Application of Energy-dispersive X-ray Fluorescence to Jewellery Samples determining Gold and Silver

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Abstract

The results from a study of the real scope of energy-dispersive X-ray fluorescence analysis in an Assay Office, in which precious metal samples must be analysed prior to their hallmarking according to Spanish regulations, are presented. The advantages and limitations of this technique for the analysis of gold and silver jewellery samples, which is one of the most significant industrial activities in the local area (Cordoba, Spain), are reported. The results of gold and silver support the use of this technique in Assay Offices, not only for screening purposes, but also as an alternative to cupellation and potentiometric titration for a number of samples. The application of the energy-dispersive X-ray fluorencence spectrometer for the detection of plating layers like rhodium and nickel is also discussed.

Keywords

X-ray fluorescence, gold, silver, jewellery, cupellation, potentiometric titration

Introduction

Cupellation is the most usual reference technique for determining the gold content of jewellery alloys in Assay Offices. This technique, based on the refining of gold, have been known to humanity a long time ago – it was first described by the Egyptians in a Cuneiform tablet dating back to around 1360 BC –. It consists on the removal of all base metals from a sample by oxidation in a cupel (a porous crucible made of magnesium oxide which absorbs the oxidised metals) placed in an oven under conditions as described by the ISO Standard 11426. The result is a pure gold-silver alloy. The removal of the silver is carried out by dissolution in nitric acid to leave a residue of pure gold which is then weighed. The ratio between the sample weights before and after the process yields the gold content of the former alloy. This technique is cheap and accurate (its precision can reach 0.02%) (1). However, it is affected by a series of drawbacks, namely:

- It is destructive.
- It determines only the gold content.
- Platinum group metals (insoluble in nitric acid) present in the samples lead to errors if they are not detected and conveniently removed.

There are some other techniques suitable for gold analysis such as touchstone, parting, atomic absorption spectroscopy (AAS), inductively-coupled plasma spectrometry (ICP). They are destructive techniques, although some of them need minute sample amounts, and most require sample preparation. Furthermore, with the exception of ICP, these methods lack sufficient accuracy.

The most common official method for the determination of silver is potentiometric titration. It is a destructive technique based on the potentiometric monitoring of the precipitation of silver chloride (ISO Standard 11427). Silver can also be determined by spectroscopic techniques, but its aqueous solutions are quite unstable and the results are not as accurate as required.

X-ray fluorescence (XRF) is a technique based on the effect that high energetic X-radiation excites at a specimen of an elemental mixture lower enegetic X-lines specific for the present elements. The source that provides photons of sufficient energy to carry this out – known as primary radiation – is, most times, an X-ray tube in which electrons are accelerated from the cathode to the anode by a high voltage. A high-energy quantum radiation is generated by interaction with the anode material. This radiation is led to the sample, in which the interaction generates a second X-ray beam, called secondary radiation, that is detected and conveniently quantified. Each element emits its unique characteristic secondary X-rays, the energy of which is related to the analyte concentration, the sample matrix, and excitation and detection conditions (2). The main advantages of the technique are its non-destructive character and the capability of determining, not only the gold content, but the whole composition of an alloy.

There are two ways in which X-ray fluorescence radiation can be discriminated into discrete elemental X-lines: by measuring either the wavelength dispersion (WDXRF) or the energy dispersion spectra (EDXRF). Wavelength dispersive X-ray fluorescence provides more accurate results than its energy dispersive counterpart (for very accurate gold analysis, wet ground sample surface has been shown to be necessary). Under this condition, the method allows the determination of gold fineness in a gold alloy with an accuracy very close to that obtained by cupellation, i.e., within the order of 0.1% (3-7). On the other hand, WDXRF is an expensive technique, with significant installation requirements and high operational costs. Furthermore, limitations in the volume of the sample chamber make WDXRF unsuitable for assaying most finished gold jewellery pieces.

Energy dispersive X-ray fluorescence (EDXRF) spectrometers use less powerful X-ray sources than those based on wavelength dispersion. Thus, the use of water cooling is unnecessary, which entails a significant economical saving. The instruments then, are cheaper and smaller than those based on WDXRF, and very accurate analytical results are achieved when a suitable set of standards is used (8), as will be shown later. The advantages of the use of EDXRF in comparison to the use of WDXRF have been described elsewhere, with particular emphasis on precious metal analysis in jewellery (9, 10).

This paper is a report on the real scope of EDXRF for the determination of gold and silver in the different types of samples that are commonly analysed in Assay Offices.

