THE USE OF ED-XRF TECHNOLOGY TO MEASURE GOLD ASSAY AFTER THE INTRODUCTION OF ISO 23345

Valerio Doppio

ED-XRF analysis techniques are becoming increasingly popular in the jewelry industry. The possibility of measuring a finished object of even complex shape, without destroying or ruining it, very quickly, is a unique attraction compared to other conventional techniques (e.g. ICP or fire assay). Despite their relative popularity, however, X-ray fluorescence-based techniques were generally relegated to a marginal role, limited to checking the rough composition, due to the perception that this type of measurement is inaccurate. Calibrating the analyzer with good references, choosing specific measurement parameters and understanding the structure of the analyzed jewelry are fundamental in allowing much more precise and accurate measurements. In our tests, we work with and on the new ISO 23345, which defines calibration, measurement and interpretation of data for fineness analysis by ED-XRF.

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INTRODUCTION

Binder The fire assay technique has been used since antiquity for analysing the fineness of precious metals in jewellery production due to its significant accuracy and reliability.[1,2,3,4] This technique involves a series of heat and chemical treatments during which non-precious elements are gradually removed from the noble alloys, until a nugget of pure gold is obtained. The nugget mass is then compared with the initial sample mass, allowing the calculation of the fineness of the materials under examination.[5] The analytical technicians must observe several precautions to ensure successful measurement and additional steps are necessary if palladium, platinum, or other elements of the platinoid group are present in the alloys. The manifold steps required by this technique and the fact that the entire procedure is handmade by operators makes the technique, while accurate and precise, vulnerable to many potential mistakes and low consistency of results.

In recent years, amongst the several other analysis techniques that have been tested for fineness analysis, the X-ray fluorescence technique (XRF) is the one that has shown the most promising results. XRF instruments are equipped with an X-ray source that excites the electrons of the atoms in the materials. The radiation emitted in turn by the electrons when they return to their ground state is detected and its energy and intensity are used to identify and quantify the atoms in the sample, thus determining its composition. The X-ray fluorescence has the advantages of being much faster than cupellation, not a destructive technique, and does not require ovens, consumables, or reagents. Furthermore, in this type of analysis, operator faults are minimised because

there are no passages strongly depending on the operator experience or on sample preparation. It is however necessary to calibrate the instrument with a series of standard materials whose composition is close to the one of the materials to be analysed to make measurements with a good accuracy, at least for gold concentration. This procedure allows the received signal to be adjusted according to the different variables specific to each instrument, measuring environment, and specifications of the alloys under analysis.

XRF is still not used for fineness measures in the ordinary jewellery companies, despite being widespread among companies and routinely used to qualitatively check the composition of unknown samples.

This analysis technique is viewed with suspicion by quality control operators because it is considered unreliable or inaccurate compared to the more traditional fire assay. It is often used to monitor the produced items but is always accompanied by control measurements performed by cupellation. A share of this uncertainty can certainly be attributed to the relatively recent development of these faster instrumentations capable of performing delicate fineness measurements, but also to the scarcity of studies and procedures describing the correct modus operandi for this measurement method, despite some exceptions. A likely source contributing to these preconceptions is the widespread use of portable fluorescence instruments designed for qualitative analysis under non-standard conditions, which are becoming increasingly common in some sectors. These instruments, which were created to meet very specific needs, do not have the same analytical capacity nor the possibilities of calibration and customisation offered by the new bench-top instruments.

The commissions within the International Organisation for Standardisation (ISO) have long recognised the potential of this technique and in 2021 the technical committee for jewellery and precious metals (ISO/TC 174) completed the creation of standard ISO 23345:2021,[6] which explicitly deals with how to configure, calibrate, and carry out an assay measurement in precious item with a bench-top energy dispersive X-ray fluorescence (ED-XRF) instrument, the most widespread variety of instruments using this analytical technique.

Accordingly, the focus of this work will be to perform fineness measurements on precious alloys with an ordinary ED-XRF bench-top instrument as well as comprehend the influence of

the alloy matrix and microstructure on the instrument response. The selection of ideal measurement conditions will be treated accordingly, confirming or complementing what is described in the aforementioned norm. At last, the fineness of commercial jewelry by Pomellato, an important luxury Italian fine jeweller, is measured. Such samples were produced by means of different manufacturing processes, to test the reliability and consistency of the technique in an ordinary jewellery quality control situation.

ENERGY DISPERSIVE X-RAY ANALYSIS BASICS

The physics at the root of the X-ray fluorescence and the corresponding spectrometry principle are extensively studied and understood by the specialist community.[5,6,7,8] A high energy source generates a beam of radiation that is focused onto the surface of the sample to be analysed by filters and collimators. The atoms in the samples absorb the energy of X-ray photons and when its magnitude is greater than the binding energy of the electrons in the inner shells, the latter are ejected from the atoms. This ionization process leaves vacancies into inner shells that are promptly replenished by electrons from outer shells with the contemporary emission of others X-ray photons whose frequency (ν) is proportional to the energetic difference of the shells involved (k_1, k_2) and to the atomic number (Z) of the element, as shown by Moseley law.[9]

$$\sqrt{\nu} = k_1(Z - k_2)$$

A detector can measure the energy of these emitted photons, which are indicative of the element species present in the material and their counts per time unit is directly proportional to the abundance of each element. The resulting spectrum, in which the number of photon counts is plotted as a function of their energy, is characteristic of the composition of the material. Consequently, the analysis of the resulting spectrum allows the quantification of each element present in the sample. ED-XRF has the drawback of X-ray limited penetration and probing depth if compared to other techniques. This means that for samples characterized by low homogeneity along the depth axis, multiple surface layers or plating as well as any other differences between the surface and the bulk of the material, other techniques that can sample a larger amount of mass are preferable.

