

XRF Analysis of jewelry using fully standardless fundamental parameter approach

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Introduction

The fineness determination of carat gold and other precious metals has been investigated using several chemical and spectroscopic methods over a number of years. The most classical and established method is the traditional Fire Assay method of measuring gold content by first chemically separating the gold content using cupellation from the rest of the material and then using high precision scales to determine the weight percentages. Fire assay, when performed according to the ISO 11426 standard has been reported to give excellent accuracy and repeatability. On the other hand fire assay is a costly and time consuming technique and it is not suitable for rapid quality control. Therefore several spectrometric techniques have been investigated for both quality assurance of manufacturing alloys and assaying of finished products (1,2). Among the different techniques Energy Dispersive X-ray Fluorescence (EDXRF) Spectroscopy has gained most popularity in recent years.

Among benefits of EDXRF technique are

- Quick assay results (typically 1 – 2 minutes) of all the elements of the alloy simultaneously
- Non-destructive measurement
- Very little or no sample preparation
- Possibility to point the x-rays on a specific point on the jewelry
- Possibility to make surface thickness profiling
- Expandability of the system to laboratory automation

This article reviews the problems associated with the traditionally used EDXRF analyzers and presents the results acquired with the aid of the newest X-ray technological innovations: fully standardless quantitative analysis software and peltier cooled silicon detectors.

2. Quantitative analysis with EDXRF

The spectrum acquired with an EDXRF spectrometer shows simultaneously the peaks of all the elements present in the alloy, Figure 1. The performance of XRF analyzers for jewelry alloys is limited mainly by two technical problems: matrix effects and detector performance.

Matrix effects, reference materials vs. fundamental parameters

The quantification of the composition of an alloy, in weight %, is made by calculating the areas of measured spectrum peaks, Figure 1, of each element with respect to each other and then

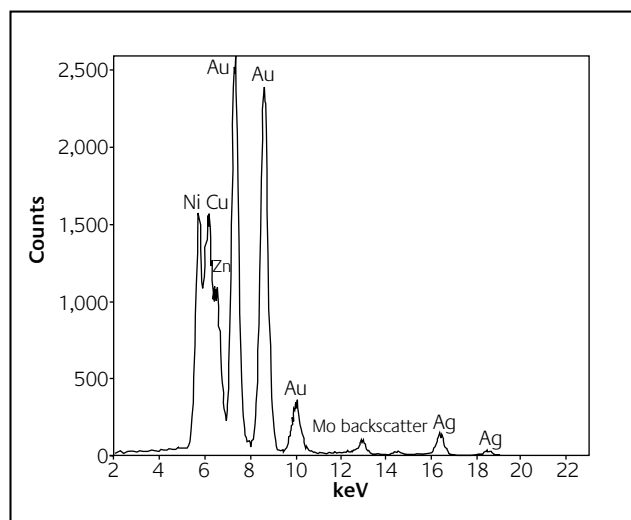


Figure 1 - X-ray spectrum of a 59.00% gold alloy containing also silver (Ag), copper (Cu), zinc (Zn) and nickel (Ni)

calculating the analysis result using a “type-matching” technique (3). Type-matching is based on comparing the measurement results of the object under study to a measurement result obtained with a reference material with a known elemental composition.

Normally, the measurement is calibrated with respect to the element of interest, e.g. gold, in jewelry. The remaining alloying elements are called *matrix*. If the elemental composition of the matrix of the sample under study is different from the reference material, the result is not dependable. Several correction techniques have been proposed to widen the applicability area obtainable with a limited set of reference materials (3, 4 and 5). However, the problem remains that, if the compositions of the reference standards do not correspond exactly to that of the sample under study, the result may be inaccurate.

Better results can be achieved with fundamental parameter (FP) calculation modeling, which is based on calculating results for all elements, not just the main element, i.e. gold (Au), silver (Ag), or platinum (Pt), but also all the elements of the matrix. Traditionally, most FP software has required also some prior knowledge about the elemental composition of the matrix and calibration with pure materials.

The new fully standardless FP program, used in the X-Inspect X10 analyzer, offers a solution to circumvent the matrix effect completely without any prior knowledge about the sample and any pure sample calibration references. Since the software calculates the concentration of all elements, it does not have a matrix at all, and consequently no matrix effect. The theoretical background of the method is explained in more detail in section 3.