2 Experimental

2.1 Instrumentation
A Fischerscope X-ray XAN spectrometer (Helmut Fischer GmbH + Co. KG, Sindelfingen, Germany) was used in this study. It consists of an X-ray tube with a tungsten anode (50kV/0.8 mA) and a silicon semiconductor detector (Peltier cooling at -30°C; energy resolution 200 eV). The chamber dimensions, HxWxD=90x320x460 mm, allow the analysis of moderate large samples. A colour video microscope allows the selection and view of the irradiated area with up to 25x magnification. Four different collimators, namely, 0.2, 0.6, 1

and 2 mm diameter, can be used, depending on the area to be analysed. The spectrometer is equipped with two primary filters, one of aluminium and the other of nickel.

The samples can be analysed either directly, using an algorithm based on Fundamental Parameters, or by calibration with a relevant set of standards.

Statgraphics Plus 5.1 (Statistical Graphics Corp.) was used for data treatment and statistical analysis.

2.2 Standards
Four certified X-ray reference materials supplied by the Sheffield Assay Office were used as standards for the analysis of gold-jewellery items. Their gold content was around 18 carats. Each reference material was analysed as follows: gold and silver were determined by cupellation in each alloy, while the rest of metals were determined by ICP-OES. The composition of these alloys can be seen in Table 1. These reference materials were certified by the United Kingdom Accreditation Service (UKAS).

2.3 Samples
About 1600 gold jewellery items, with gold content ranging between 6 and 24 carats, were analysed by X-ray fluorescence in order to determine their composition. Among them, 600 were also analysed by cupellation for the sake of comparison. The samples belonged to two main groups: finished articles and ingots of alloys that are analysed before the jewellery item manufacture. In the former case the samples were analysed directly, without any manipulation; on the other hand, alloys were polished in order to remove the outer layer, that can be dirty and oxidised. The calibration set used was the same for all the samples, independent of their gold content and manufactured character of the pieces.

3 Results and discussion

3.1 Optimisation of the working conditions
The experimental variables that can affect the EDXRF analysis were optimised by an experimental design in order to obtain the best results (minimum error) as compared with the nominal value obtained by cupellation. The variables were: voltage, collimator diameter, collection time and the use or

Table 1

Percentage composition of the reference materials used as standards in the X-ray fluorescence analysis of gold-jewellery items, and the corresponding standard deviation.

	18CT YELLOW	CLA100 40.1	18CT RED	G18HWS
Au (%) ± SD (%)	75.47 ± 0.05	75.09 ± 0.05	75.36 ± 0.05	75.70 ± 0.05
Ag (%) ± SD (%)	16.35 ± 0.05	16.05 ± 0.05	5.57 ± 0.05	–
Cu (%) ± SD (%)	5.95 ± 0.10	9.15 ± 0.15	19.50 ± 0.30	8.84 ± 0.14
Zn (%) ± SD (%)	–	–	–	2.90 ± 0.05
Ni (%) ± SD (%)	–	–	–	12.40 ± 0.20
Pd (%) ± SD (%)	–	–	–	0.41 ± 0.02
Cd (%) ± SD (%)	1.83 ± 0.30	–	–	–

Table 2

Tested ranges and optimum values for the experimental variables that can affect the EDXRF analysis.

Variable	Tested range	Optimum value
Voltage	10-50 kV	50 kV
Collimator diameter	0.2-1.0 mm	0.6 mm
Collection time	60-180 s	60 s
Use of primary filter	Al, Ni, none	Ni

not of primary filters. The ranges over which these variables were studied and the optimum values found are listed in Table 2.

A full two-level factorial 2^4 design (16 randomised experiments) was performed plus three replicates of the centre point. The conclusions obtained from the experimental design were that the only influential variable with a positive effect is the high voltage, so analyses were carried out at its maximum value, i.e., 50 kV. The collimator diameter was not influential for all the response variables, but it was significant in some cases and its effect was positive, so the use of the maximum value was advisable. However, the shape of most samples makes the use of a collimator bigger than 0.6 mm impossible. The effect of the collection time between 60 and 180 seconds was not significant, so 60 seconds were chosen to obtain the best speed of the analysis. The use of primary filters did not seem to affect the analysis.