Several articles and technical procedures have been published in recent years, focusing both on methods to increase the accuracy

of the measurement and to investigate the most suitable surface preparation method for the specimens.

It has been shown that more accurate results can be obtained on XRF analyses when the surface roughness is reduced by grinding with at least the 1200 grit sandpaper. Further polishing does not have any appreciable influence, at constant excitation current.[9] Manufacturer guidelines and good laboratory practice for these instruments suggest the use of flat samples so that the radiation is collected completely by the detector. When this is not possible, reference and calibration samples should be made so that they have a structure and surface finish as close as possible to the one of the real samples.

The procedure described in document ISO 23345:2021, based on results of internal tests, calls for calibration samples whose composition is as close as possible to that of the sample to be measured, defining maximum deviations of approximately 50‰ for major elements and allowing minor elements below 5‰ and trace elements to be neglected.[6] The same regulation standardizes the measurement procedure as follow: for each sample, the XRF analysis has to be repeated at least three times in three different points in order to evaluate the statistical variability of the measurement and avoid the influence of outlier data due to random errors. Moreover, the regulation defines the acceptability limits for these data on the base of the difference between maximum and minimum measured values.

EXPERIMENTAL METHODS

In this work, the gold fineness was measured by means of a FISCHERSCOPE X-RAY XAN 252 (Helmut Fischer) fluorescence apparatus. The instrument is equipped with a 500 μm aluminum filter to cut off the light-elements contribution to the spectrum while the applied voltage was set to 50 kV.

It is well known[11] that the acquisition time is directly proportional to the scanning counts of all elements, therefore the signal-to-noise ratio. On the other hand, it has been proven that the correlation coefficients and the accuracy of the measurements do not depend on the exposure time. The acquisition time was set at 30 seconds according to just mentioned correlations to find a good compromise between signal-to-noise ratio and amount of analysis per unit of time.

The instrument is equipped with four interchangeable collimators

of different aperture sizes (0.2, 0.6, 1.0, 2.0 mm). The use of the largest collimator possible, which depends on the sample target area, morphology and extension, is mandatory according to ISO 23345:2021,[6] but the productive method and the thermo-mechanical history of the jewellery items are not taken into consideration.

A set of measures has been scheduled to understand whether the collimator choice and the alloy microstructure influence the assay analysis in terms of both grain size and phase distribution, which are a consequence of the alloy solidification rate and possible thermo-mechanical treatments present in the production line (cold working and annealing processes).

The average grain size for 18K golds produced by investment casting is typically in the range 100 - 1000 μm.[12] This implies that different collimators would change the X-ray beam cross-section interacting with the sample, resulting in a change in the portion of the alloy contributing to the fluorescence signal. Moreover, at constant collimator size, the smaller the grain size, the higher the number of grains involved in the analysis, thus obtaining a signal originated from a more representative portion of the sample.

In this regard, a 5N red-gold alloy (18K) was solidified by three different processes with different solidification rates, so that the resulting specimens had a gradient of microstructure dimensions. The grain of the samples produced this way have an average size of 167 μm, 353 μm and 3480 μm which from now on will be labeled as small, medium, and large grain respectively. The correlation between the collimator size and the microstructure of each sample is shown in Figure 1.

The gold content was measured for each item with an uncalibrated method by means of 0.6 mm and 2.0 mm collimators to investigate the internal or intrinsic error of the instrument and possible composition differences. The gold content was measured repeating the analysis twenty times and averaging the results. The single measurements are plotted in Figure 2 while the average values are listed in Table 1.

The uncertainties of the measurements are calculated through the standard deviation. They appear modest and according to a variance F-test are independent from both the collimator and the grain size in the case of the small and medium grain samples. On the contrary, the uncertainty resulting from the large grain microstructure is much larger than the previous cases when using

the smaller collimator and its difference from the results obtained with the larger one is high enough to be statistically significant, according to the F-test (Figure 3).
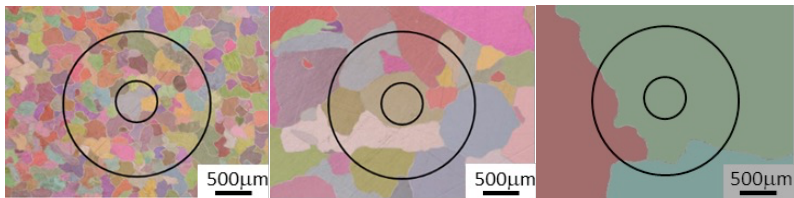

Figure 1: Microstructures of small (left), medium (center) and large (right) grain samples, compared to 0.6 mm and 2.0 mm.

Table 1: Average fineness for small, medium and large grain samples and both collimators.