X-ray detectors and overlapping spectrum peaks

Overlapping peaks in the measured X-ray spectrum can reduce the accuracy significantly. Peak overlapping occurs when the energies of spectrum lines of two or more elements are close to each other. In practice, if two peaks are closer than 400 eV to each other (see Figure 1.), the overlapping may affect the analysis result. This is the case particularly with gas filled proportional counter detectors, which have been in wide use in low-cost XRF analyzers earlier. Today, the new peltier cooled silicon detectors offer an affordable solution with energy resolution, expressed in Full Width Half Maximum (FWHM) of a peak well below 300 - 400 eV (6). However, overlapping can still be a problem, in particular when trying to separate Pt-Ir or Pt-Au containing alloys with a high concentration difference between the two elements. For example, where the concentration of one element is over 90% weight and the other below 3%, the accuracy can be affected.

In order to employ an FP calculation routine, most of the individual spectrum peaks need to be reasonably separate from each other in order to get unambiguous information about the spectrum. In practice, this can be achieved only with silicon based detectors.

3. Basic theoretical principles of the X-Inspect fully standardless FP analysis

The quantification of the X-ray spectrum using FP calculation is based on the theoretical expression of XRF intensity as a function of sample composition. In order to be able to calculate all information from the spectrum without any standards, the mathematical modeling needs to include all phenomena that occur, when the X-rays are interacting with the material of the sample. In the following, we list briefly these physical processes:

- Calculation of X-ray Fluorescence radiation yield relies on the measured values for photoelectric cross-section, the Coster-Kronig transitions and up-to-date mass attenuation coefficients established in previous research.
- Calculation of the production of secondary fluorescence, which depends on the energy difference between the various fluorescence lines and absorption edge energies and can be significant in some cases.
- Other phenomena which need to be taken into consideration are escape peaks, instrument function parameters, X-ray tube spectrum, etc.
- Measured energy spectrum is the sum of the fluorescence lines from different elements and the contributions from other scattering processes, which are treated as a background.

The quantification process starts by first obtaining the qualitative information of the elemental composition from the measured fluorescence spectrum. This can be used as a starting point of an iterative method that leads to quantitative information. In other

words, it is possible to investigate directly from the spectrum the elements that are present in the sample. No other assumptions concerning the sample are made, except that it contains only elements with observable fluorescence lines.

The FP calculation method can result in having more data and consequently better statistical accuracy than using a type matching calculation for a spectrum, which has been measured with the same hardware. This is caused by the fact that the fluorescence fitting components are the fluorescence lines due to all of the elements in the sample and the iterative whole-pattern fitting procedure contains all the fluorescence lines of the corresponding element, not just individual peaks.

Another major advantage of using all fluorescence lines together is that it works well in cases where, for example, fluorescence peaks of adjacent elements overlap and cannot be separated. The program works well, even if the sample contains all the elements from titanium to zinc with badly overlapping fluorescence lines and with strong secondary fluorescence contributions.

A full mathematical treatment of the calculation principle of the X-Inspect program has been presented earlier in reference (7). Today, the software includes also a full modeling for continuous X-ray tube spectrum, the possibility to use correction factors, customize detection limits and advanced tools for handling the measurement results and transferring data.

4. Accuracy and results with gold alloys

Accuracy

Accuracy is a very important value since it tells the user what is the uncertainty of the results shown by the analyzer. Statistically, however, there is no exact way to establish a "correct" accuracy reading, especially in XRF. Therefore the accuracy value is in many cases empirically determined or based on assumptions or different statistical calculations.

The evaluation of the accuracy of X-Inspect fully standardless method has two different approaches:

First, each X-Inspect XRF analyzer is calibrated with Certified Reference Materials (CRMs) so that the measurement result acquired with the analyzer is close to nominal values of CRMs without any references.

Secondly, an absolute value for the elemental accuracy (in weight percentages) is obtained from the average calculation of the nominal values of the differences. A measure of combined accuracy is calculated as an average of the sum of the differences (*not* a sum of absolute values).