3.2 Analysis of gold

The direct analysis of gold alloys by EDXRF using the Fundamental Parameters method provides higher estimation of the amount of gold in the samples than that obtained by cupellation, as can be seen on Table 3, where the results obtained by cupellation, EDXRF with a calibration set and EDXRF without calibration for a series of home-made reference samples, with gold content ranging from 99.97% to 50.06%, are shown. These samples have been analysed ten times by each technique and their composition was also

studied by other techniques as well (11). As can be seen, the estimated amount of gold without using any standard is usually higher than the values provided when a calibration set is used. In most cases, the differences between the calibrated results and those obtained by cupellation are smaller than the differences when the uncalibrated values are considered, so all the gold samples in this study were quantified by calibration. The higher estimation of gold when using only the Fundamental Parameters method is due to the fact that this is a theoretical method, based on the spectra of pure elements. In our case, we have alloys and the presence of some metals can interfere with the quantisation of others. Thus, some emission lines of copper overlap with some of gold, so the determination of gold by the Fundamental Parameters method in samples containing copper is not so accurate as the determination by calibration using a proper set of standards. On the other hand, when no overlapping can take place (for instance in silver/copper alloys, where the spectral lines are clearly differentiated), the direct analysis of the samples using the Fundamental Parameters method yields very accurate results.

The comparison of the results provided by EDXRF with those obtained by cupellation (expressed in parts per thousand in both cases) was carried out by linear regression.

3.2.1 Determination of the gold content in alloys

The results obtained were better as the sample gold content approached 18 carats, which is the concentration of the reference materials used as standards. Figure 1 shows the plots of gold content obtained by EDXRF against the gold content provided by cupellation for the three groups in which the alloys were divided, namely, 70-80%, 50-70% and less than 50% gold. Each plot also shows the regression equation and R^2.

Figure 1a plots the results obtained by EDXRF against those corresponding to cupellation for alloys with gold content ranging between 70 and 80%. The number of

Table 3

Differences in the gold determination of nine house-made Au/Ag/Cu reference samples, (the gold content of which was determined by cupellation), when compared with the results obtained by EDXRF with and without calibration (each sample was analysed ten times).

Au_{cup}: *gold content of the reference sample determined by cupellation.*

$Au_{EDXRF\,ws}$: *gold content determined by EDXRF using calibration.*

$Au_{EDXRF\,wos}$: *gold content provided by EDXRF directly, without the use of standards.*

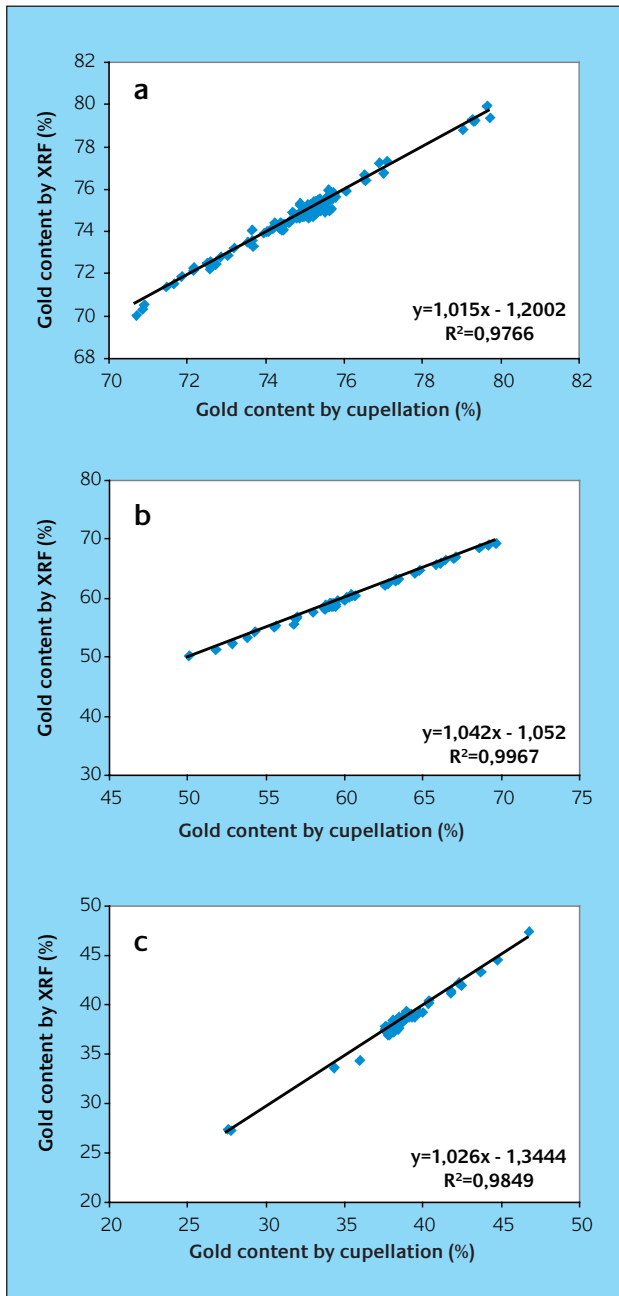| Sample	Au_{cup} (%) ± sd	$Au_{EDXRF\,ws}$ (%) ± sd	$Au_{EDXRF\,wos}$ (%) ± sd
Au 2	99.97 ± 0.03	99.95 ± 0.02	99.87 ± 0.03
Au 3	89.93 ± 0.04	89.91 ± 0.10	89.96 ± 0.09
Au 4	80.05 ± 0.01	79.98 ± 0.11	80.39 ± 0.08
Au 6	76.00 ± 0.04	75.82 ± 0.12	76.24 ± 0.12
Au 9	73.89 ± 0.02	73.82 ± 0.12	74.61 ± 0.11
Au 10	69.89 ± 0.02	69.86 ± 0.11	70.65 ± 0.15
Au 11	60.07 ± 0.02	59.84 ± 0.29	60.72 ± 0.10
Au 14	58.08 ± 0.03	58.02 ± 0.15	58.63 ± 0.14
Au 15	50.09 ± 0.02	49.86 ± 0.16	50.76 ± 0.16