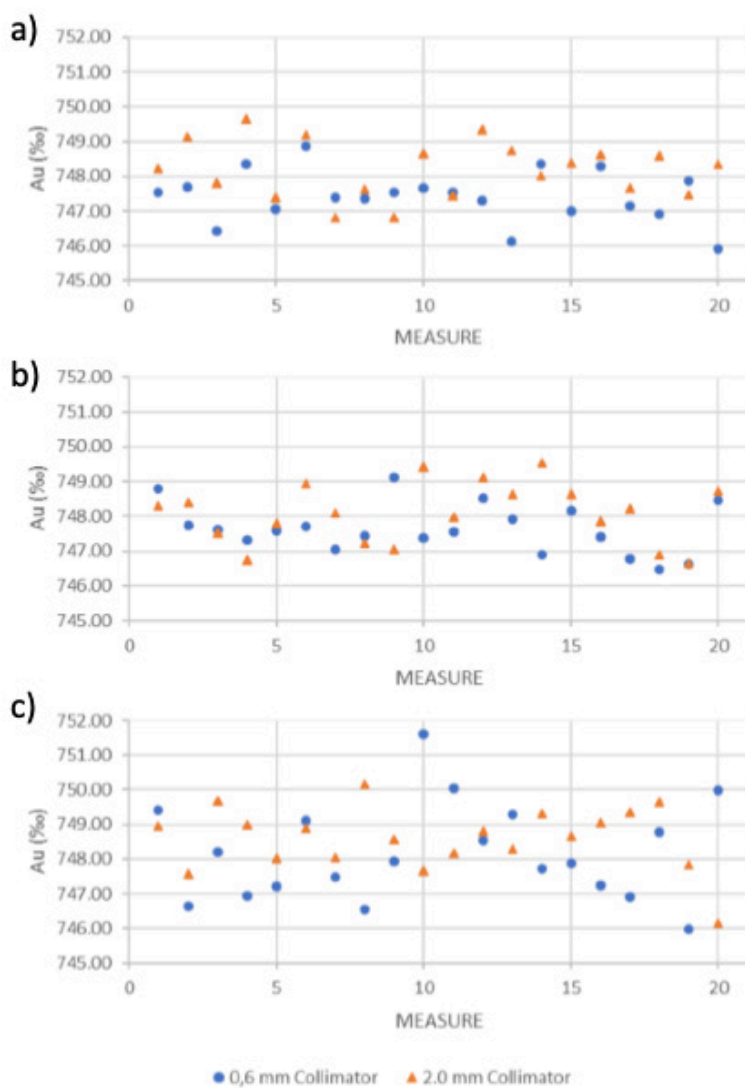| GRAIN SIZE (μm)	COLLIMATOR SIZE (mm)	AVERAGE GOLD CONTENT (‰)
167	0.6	747.4 ± 0.7
	2.0	748.2 ± 0.8
353	0.6	747.6 ± 0.7
	2.0	748.1 ± 0.9
3480	0.6	748.2 ± 1.4
	2.0	748.7 ± 0.7

Figure 2: Fineness analysis for 20 samples with small (a), medium (b) and large(c) grain samples and both collimators.

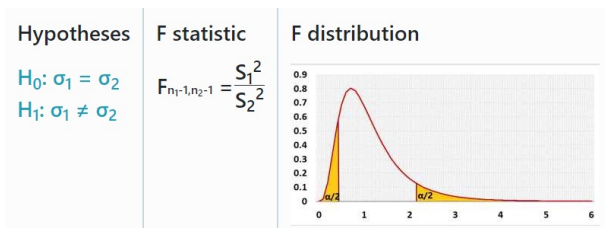| Hypotheses	F statistic	F distribution
$H_0: \sigma_1 = \sigma_2$ $H_1: \sigma_1 \neq \sigma_2$	$F_{n_1-1, n_2-1} = \dfrac{S_1^2}{S_2^2}$	

Figure 3: F test hypotheses and calculation: S_1 and S_2 are the standard deviations and n_1 and n_2 the sample sizes of the two sets of data.

This behaviour could be related to the relationship between the collimator and grain sizes. In case of very large grain sizes and very narrow collimator, the spectrometer may reveal slight compositional differences, then being subjected to potentially larger measurement uncertainty or requiring several repetitions of the measurement until a good statistical agreement is reached. The slight compositional difference amongst grains could be ascribed to incipient coring mechanism and ordering transformations in polycrystalline microstructure[13], although additional investigations are required for a deeper understanding of the phenomena.

In practice, it is then always advisable to use the larger collimator, which allows to probe a larger material volume and reduces the possible local variations of composition. However, these local variations can be bigger with respect to those encountered in cupellation because the number of atoms involved in the traditional fire assay technique is significantly larger, depending on collimator size and alloy composition.

The energy of the incoming X-ray beam onto the analysed material is much larger than the one of the emitted fluorescence X-rays. Therefore, the sample thickness (t) contributing to the XRF signal coincides with the thickness from which the characteristic X-rays of each element can escape the surface of the material and can be calculated through the Beer-Lambert equation.[14]

$$I = I_0 e^{-\mu t}$$

In this equation, I and I_0 are the final and initial intensities. The linear absorption coefficient (μ) has been calculated for the red gold alloy composition considering the most energetic X-ray transition generable by the 50kV set in the instrument. Under these assumptions, the total volume involved in the XRF signal is taken into consideration. The linear absorption coefficient for each element in the specific alloy has been calculated considering

the relative species abundance by means of the weight fraction f_i according to the relationship:

$$\mu = \rho_{alloy} \sum_i f_i \, (\mu/\rho)_i$$

The absorption coefficient through each element is obtain from literature tables.[15] It is worth noticing that different elements would have different escape thickness, thus a different number of atoms take part in the XRF analysis. An assumption often used for the calculation of the thickness is to consider the depth from which the outcoming radiation intensity is 5% of the originally emitted one. The number of atoms for each element was calculated in this way and summed to obtain the total number of atoms involved in the XRF signal of the alloy, to be compared with the number of atoms of the volume involved in fire assay, calculated from sample weight and alloy density. The result shows that the fire assay involves approximately 60 times more atoms than the ED-XRF analysis with the 2.0 mm collimator and 650 times more atoms than the 0.6 mm collimator.

On the base of the above-mentioned results, the 2 mm collimator was chosen to be used for all successive analysis, being the most suitable collimator compatible with the analysed samples.

Once the measure parameters were selected, a set of three different 18K alloys representing different commercially widespread colours and compositions used in jewellery making were chosen for the fineness measure. The selected alloys were a 3N yellow alloy, a 5N red alloy and a palladium-based standard-white alloy.

Table 2: Alloy composition of measured samples.