Table 1 - Nominal and measured (fully standardless) values for a set of CRMs of ref. (8)

Measured values for single measurements [weight-%], X

Sample	Ni	Cu	Zn	Pd	Ag	Au	Σ
Au1					66,67	33,33	100,00
Au2		21,61			45,42	32,96	99,99
Au3		19,75		31,95	10,95	37,35	100,00
Au4	32,29	10,88			20,54	36,3	100,01
Au5	7,98	23,24	5,08		26,49	37,21	100,00
Au6		12,21		24,75	13,05	50	100,01
Au7				14,17	28,54	57,29	100,00
Au8	14,9	11,98	7,09		7,37	58,67	100,01
Au9	16,91	15,23	9,85			58,01	100,00
Au10	12,84	9,65	2,5			75,01	100,00
Au11	15,07			9,64		75,28	99,99
Au12	25,21					74,79	100,00
Au13		5,37			2,65	91,97	99,99
Au14		4,19				95,81	100,00
Au15		1,47				98,53	100,00

Nominal values for CRM samples [weight-%], S

Sample	Ni	Cu	Zn	Pd	Ag	Au	Σ
Au1					66,59 ± 0.04	33,32 ± 0.04	99,91
Au2		21,98 ± 0.05			44,65 ± 0.05	33,35 ± 0.03	99,98
Au3		20,10 ± 0.07		32,44 ± 0.09	10,57 ± 0.04	37,07 ± 0.08	100,18
Au4	32,43 ± 0.10	10,53 ± 0.05			20,00 ± 0.07	37,06 ± 0.06	100,02
Au5	8,96 ± 0.06	23,83 ± 0.07	4,92 ± 0.05		25,09 ± 0.08	37,14 ± 0.05	99,94
Au6		12,53 ± 0.05		24,96 ± 0.04	12,54 ± 0.05	49,99 ± 0.07	100,02
Au7				14,43 ± 0.06	27,68 ± 0.04	57,88 ± 0.04	99,99
Au8	14,57 ± 0.07	11,98 ± 0.05	6,74 ± 0.05		7,64 ± 0.01	59,01 ± 0.07	99,94
Au9	16,87 ± 0.09	15,31 ± 0.05	9,74 ± 0.06			57,81 ± 0.09	99,73
Au10	12,89 ± 0.05	9,64 ± 0.05	2,60 ± 0.03			74,83 ± 0.06	99,96
Au11	15,05 ± 0.05			10,00 ± 0.05		74,95 ± 0.06	100,00
Au12	24,94 ± 0.06					74,98 ± 0.04	99,92
Au13		5,28 ± 0.04			2,76 ± 0.04	91,67 ± 0.06	99,71
Au14		4,02 ± 0.03				96,00 ± 0.05	100,02
Au15		1,40 ± 0.01				98,60 ± 0.05	100,00

Difference [weight-%], $X - S$

Sample	Ni	Cu	Zn	Pd	Ag	Au	Σ
Au1					0,08	0,01	0,17
Au2		-0,37			0,77	-0,39	1,15
Au3		-0,35		-0,49	0,38	0,28	1,04
Au4	-0,14	0,35			0,54	-0,76	1,02
Au5	-0,98	-0,59	0,16		1,40	0,07	3,19
Au6		-0,32		-0,21	0,51	0,01	1,03
Au7				-0,26	0,86	-0,59	1,13
Au8	0,33	0,00	0,35		-0,27	-0,34	1,02
Au9	0,04	-0,08	0,11			0,20	0,50
Au10	-0,05	0,01	-0,10			0,18	0,20
Au11	0,02			-0,36		0,33	0,37
Au12	0,27					-0,19	0,35
Au13		0,09			-0,11	0,30	0,48
Au14		0,17				-0,19	0,15
Au15		0,07				-0,07	0,07

Table 1 - Continued

Accuracy [weight-%]

	Ni	Cu	Zn	Pd	Ag	Au	Total
	± 0,26	± 0,22	± 0,18	± 0,33	± 0,55	± 0,26	± 0,79

Precision [weight-%]

Sample	Ni	Cu	Zn	Pd	Ag	Au
Au8	0,11	0,09	0,11		0,12	0,14

Table 1. shows the results of CRM samples, manufactured by the Polish Mint (8). All results are obtained with one set of fundamental parameters and using the analyzer completely without reference measurements. The information about the accuracy of X-Inspect analyzer follow EURACHEM/CITAC and ISO guidelines (9, 10).

