Non Destructive Analysis of Gold Alloys Using Energy Dispersive X-Ray Fluorescence Analysis

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Gold alloys can be analyzed quickly and in a non-destructive manner using energy dispersive x-ray fluorescence analysis (ED-XRFA). Two factors determine the accuracy of the measurement; the repeatability precision of the instrument and the inhomogeneity of the sample. In principle, the first can be kept low, all be it, at the expense of the measurement time, which is typically between 100 sec and 1000 sec. Values of 0.1%¹ or better, matching the accuracy of the cupellation method (fire assaying), are possible.

Inhomogeneous element distribution influences an individual measurement result. As the analyzed volume is determined by the measurement spot size, measurements should be made with as large a collimator as possible and repeated at different places. Statistical evaluations will then provide reliable statements about the uncertainty of the mean value.

Whether it is preferable to use instruments with a semiconductor detector or with a proportional counter tube depends on the specific application and will be covered in greater detail later in this report. In addition, and to a limited degree, ED-XRFA permits the detection of coatings on the surface. It also allows for the differentiation between solid Au alloys and Au alloy coatings. Metallurgic constituents can also be examined using special micro ED-XRFA techniques.

1 Destructive and Non-Destructive Methods

Analysis is the process of separating or isolating the individual components of the sample of interest. Thus, the analytical chemist “breaks down” the substance to be analyzed into its components and usually, thereafter, the object of the analysis is destroyed and can no longer be used; at most, the remains will have a certain material value. Often, taking a small sample for analysis is of no consequence, soil samples come to mind, for example. However, the situation becomes more problematic when samples should not be destroyed, such as valuable pieces of jewelry, works of art or elaborate machine components. It may not be a problem if one were to remove only a very tiny piece, possibly from an area that is generally not visible. However, the analysis error increases with decreasing sample mass due to uncertainties in weighing. More importantly, however, is the question as to whether the sample is indeed representative of the entire object. These questions can be answered only by using statistical methods – and this means several tests with many samples and removal of more material.

The solution appears to come from non-destructive analysis techniques. Non-destructive methods are based on the interaction between radiation (electromagnetic or acoustic radiation or even particle radiation) and the sample, whereby a conclusion regarding the sample's properties is drawn from the response signal. To evaluate the response signal, models of the interaction mechanism are required, which can be verified using samples with known compositions (standards).

The advantages and disadvantages of a certain destructive and a certain non-destructive method must be investigated individually for each application. Often, what cannot be accomplished with one technology, another will be able to do and vice versa. This report is concerned with the analysis of precious metal alloys, as for example used in jewelry. The determination of gold (range 33-100%) in a matrix consisting of Ni, Cu, Zn, Pd, and Ag /1/ plays the most important role. The officially recognized method for gold is the so-called cupellation method (fire assaying, cf. e.g., /2, 3/). Due to the great reputation of this classical (destructive) analysis method, one wonders whether it makes sense to introduce an additional method. – In reality x-ray fluorescence analysis offers so many advantages that it is already used as a complement to traditional analysis techniques and its use will most likely become even more widespread in the future /4,5,6/.

This report shall highlight the following capabilities of x-ray fluorescence analysis:

- a) Non-destructive method,
- b) Measurement results of great accuracy,

- c) Fast,
- d) Detection of inhomogeneities (micro analysis) is possible,
- e) Accompanying elements (Ni, Cu,...) are also detected,
- f) Top coatings that falsify the analysis can be recognized,
- g) Differentiates between solid alloys and coatings.

Essentially, only one disadvantage is inherent to the method; the analyzed depth is only a few micrometers. When evaluating this disadvantage, one should take note that only a small part of the specimen is analyzed with the cupellation method.