ALLOY	Au (‰)	Ag (‰)	Pd (‰)	Zn (‰)	Ga (‰)	In (‰)	Cu (‰)
3N YELLOW	752.0	116.6	-	5.0	-	-	BAL.
5N RED	752.0	44.6	-	2.5	-	-	BAL.
PD WHITE	752.0	-	129.6	-	5.0	14.9	BAL.

Each series of samples was produced by means of two different manufacturing processes.

The first one was optimised to obtain samples with a microstructure consisting of medium fine grains (approximately 300 µm). This process involved an initial melting followed by water cooling and mechanical deformation. The second production process has been optimised so that the same composition gives a grain size of over a millimetre and consisted of an ordinary investment casting whose cooling time has been altered. An example of the samples treated in this work is reported in Figure 4. In both cases, the samples were flattened, ground with 2500-grit sandpaper and polished with 3 µm diamond suspension before the XRF analysis. The surface finishing achieved this way is comparable to the standard jewellery finishing procedure resulting from 800-1000 sanding and successive paste-polishing, which allow us to compare our results in the same working condition of a standard production line.[8]


Figure 4: Example of measured samples.

For calibration and verification of the instrument, the instructions of ISO procedure 23345 are followed. A series of three specimens was prepared by mixing the same master alloy used to prepare the samples with an increasing gold content of 740, 750, and 760 thousandths respectively. This procedure was repeated for each investigated alloy. A calibration line for each composition-dedicated analysis method was obtained with these samples. In all the methods we declared all the non trace elements contained in the composition, according to Table 2.

The real gold content value in the calibration samples was determined through the fire assay method. ISO 23345 permits to avoid minor elements (<0.5‰) in the production of the standard,[10] but dictates that the elements must be declared during the preparation of the calibrated method, leaving room for different

interpretations concerning the role and the influence of these elements on the calibration.

For sake of completeness, zinc has been considered while dealing with the red-gold alloy for a preliminary study. The zinc Kα transition, in fact, stands in the energy interval of a secondary gold transition (Figure 5). The working principle of the spectrometry fluorescence instrument consists in normalizing the results, thus there might be some miscalculation in the deconvolution of the signals and in the following element quantification due to the low zinc amount in the alloy.

Two different methods were created to investigate the evaluation of the gold content as a function of the zinc presence. The first one contained all the elements present in the alloy (Au, Cu, Ag, Zn) while the zinc was omitted in second one. Both methods were calibrated using the same standards. Then, 30 samples alloyed with 752‰ gold were analysed. Their fineness was confirmed through fire assay. The average gold content is 750.9 +/- 0.7‰ and 751.7 +/1 0.5‰ for the method with and without zinc, respectively. Figure 6 shows the XRF analysis of single specimens compared with the corresponding fire assay reference being 751.6 +/- 0.2‰.
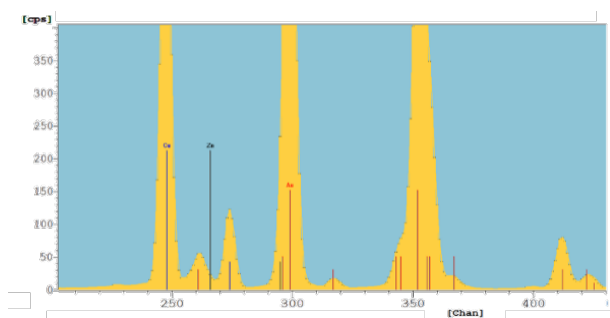
Figure 5: XRF spectrum of 5N Red alloy, elemental spectral lines in evidence.
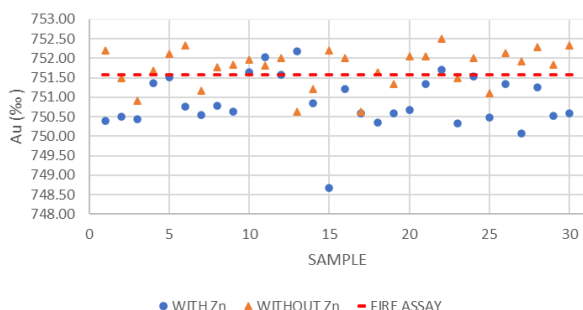
Figure 6: Influence of the zinc declaration within the analysis method on the fineness of 5N Red alloy.

The method without zinc measures the gold content in agreement with the fire assay, while the one including zinc differs by a significant amount. The inclusion of the interfering element at low concentration into the analytical method can affect the outcoming gold content, thus confirming the recommendation from the norm.[6] Consequently, for each alloy it is preferable to perform a preliminary study before the determination of the gold content to evaluate the potential interferences belonging to trace elements. Future works may be focused on the determination of the limit over which the presence of minor elements introduces a relevant error in the gold fineness measure, and if this effect is only relevant if the minor element spectral line is partially or totally overlapped with one of the gold spectral lines. For this reason, the zinc has not been included in the calibration methods of the red and yellow gold alloys treated in this work.

DATA ANALYSIS

3N Yellow Alloy
Figure 7 shows the result of the microstructure analysis of the samples produced in yellow gold alloy. The average grain sizes for the two production processes are 232 +/- 89 μm and 1412 +/- 756 μm for 3N YELLOW MEDIUM GRAIN and 3N YELLOW LARGE GRAIN, respectively. A series of measurements was performed with this method on 30 different samples. Each measurement was averaged over five shots taken within the sample area. The results are plotted in Figure 8. The measured average gold content for the medium and large grain samples is 751.99 +/- 0.43‰ and 752.68 +/- 0.75‰, respectively. The small difference in fineness between the two series can be explained by the different production method used to produce the samples. 3N YELLOW LARGE GRAIN series