accuracy with respect to one element by using correction factors. The correction factors can be established by selecting a few samples as internal standards and calibrating the factors for one element with them, as demonstrated in Table 2

Precision

The term 'precision' is used to describe how well the measurement system is able to generate repeatable results. In other words, how close two or more replicate analysis results are to each other statistically when the conditions are kept the same. Precision is defined as a standard deviation of several repeated analysis results at the same conditions (same sample, same measurement time, same operator, etc.). Precision is normally an absolute value. If a relative precision of the instrument is required, the coefficient of variation is used rather than standard deviation. X-Inspect gives the results expressed as absolute values of weight percentages. The precision of each X-Inspect analyzer unit is determined individually and the results obtained can be found from the Measurement Certificate.

Correcting instrumental errors with selected references

The fully standardless results give a good overall view for completely unknown samples giving a reasonable accuracy for all elements simultaneously. However it is possible to improve the

Table 2. Measurement results for a subset of CRMs of ref. (8) by correcting the instrument error for gold.

Measured values for single measurements [weight-%], X

Sample	Ni	Cu	Zn	Pd	Ag	Au	Σ
Au9	17,01	15,33	9,87		-	57,79	100,00
Au10	12,97	9,74	2,53		-	74,76	100,00
Au11	15,23			9,74	-	75,03	100,00

Difference [weight-%], X - S With correction factors

Sample	Ni	Cu	Zn	Pd	Ag	Au	Σ
Au9	0,14	0,02	0,13		-	-0,02	0,56
Au10	0,08	0,10	-0,07		-	-0,07	0,29
Au11	0,18			-0,26	-	0,08	0,44

Difference [weight-%], X - S Without correction factors

Sample	Ni	Cu	Zn	Pd	Ag	Au	Σ
Au9	0,04	-0,08	0,11		-	0,20	0,50
Au10	-0,05	0,01	-0,10		-	0,18	0,20
Au11	0,02			-0,36	-	0,33	0,37

Table 3 - Typical achieved detection limit values [weight-%] for some selected elements

Cu	Pd	Ag	Au
0.26	0.14	0.57	0.59

Detection Limit, Determination Limit and Quantification Limit

The detection limit (DL) is defined as a statistically determined value above which the reported concentration can be reliably differentiated from a zero concentration with a specific probability. There are many procedures for calculating the detection limit in X-ray spectroscopy. The factors that determine the detection limits in XRF analysis are the measurement time, X-ray tube accelerating voltage and current, elemental sensitivity and sample composition. In XRF, the DL is usually defined as three times the standard deviation of the background. Detection limits for some elements are presented in Table 3.

A closely related concept is determination limit or quantification limit (QL), which is the lowest concentration of element in a sample that can be analyzed with a precision that is high enough to allow comparisons among measurements. Determination limit in XRF is normally defined as ten times detection limit (also denoted as 10-sigma, 10-σ).

Statistical standard deviation

The X-Inspect software shows the standard deviation (STDV) value for each measurement. In practice, when the number of repeated measurements is large ($n \geq 10$), the standard deviation values obtained from them approaches the STDV value shown by the analyzer for a single measurement. Therefore, the single measurement STDV, shown by the analyzer, can be used as an assumption of the standard deviation of the repeated measurements and consequently as an assumption of precision, 1/3 of detection limit or 1/10 of quantification limit.

The statistical STDV is inversely proportional to the square root of measurement time, as illustrated in Figure 2.