2 How does the x-ray fluorescence analysis (ED-XRFA) work?

The x-ray fluorescence analysis belongs to the non-destructive methods mentioned above. Its elementary interaction mechanism is the photo effect. The fluorescence radiation used for the analysis is emitted as a result of the ionization of an inner electron shell. The energy of this radiation is characteristic for each element. The intensity distribution of the radiation component ("spectrum") detected by a detector becomes the foundation for drawing conclusions about the chemical composition of the sample. While Fig. 2 schematically demonstrates the method, reference shall be made to textbooks such as [7] for a more detailed description.

In the x-ray tube T, electrons are accelerated from the cathode c to the anode a. A high-energy quantum radiation is generated by the interaction with the anode material,

mostly W (tungsten). A filter PF in the primary radiation path modifies the energy composition ("spectral density"). A collimator C defines the area of the interaction with the sample S. The size of the measurement spot can typically be set using exchangeable collimators. For very small measurement spots, special x-ray optics are used in place of the collimators. If the instruments are equipped with a programmable motorized measuring stage, the measurement can easily be automated to take place on several samples or at many points on one sample. The detector D registers the fluorescence radiation, which is used to determine the composition. The signals of the detector must be converted by suitable electronics E (amplifier, analog/digital converter) to an impulse amplitude spectrum

Figure 2
Principle of the x-ray fluorescence analysis

Figure 1
The XRF system Fischerscope X-Ray XAN is used for assaying jewelry samples in the Sheffield Assay Office, UK

Figure 3
Analysis of a gold ring by the Fischerscope® XDVM-W

(Fig. 5), which then serves the evaluation software as a foundation for computing the results. These may be the contents of the individual elements that are present in the sample.

The examples presented in this report refer to two different detector types: proportional counter (Fischerscope® types XDVM-W and XUL) and PIN diode detector (Fischerscope® types XDAL and XAN, cf. Fig. 1).

The XDVM-W and the XDAL include a motorized stage for automatic analysis of a large number of parts. Measurements at different positions of one sample or scans can be made automatically.

A measurement result for a rough estimate is available within a few seconds. Sample preparation is not required and it is not necessary to generate a vacuum. The only problem is positioning the area used for the measurement perpendicular to the primary X-ray beam. Simple mechanical positioning aids are very useful for this purpose. Positioning is simplified for instruments that measure “from below” by simply placing the measurement area on the protective foil (XAN, XUL). This geometry is ideal for flat parts. In any case,

Table 1

Repeatability precision of the Au concentration for a few typical applications (Fischerscope® XDVM-W, 60 sec measurement time) /10/. At times, different collimators (meas. spot sizes) have been used. The first line shows the standard application

No.	Application	Meas. spot size (mm)	Au (%)- Ag (%)-Cu (%)	u _{rep} (Au) (%)
1	AuAgCu	0.6	59 - 4 - 37	0.035
2	AuAgCu	0.6	59 -30 - 11	0.050
3	AuAgCu	0.25	59 - 4 - 37	0.074
4	AuAgCu	0.25	59 -30 - 11	0.067
5	AuAgCu	0.09	59 - 4 - 37	0.26
6	AuAgCuZn	0.6	59 - 4 - 37	0.26
7	AuAgCuZn	0.25	59 - 4 - 37	0.1
8	AuAgCuZn	0.09	59 - 4 - 37	0.32

the cross-hair of the video image shows the position where the sample is analyzed. Fig. 3 depicts the WinFTM V.6 /8/ screen for the analysis of a gold ring. The video image shows the analyzed area.

Only the elements of interest, Au and Ag are displayed. The uncertainty of the Au reading (see below) is about 0.1%. This value is mainly limited by the standards used for calibration. Experimental data: 10 measurements with 100 s. Measuring spot size is about 0.3 mm diameter.

3 Measurement uncertainty (accuracy) in the x-ray fluorescence analysis (ED-XRFA)

Measurement uncertainty u indicates an estimated value of the difference of the displayed value to the true value. The established terms “error” or “accuracy” are to be understood in this spirit. We generally differentiate between random and systematic error portions. The first can be determined using statistic methods (Point 3.1), while the latter can only be determined by measuring known samples (standards) and can then be corrected (Point 3.2). When speaking about evaluation software, reference is made exclusively to WinFTM® /8/.