was produced by lost wax investment casting and zinc loss and oxidation phenomena can increase final fineness for some extent.
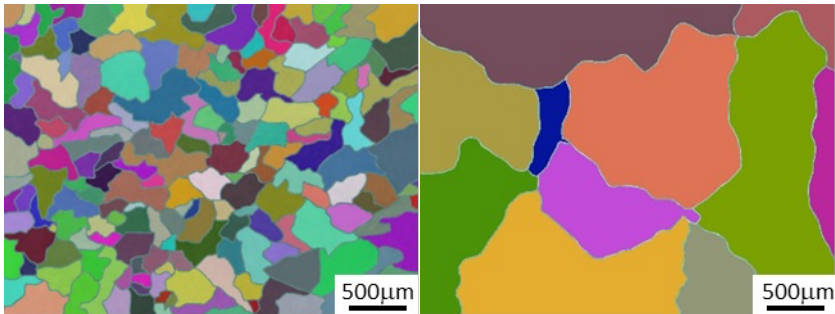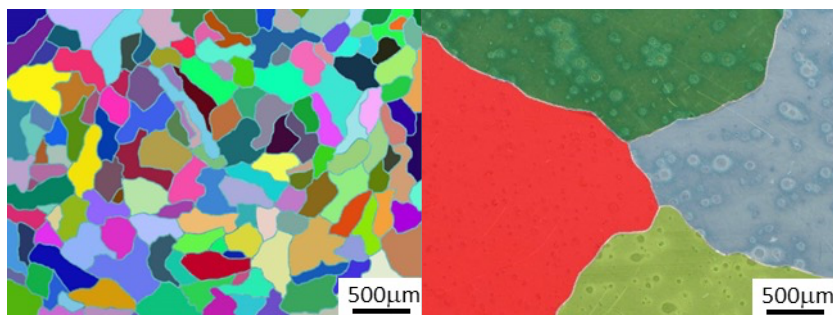

Figure 7: Grain structure of medium grain (left) and large grain (right) samples of 3N Yellow alloy.
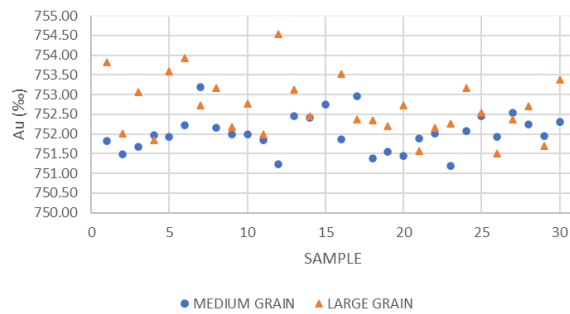
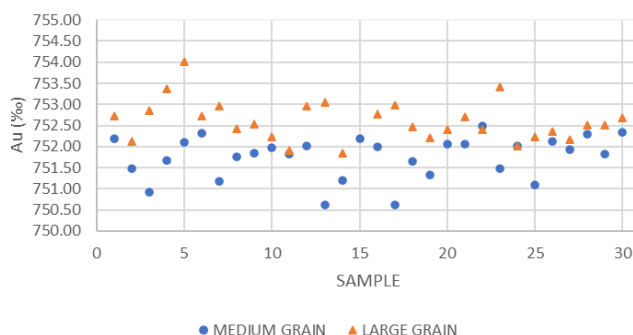*Figure 8: Comparison of fineness of 3N Yellow alloy depending on grain dimension.*

5N Red Alloy

The microstructures of the red alloy samples, whose mean grain sizes result in 250 +/- 85 μm (5N RED MEDIUM GRAIN) and 2550 +/- 1136 μm (5N RED LARGE GRAIN), are reported in Figure 9.

Figure 9: Grain structure of medium grain and large grain samples of 5N Red alloy.

The fineness averaged over 5 measurements per sample is plotted in Figure 10. The average gold content for the medium and large grain samples is 751.75 +/- 0.50‰ and 752.56 +/- 0.40‰, respectively.

The standard deviation of the two series is nearly identical, so that it is not possible to appreciate an effect of the grain size on the data dispersion for this composition, as previously discussed.


*Figure 10: Comparison of fineness of 5N Red alloy depending on grain dimension.*

Pd White Alloy

The microstructures of the Pd white alloy samples, whose mean grain sizes result in of 331 +/- 136 μm (Pd WHITE MEDIUM GRAIN) 1126 +/- 290 μm (Pd WHITE LARGE GRAIN), are reported in Figure 11. The calibration was performed by including minor elements in the method due to the fact that both indium

