be the case when investigating the 750 gold samples (Table IV). Values for the 750 standard, however, varied by a maximum of only ± 0.4 per cent. The impurity levels were also found to be fairly constant regardless of preparation method. No Mg, Fe or Cr was detected in the standard, however, and Si levels were found to be <0.1 per cent and, therefore, could not be interpreted with certainty.

Perhaps the most interesting result in Table IV is the relatively high gold and low silver content of the unpolished standard compared with samples 11-16. It appears that the act of polishing may either remove gold, leaving a higher apparent concentration of copper and silver, or promote diffusion of alloy constituents to the surface (the effects of surface heating generated by polishing have been discussed by Samuels [4]).

Results of EDS analyses carried out on the white and yellow rings of German origin (Table V) illustrate that surface topography has a strong influence on the extent to which particle entrapment may occur. This is also illustrated by the analysis of sample 10, the earring of French origin. On certain regions of the surface of this sample, polishing debris has accumulated, forming a deposit, rather than an entrapped layer. As a consequence, the compositional analyses of such regions were found to be high in iron and more closely resembled the composition of rouge given in Table II.

Results from the analysis of sample 9 (a 750 gold earring of French origin) are of particular interest because the sample is known to have failed the assay test. The EDS results once again indicate a substantial variation in composition over the surface; gold contents in

Fig. 3 SEM micrograph of embedded particles between claws on the German ring in Figure 1

analyses 9a and 9d differed by 7.2 per cent. Whether such variations could result in assay failure would depend not only on their magnitude but also on the volume over which they extend. It should be remembered that although the technique of EDS provides information generated from a depth in the sample comparable to the finest scrapings collected for assay, the length and width of a typical scraping (and hence the total volume) analysed during assay may be at least an order of magnitude greater. Therefore, if composition variations are on a fine enough scale, an assay scraping would represent a good average sample.

LAMMS analysis of sample 9 not only confirmed the composition variations detected by EDS but also provided depth analysis. Results confirmed the presence of

contamination and also indicated significant sub-surface impurity levels which appeared to reach a maximum at a depth of 0.2 - 0.3 μm below the surface.

Conclusions

1). Many of the polished gold samples contain embedded contaminant particles. LAMMS depth profiling indicates that the highest levels of contamination are found below the surface.

2). Many of the samples tested exhibited substantial variations in composition over their surfaces. The magnitude of the volumes over which these extend may influence the outcome of an assay.

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Fig. 4 LAMMS analyses of an earring (sample No. 9) at varying depths of analysis: a). about 0.1 μm ; b). about 0.2 μm ; c). about 0.3 μm ; d). about 0.5 μm ; e). about 2.0 μm . The vertical axis represents relative ion current