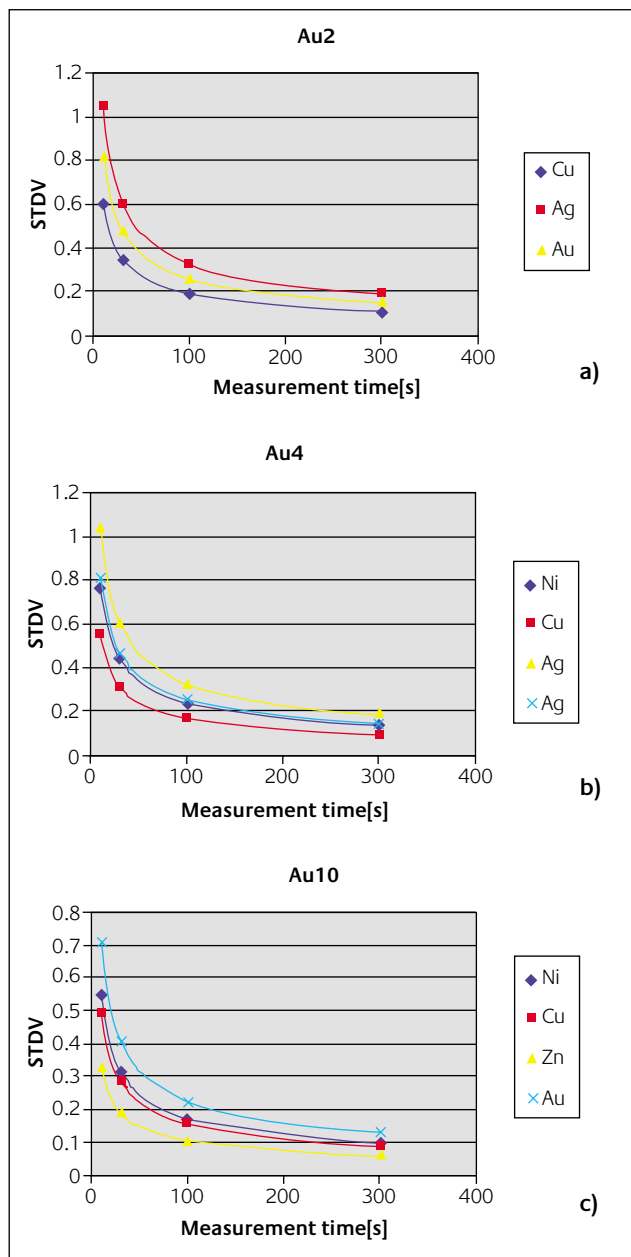


Figure 2 - STDV as a function of measurement time for three gold alloys. a) 33.5% gold, b) 37.06% gold and c) 74.83% gold.

Overlapping peaks

A potential source for a deterioration of detection limit is the overlapping of spectrum peaks of neighboring elements. Peak overlapping occurs when the energies of spectrum lines of two or more are close to each other. The overlapping can be classified in three categories according to the detected X.-ray line series (K-lines or L-lines) in the spectrum.

Overlapping L-lines

Typical examples are PtIr or PtAu alloys with a high concentration difference between the two elements. In cases where the concentration of one element is over 90% wt. and the other is below 5%, the accuracy of X-Inspect may be (but is *not*

necessarily) affected. However, the problem can be overcome by purchasing a CRM standard for the particular alloy and finding out the correction factors for the FP program empirically.

Overlapping K-lines

Overlapping of K-lines is not a problem for elements in the range technetium to iodine (atomic number, $Z = 43 - 53$). However, inaccuracy may arise when analyzing lighter neighboring transition metals ($Z = 21 - 41$). A high K-line fluorescence peak can have a tail (an increased background) of about 0.5 – 1 keV below the K-line peak energy. This tail affects the DL and accuracy when measuring K-lines of neighboring elements just below the high concentration peak. For example: the measurement of 3% nickel in the presence of 97% copper.

Overlapping K-lines with L-lines

There are a few rare cases where the K-lines of lighter elements coincide with L-lines of heavy metals. The worst case occurs when the concentration difference is over 90% and the major constituent is measured from L-lines. Examples include high platinum – low gallium and high gold – low germanium alloys.

Inhomogeneity of the samples

Mixing different pure metals as an alloy does not necessarily occur homogeneously. Instead, there may be local areas with a significant deviation from the average composition of the sample. This can be caused by formation of different phases between metals according to the laws of thermodynamics. Therefore, it would be beneficial to know the degree of inhomogeneity in the sample and judge from that knowledge whether the result obtained from a local area gives a satisfactory description about the total composition of the sample.