and gallium spectral lines do not overlap with gold fluorescence wavelengths, nor other major element signals as shown in Figure 12.
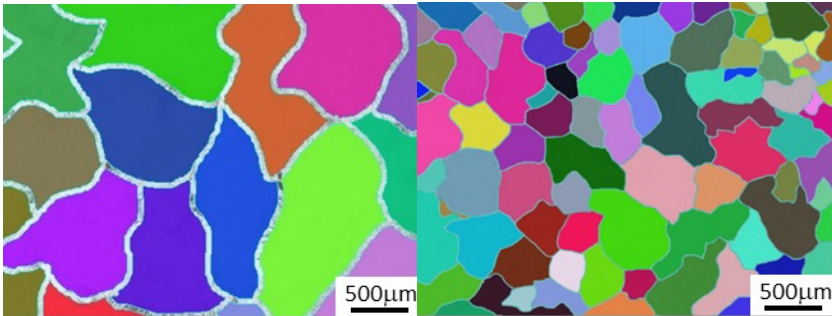
Figure 11: Grain structure of medium grain and large grain samples of Pd White alloy.
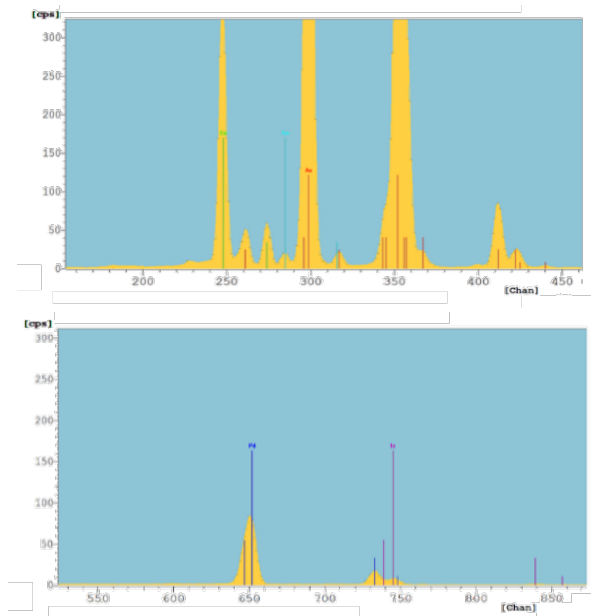
Figure 12: XRF spectrum of Pd White alloy, elemental spectral lines in evidence.
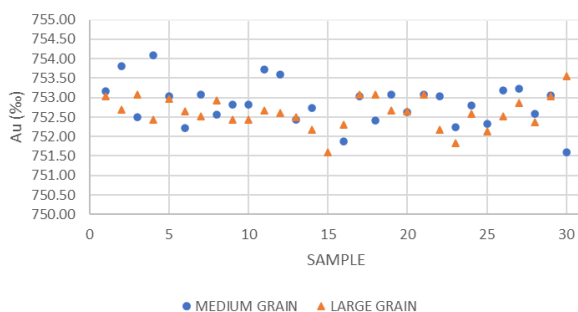
Figure 13: Fineness of Pd White alloy depending on grain dimension.

The measurements were carried out as previously mentioned and the results are represented in Figure 13. The measured average gold content for the medium and large grain samples is 752.85 +/- 0.47‰ and 752.66 +/- 0.37‰, respectively. In this case no fineness difference was observed between the two production processes which supports the thesis according to which zinc evaporation is responsible for the increasing gold content in investment casting samples.

Based on the analytical data, with the instrumental parameters used, there is no statistical difference between samples with medium and large grain size in white and red gold. The standard deviation of the measurement series is generally in the range of half a thousandth (0.5‰), which is comparable or even better with respect to values normally associated with the repeatability of the cupelling technique. Repeatability values associated with cupellation rise to about 1‰ in the case of compositions containing palladium. Only in the case of yellow gold, standard deviation for the samples with larger grains seems to increase probably due to an increase in local inhomogeneity, but is still less than a thousandth, showing that the technique can perform comparable or close to that of cupelling. It could be assumed that slightly higher local inhomogeneity more evident in surface fluorescence analysis into yellow coarser microstructure may depend on the presence of a somewhat larger difference in solid phase composition percentages, i.e. primary alpha phase and ordered intermetallic species mass fractions.
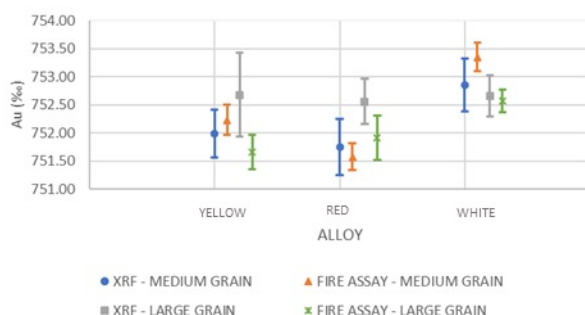
Figure 14: Fineness comparison for each alloy as a function of the grain dimension and the analysis technique.

The average gold content values for all samples are shown as a function of the gold alloy in Figure 14, from which it is possible to compare the differences between the two techniques in the determination of the gold fineness. XRF and cupellation results for both the medium grain size samples and the large ones are in perfect agreement within their relative uncertainties, the latter being slightly larger because of the number of measures performed during the study, while the cupellation is conditioned by the normed methodology which defines all the measures differing from more than 0.5‰ as not valid. By considering this same theoretical rule for the XRF technique, it is possible to observe that for each gold alloy colour family the great majority of the measures stand in between the same interval, although there are few points that are out of the acceptable range. In the fire assay method such measure would be repeated, which for the XRF is an easy and rapid. In other words, ED-XRF and fire assay provide the same quantitative analysis of the gold content and the two techniques can be considered as equivalent under certain experimental conditions and using samples compatible with this type of analysis. The greatest advantages of the XRF consist of being a non-destructive technique, besides being cost and time saving.

We chose to perform a statistical analysis on the standard deviation values obtained, to confirm whether the differences obtained were significant. An F-test on the variances obtained in the two yellow gold groups showed that the standard deviations are sufficiently different to be considered distinct. This means that we can assume that the larger grain size and the resulting inhomogeneity of the alloy in the area sampled by the instrument influenced the determination of the gold's fineness. Not only does the fineness measured by the instrument fall just at the limit of the respective experimental errors with the cupellation, but the standard

deviation also shows a greater dispersion of the different readings compared to the series with medium grain size.

A different situation occurs with both red gold and white gold. The average values of the fineness measured with the XRF coincide, net of experimental errors, with the cupellation ones. Furthermore, the F-test on variances tells us that the difference between the standard deviations of the respective medium and large grain series is not large enough to be statistically significant. Therefore, we cannot detect a significant difference for red and white gold alloys in the behaviour of the instrument on medium and large grain samples.

ANALYSIS METHOD MATRIX INFLUENCE

As the uncertainties on the determination of the gold content were found, the focus spontaneously shifts on the opportunity to analyse the gold assay of other alloys using the XRF methods. ISO 23345:2021 already requires calibration to be made with standard samples in which all major elements differ for up to 50‰ to the composition to be analysed, but according to our knowledge no practical investigation on this limit was considered during the regulation writing.