Figure 1

Results of the comparison between the values obtained in the analysis of gold alloys by EDXRF against those provided by cupellation by linear regression: a, alloys with gold content between 70 and 80%; b, samples with gold content ranging between 50-70%; c, samples with less than 50% in gold.

samples in this plot is 218, after having removed 4 samples with Studentized residuals higher than 3 in absolute value. The P-value in the ANOVA table is less than 0.01, so there is a statistically significant relationship between the results obtained by EDXRF and those provided by cupellation at the 99% confidence level. The mean absolute error is 0.15%; this is the average of the residuals and it is within the order of the experimental error of both techniques in routine analysis, i.e., not under their optimal working conditions.

The results for samples with gold content between 50-70% are plotted in Figure 1b. The number of samples is 68 after the removal of three of them that had unusually large Studentized residuals. The P-value in the ANOVA table is less
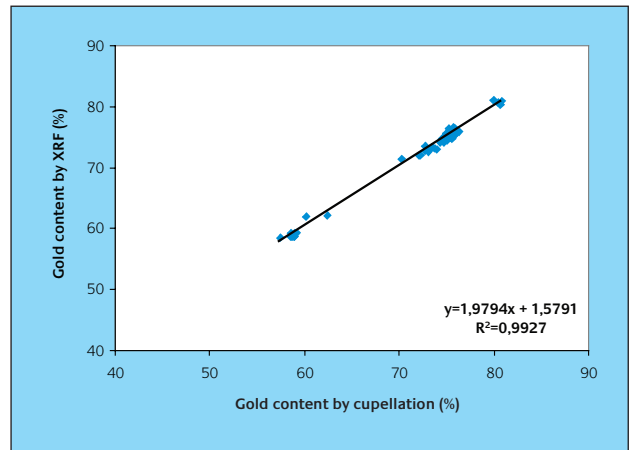

Figure 2

Comparison between the results of the analysis of gold finished articles obtained by EDXRF against those from cupellation by linear regression, as well as the corresponding equation and R^2.

than 0.01, i.e., a statistically significant relationship exists between the results obtained by EDXRF and those provided by cupellation at the 99% confidence level. The mean absolute error is 0.18%.

Figure 1c depicts the regression between the results provided by EDXRF and those corresponding to cupellation for samples with a gold content lower than 50%. The number of samples in this case is 64 (one sample was removed due to its large residual). Again, there is a statistically significant relationship between the results obtained by EDXRF and those provided by cupellation at the 99% confidence level, with a mean absolute error of 0.26%.

3.2.2 Determination of the gold content in finished articles

As mentioned before, the samples were analysed directly, so larger errors in the determination of gold were expected because of the finishing treatments used in some of the samples (mainly, the hollow ones), which can change the alloy composition on the surface. The comparison of EDXRF with cupellation by linear regression is shown in Figure 2, as well as the corresponding equation and R2. The mean absolute error is 0.27% (163 samples, after the removal of three samples with Studentized residuals higher than 3 in absolute value), which is higher than that corresponding to alloys within the same composition range. As mentioned before, this is due to finishing treatments. Although in some samples the differences in composition between the inner and the outer parts are negligible, in some others the differences can be very significant. This is particularly true in some hollow samples, which are made around a copper core. Once the item is finished, it is treated with nitric acid in order to dissolve the core, but part of the alloy copper in contact with the acid is also dissolved, so the composition in this part is different from the rest of the item. This is a very local effect, on the sample surface but, as EDXRF analyses a very small volume (the penetration of the beam in metallic samples depends on the matrix, but it scarcely exceeds some tens of microns), it must be taken into account.