A way to measure the homogeneity of a sample statistically is Snedecor's F-test (11). F-test calculates if the difference between two measurement series is statistically significant indicating inhomogeneous sample. As an example, we have calculated the standard deviation for two different measurement series for gold from the same eight carat gold sample, Table 4. In the first series, the measurement location has been altered randomly whereas, in the second series, the measurement location was held the same. When the calculated P value, which is associated with the F-test,

Table 7 - F-test results for two series of measurements. The measurement time in each case was 300 s

	Random location	Same location
	33.77	33.09
	33.5	32.22
	33.68	32.91
	33.54	33.06
	34.96	32.94
	33.33	33.08
	33.32	32.69
	33.22	32.86
	33.46	32.85
	33.43	32.65
STDV	0.50	0.18

P = 0.0060

is less than 0.05 ($P < 0.05$), the conclusion is that the two standard deviations are statistically significantly different. Therefore, we would assume the sample is inhomogeneous.

5. Using XRF equipment as a quality control tool in manufacturing or assaying

When setting up an analysis instrument as a part of the manufacturing or testing process control, it would be good to clarify what kind of improvement is expected in the process.

Define the objectives for measurements

Before implementing a sampling and analysis programme, consider the objectives for the particular measurement. For what purpose is the data being collected? What types of decisions will be made as a result of the data? What are the action-levels for the analytes you are testing at the site? What is known about the extent and distribution of the contaminant? What are the implications of possible misclassification of samples?

The answers will help to determine the precision and accuracy you need to attain for different phases of the programme. These, in turn, will help you to determine sample collection procedures, preparation methods, measurement time, and the requirements for quality assurance and laboratory support.

Standard Operating Procedure (SOP)

To obtain good test data, it is essential to develop a written Standard Operating Procedure for sampling, measuring, and reporting data. A systematic procedure will help you to produce data of uniform quality. Typically, the Standard Operating Procedure is a written document that details the steps to be taken in handling the samples, standards, equipment, and data, including quality assurance measures, such as calibration checks and laboratory confirmation.

In jewelry industry, there are usually two type of needs:

- Quality control of alloy manufacturing process (alloy manufacturers)
- Testing of the fineness of finished jewelry products (assay offices, jewelry wholesalers, factories)

When manufacturing alloys the elemental composition needs usually to be known very accurately. There, it is usually important to know, very precisely, both the fineness of precious metal and composition alloying elements, which affect the color, casting properties, etc.

When assaying just the fineness of gold of finished products, it is, for most cases, quite satisfactory just to make one 2-3 minute measurement to establish that the item is clearly corresponding the nominal quality (hallmark). For example, in the case where the analyzer gives a result of 58.50% gold for a nominal 14 kt gold ring. If the STDV for gold is 0.14% with a 2 min measurement time, it can be said with a 99.96% probability (3 times STDV) that the ring contains over 58.08% gold, which is still over the legally required lowest limit of 58.03% (in some countries).

Therefore, when assaying finished products, the measurement time needs to be made longer (or multiple measurements be made) only when you get results that are close to the limit 58,03%. Then a better precision (smaller stdv) is needed to ensure that even if the fineness is a borderline case, it is still reliably over the limit.

The authors propose the following SOP for fineness testing:

- 1 Make one measurement with 2 or 3 minutes (depending on the displayed STDV)
- 2 If the fineness is over 2 times STDV + the required minimum value, the sample is clearly satisfactory
- 3 If the sample is close to the minimum value, repeat the measurement 1 or 2 times more. Also, make sure that the sample positioning and other conditions are certainly according instructions. If the average of measurements is still over minimum value, the sample is satisfactory
- 4 If, after multiple measurements, the result is still right on the borderline, use a comparative measurement method (usually fire assay).
- 5 If, after repeated measurements, the result is showing an undercarated value, there is likely a problem with the alloy.

A similar SOP is, in fact, already in use in several European assay offices that use XRF in their daily work. In this way, the use of the fire assay method can be reduced in function to just a backup method for the most difficult cases (12).

6. Summary

The newest development in XRF software and X-ray detectors have both improved the accuracy and made it possible to analyze all kinds of alloys, using only a few or no reference samples.

When doing a quick assay of finished alloys (Au, Ag, Pt, Pd,

etc.), it is possible to operate fully without references with the X-Inspect analyzer. The X-Inspect software is factory calibrated to give correct results for any alloy combination with an instrument error, typically less than 0.2-0.3%.

For quality control in a jewelry manufacturing plant, it is possible to reach an accuracy of 0.1% by using just a few internal standards and still cover a wide range of variable alloying matrices.

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