Each of the previous alloys was analysed by using ten medium grain and ten large grain samples by means of a calibration method each time different to check the accuracy of the gold assay. We can refer to this approach of using a calibration belonging to another colour family as "cross-referencing" method and it might be useful to reduce the analysis lead time and cost.

The fineness analysis performed for each series of samples using the calibrated methods for the series of different composition created during the previous phase is reported in Table 3.

Table 3: Average fineness deviations for medium and big grain samples when measured with different colour family methods.

		AVERAGE FINENESS DEVIATION		
		YELLOW GOLD METHOD (‰)	RED GOLD METHOD (‰)	WHITE GOLD METHOD (‰)
3N YELLOW ALLOY	MEDIUM GRAIN	-	2.6 ± 0.5	104.5 ± 0.3
	LARGE GRAIN	-	2.0 ± 0.6	104.0 ± 0.5
5N RED ALLOY	MEDIUM GRAIN	-2.6 ± 0.5	-	34.4 ± 0.5
	LARGE GRAIN	-1.9 ± 0.5	-	33.9 ± 0.6
Pd WHITE ALLOY	MEDIUM GRAIN	136.3 ± 3.5	135.0 ± 0.7	-
	LARGE GRAIN	135.3 ± 0.5	136.5 ± 0.8	-

As palladium is not present in the 3N yellow and 5N red methods, the white alloy measured through the 3N yellow and the 5N red calibrations results in a consistent overestimation of the gold content. The error on the measurements is about the same (~135‰) for the two methods. Such misleading could be attributed to the software algorithm which normalizes the sum of the total concentrations at one thousand thousandth (1000‰), thus increasing the relative amount of the selected elements by not considering the missing ones. Another possible source for this error is the spectral interference of the secondary wavelength of palladium, which tends to increase the signal of gold and is not normalised in the red and yellow methods due to the absence of this element in the calibration standards. On a practical level, no use can be made of calibrations derived from standards whose elements are different from those contained in the sample to be analysed. This was confirmed by measuring the red gold alloy and the yellow one with the Pd White alloy method where the discrepancy remains significant and in the order of 34-105‰.

The same basic principle applies for systems whose composition differs from the one used for the calibration. The extension of such difference and its possible relationship function has not been studied from the scientific community, yet. As a matter of fact, fineness measurements of red gold using the yellow gold method result in an underestimation of 2.6‰ for the medium grain and of 1.9‰ for the large grain. A similar behaviour is observed for the yellow gold alloy fineness measured with the 5N red gold method where a discrepancy of 2‰ and 2.6‰ is obtained for large and medium grain size samples, respectively. The relative difference in copper and silver amounts is responsible for the measurement error and works in opposite directions, although the origin of the miscalculation is once again probably associated to the software normalization process.

Certainly, what emerges from this first analysis is the importance of analysing the gold fineness using methods calibrated with alloys having the closest composition possible to the unknown sample for the purpose of obtaining accurate measurements. No significant trends were identified during these analyses that could be traced back to grain size and microstructure in general.

We performed XRF measurements on 10 5N red gold samples (18K) to investigate the limit within which a method is effective and accurate in determining the fineness of gold, even if it has been calibrated with a composition different from the one to be measured. The specimens, for which we already have the results

obtained with the corresponding method and the 3N yellow gold alloy method, were additionally measured with three other methods based on a 4N composition, a 6N composition and a different 5N composition, all defined as by the gold alloy colour standard, ISO 8654:2018.[16] The average results are represented in Table 4.

Table 4: Average fineness deviations for medium and big grain samples when measured with close colour family methods.

| | | AVERAGE FINENESS DEVIATION | | | | |
		3N YELLOW GOLD METHOD (‰)	4N PINK GOLD METHOD (‰)	5N RED GOLD METHOD (‰)	5N ALT. RED GOLD METHOD (‰)	6N RED GOLD METHOD (‰)
5N RED ALLOY	MEDIUM GRAIN	-2.6 ± 0.7	-2.7 ± 0.2	-	-0.8 ± 0.6	-0.7 ± 0.9
	LARGE GRAIN	-1.9 ± 0.8	-3.0 ± 0.5	-	0.5 ± 0.6	-0.4 ± 0.7

As seen from the table above, each variation in calibration composition is reflected in a slightly different value of the average fineness value for the sample series. This variation is small, and within the tolerance limit defined by the standard deviations, in the case of the methods for 5N red gold of alternative composition and 6N red gold. The variation, however, becomes important as the concentration of the major elements in the calibration samples varies more and more from the reference composition. This leads to important errors for the values obtained with the 4N pink gold and 3N yellow gold methods, the value of which was also presented in the previous table. Remarkably, even a method calibrated with standards belonging to the same colour family can show a certain discrepancy from the fineness value obtained with the official method. This suggests that the ideal practice would always be to calibrate with a standard whose composition reflects that of the samples to be analysed later.

ANALYSIS ON SEMI-FINISHED JEWELLERY ITEMS

Given the results and experience obtained along this study, it was decided to carry out a series of measurements on semi-finished jewellery samples produced by the Italian fine jewellery company Pomellato, which contributed to this study by supplying a series of rings produced both by lost-wax investment casting and by hollow round bar machining. The rings (Figure 15) are part of commercial line "Nudo" (mechanical working) and "M'Ama Non M'Ama" (investment casting), respectively. Such samples are produced with a 18K pink gold alloy.