Analysis of rhodium-plated jewellery. The use of an outer rhodium layer in white gold jewellery is very common in the last few years. A high percentage of the jewellery items provided with diamonds belong to this category. The high price of much of these items (some of them are unique jewels) affords a special interest in their non-destructive analysis. Furthermore, rhodium is an interference in the gold determination, because it is not absorbed by the cupel and it is also insoluble in nitric acid.

EDXRF can play an important role in the analysis of this type of samples because it enables both the analysis of the composition of the underlying alloy and the measurement of the rhodium layer thickness. During the time the present study was carried out, a great number of rhodium-plated pieces were analysed with good results, although in most cases their gold content provided by cupellation was not available, so no statistical comparison was carried out.

3.3 Analysis of silver

Direct analysis of silver samples by the Fundamental Parameters algorithm is more accurate, as compared with potentiometric titration, than in the case of gold determination and its cupellation counterpart. However, in order to obtain proper accuracy, the samples usually need to be ground, since silver can easily suffer from corrosion and the finishing treatments used in silverware manufacture change the outer composition of the item. Thus, the results provided by direct analysis of ground Sterling silver samples as compared with those obtained by potentiometric titration are plotted in Figure 3, where the regression equation and R^2 are also shown.

ANOVA makes clear that there is a statistically significant relationship between the results obtained by EDXRF and those provided by potentiometric titration at the 99% confidence level. The mean absolute error is 0.22%.

It is worth noting that direct analysis of intact samples can lead to significant errors in the determination of the silver content. This is a serious drawback but it can be overcome by
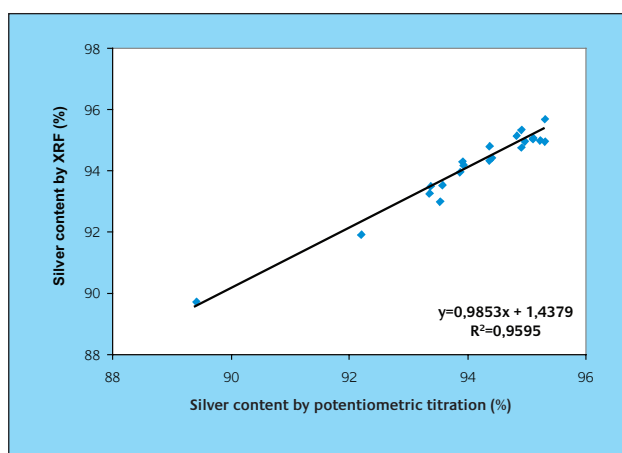
the use of an "internal standard", i.e., one of the items of a series is analysed by potentiometric titration and it is taken as the "standard" for the calibration of the rest of the samples in the series. This is an alternative to potentiometric titration when a high number of identical objects must be analysed in order to fulfil the regulations, owing to the fact that potentiometric titration is a destructive technique.

3.3.1 Rhodium-plated silverware

As well as in the case of gold jewellery, some silver items can be rhodium-plated in order to have a whiter shade. Thus, the discussion carried out for rhodium-plated gold jewellery pieces is valid here.

3.3.2 Nickel-plated items

Throughout the time in which this study was developed, some imported silver samples were found to yield low silver values (less than those permitted by law) when analysed by potentimetric titration. Their analysis by EDXRF, demonstrated that they have an outer nickel layer. Once this layer was removed, the silver values were those permitted by law. This layer is added in order to make the piece whiter but, as nickel is not an expensive metal, the layer thickness is wide enough to alter the weight of the sample. EDXRF allows the construction of measuring methods in which the nickel-layer can be taken into account and the underlying alloy composition can be determined.

4 Conclusions

The present results illustrate the usefulness of EDXRF in Assay Offices, not only as a screening technique that can replace touchstone (with a number of obvious advantages over it), but also as an alternative to cupellation for the analyses in which the results provided are accurate enough, and as a complementary technique when the whole composition of the sample must be determined. Thus, the analyses of polished alloys and solid gold finished items can be carried out by EDXRF, at least as a way of increasing the number of samples analysed without deterioration of the client's goods.

Furthermore, EDXRF offers the possibility of analysing multi-layered samples without the necessity of removing any of them.

For all the above mentioned reasons, in the authors' opinion EDXRF is a highly advisable technique in Assay Offices.

Acknowledgement

Figure 3
Linear regression of the results of silver determination by EDXRF and potentiometric titration as well as the corresponding equation and R^2.

In the figure:
y=0,9853x + 1,4379
R^2=0,9595

Axis labels: Silver content by XRF (%) / Silver content by potentiometric titration (%)

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