We used the same setup as during the previous phases: a FISCHERSCOPE X-RAY XAN 252 (Helmut Fischer) fluorescence apparatus equipped with a 500 µm aluminium filter, 50 kV, 30 seconds measure time. We produced a calibrated method as laid down in the ISO 23345:2021, using the same alloy composition to produce the calibration standards, but not declaring zinc in the analysis method due to the consequences of our above results. The 2 mm collimator was not suitable for these samples due to the size of the rings. The larger collimator compatible was the 0.6 mm one. As stipulated in the regulations,[6] three points per object were sampled, at each of which three measurement repetitions were carried out, accepting measurements only when the difference between them was less than 1.2‰, repeating them otherwise. The resulting fineness are shown in Figure 16.

Figure 15: Example of semi-finished Pomellato's "Nudo" ring (left) and "M'Ama Non M'Ama" ring (right).
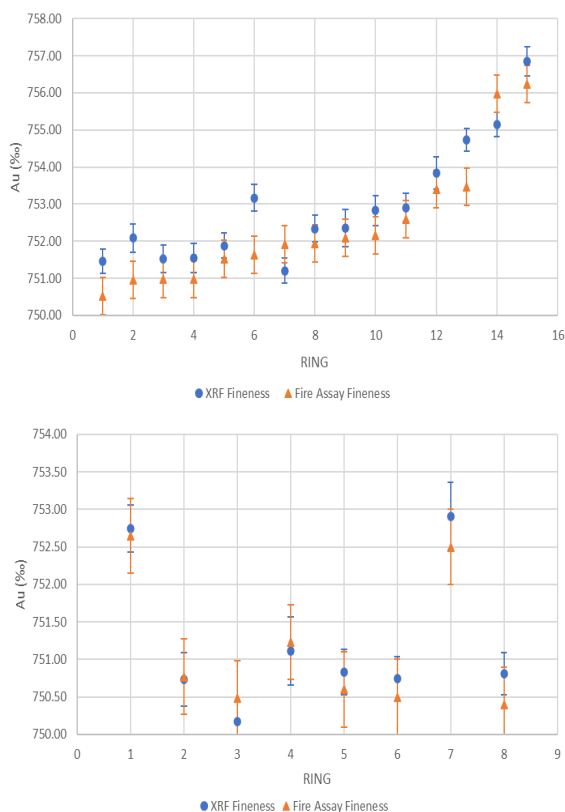
Figure 16: Comparison of fineness of Pomellato rings produced by investment casting (a) and mechanical working (b) process.

As far as the "M'Ama Non M'Ama" series is concerned, a good correspondence is generally observed between the value obtained by the classical cupping technique and ED-XRF, regardless of the model variant and the fineness. Besides few exceptions, the two fineness values coincide within the error limits consisting of the standard deviation for the XRF repeats, and the maximum limit of 0.5‰ defined by the cupping norm for repeats of the same sample. Even when the error intervals of the two measurements does not overlap (only 4 samples in the entire series), the distance between the mean values is still no greater than 1.5‰. We believe that it is possible to optimise the XRF procedures for measuring this type of sample e.g. by compensating for the small size of the collimator with a longer analysis time or a higher number of repetitions. The sampling might be struggling in this kind of samples due to the small dimensions involved and the eventual local composition variability coming from the production process.

Increasing the number of repetitions and improving the choice of points to be analysed on each piece so that they are more meaningful and less subject to environmental influences is likely to be a straightforward way to improve the results accuracy. Concerning the compositional variability statement, an indirect confirmation was found analysing the "Nudo" series manufactured through mechanical processing, which generally guarantees greater homogeneity of composition with respect to investment casting. In this case, all the values obtained with the XRF technique are fully in agreement and well within the confidence intervals of those obtained by fire assay. This demonstrates the excellent response of the instrument on this type of item, despite the use of a small collimator.

CONCLUSIONS

During this research, several 18K alloys representative of the main colours used in jewellery making were cast. The samples were polished and subjected to compositional analysis with a commercial ED-XRF after constructing a calibrated method for each one based on the recent ISO 23345:2021.

The importance of calibrating each method with a good quality standard, whose composition is as close as possible to the target alloy, was confirmed. Nonetheless, it was observed that minor deviations in the measured fineness can arise from alloys with different compositions despite consisting of the same elements. Such deviations become very important for alloys containing different elements, even though the calibration always refers only to the gold signal.

One of the elements generally present in the alloy as a minority element is zinc. Its emission lines partially overlap with spectral lines of gold, thus influencing the measurement of gold fineness depending on whether it is present in the standard and among the elements defined by the measurement method, although further investigation is needed to better define this influence and whether it is limited to zinc or affects more secondary elements.

Additionally, the influence of the sample microstructure on the analysis result was investigated as well as the importance of the collimator choice. The use of a sufficiently large collimator (2.0 mm) allowed to obtain a standard deviation comparable or slightly above the acceptability limit for duplicate tests defined by ISO 11426:2021 for cupping. The use of a smaller collimator (0.6 mm) on a sample with very large microstructure can lead to

a measurement uncertainty increase. This again emphasizes the importance of sampling the largest possible area, i.e. using the largest collimator compatible with the sample to be measured.

Considering these results, it can be said that the use of ED-XRF to define the fineness of gold in jewellery is possible, at least for elements whose nominal composition is known so that a calibration can be performed. The levels of accuracy are comparable to those of cupping under suitable measuring conditions. Moreover, as ED-XRF is a non-destructive technique and has much shorter measurement times, a statistically larger number of analyses can be performed. Another important key aspect of ED-XRF consist of being less dependent on operator steps, thus limiting human error sources. On the other hand, the limitations of the XRF technique must also be considered. Peculiarities related to sampling, surface inhomogeneities, microstructure length scaling problems, surface treatments or plating can significantly influence or compromise the measurement.

The ISO 23345:2021 standard is an excellent starting point for any company interested in carrying out this type of measurement. As more and more data are collected, calibration and analysis methodologies refined, definition of errors and limits of uncertainty (which are still relatively wide now) corrected, this normative will become a fundamental document for companies who want to approach ED-XRF technique.

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