3.1 Precision

If the measurement is repeated very often in one laboratory using one instrument, the result will fluctuate corresponding to a normal distribution, where the distribution parameters (can be closely approximated to the standard deviation s . For an individual measurement result x , this means that with a probability of 68%, the true value will be within $x \pm \sigma$. For 95%, $x \pm 2\sigma$ applies, and for 99.7%, $x \pm 3\sigma$. We identify the repeatability precision u_{rep} (cf. also /9/) with this distribution parameter σ , which is dependent on measurement time. The longer the measurement, the smaller u_{rep} will be. The WinFTM® program can calculate $\sigma = u_{rep}$ from the measured

Table 2

Repeatability precision u_{rep} of the Au concentration for a few typical applications (Fischerscope® XDAL, 60 sec measurement time, meas. spot size 0.7 mm)

No.	Application	Au (%)- Ag (%) -Cu (%)	XDAL u_{rep} (Au) (%)
1	Au Ag Cu	59 - 4 - 37	0,182
2	Au Ag Cu	59 -30 - 11	0,280
3	Au Ag CuZn	59 - 4 - 37	0,219
4	Au PdAg NiCuZn	59 - 4 - 37	0,344
5	AuPt PdAg NiCuZn	59 - 4 - 37	0,342
6	AuPtIr RhPdAg CrCoCuZnNiMolnSn	59 - 4 - 37	0,617

spectrum, such that no elaborate measurement series are required to determine the repeatability precision (estimation of the random measurement error). The often used expansion factors $k=1, 2$ or 3 for the various confidence levels can be set in the program. $k=2$ means $\pm 2 \sigma$ with a confidence level of 95%.

3.1.1 Proportional counter tube or semiconductor detector?

For gold analysis a value of $u_{rep} = 0.02 \dots 0.1\%$ is of interest, because it corresponds approximately to the precision of the cupellation method (to the best of our knowledge detailed studies about its measurement uncertainty have not yet been published). Typical ED-XRFA measurement times are between 100 sec and 1000 sec. If a high sample throughput is important, that is, where short measurement times have priority, good results can be achieved using proportional counter tube instruments [10]. However, a prerequisite is that the composition is known qualitatively. Tab. 1 provides examples.

Here, using a relatively simple instrument, an attempt is made to implement a fast and precise measurement, which appears likely, due to the high count rate. Usually, for most applications with about 14 ct alloys, a repeatability of better than 0.1% can be achieved with measurement times of one minute. If one removes applications # 5 and # 8 which use very small collimators, # 6 remains as the only “poor performance”. This application clearly shows the limits of a proportional counter tube instrument. While the high intensity of the detected radiation component enables the “best” precision of application # 1, it also reduces the energy resolution. Herein lies the weakness of the proportional counter tube. When several elements which are adjacent to one another in the periodic system, such as Cu and Zn, need to be analyzed simultaneously, the detector struggles to distinguish between the individual radiation components.

The only difference between applications # 1 and # 6 is that in # 6, a value for Zn is also requested. The sample is the same. The limits of the proportional counter tube are highlighted - it fails if many elements are to be detected simultaneously. The evaluation calculation in these cases has the task of separating adjacent, overlapping peaks in the spectrum of the fluorescence radiation. For example, the common application of Pt in gold alloys or Au in Pt alloys cannot be solved with a proportional counter tube instrument.

Tab. 2 shows results for the same samples, this time using an instrument with a semiconductor detector. Again, the u_{rep} (Au) values reflect the repeatability precision for various measurement applications.

For more complex sample compositions, where many elements are to be measured, the results are significantly better when using a semiconductor detector. On the other hand, for the application AuAgCu with only 3 elements, the simple proportional counter tube is superior. Fig. 4 schematically illustrates this fact, while Fig. 5 shows the underlying different energy resolution.

The sample with the spectrum shown in Fig. 5 has also been measured with both instruments under repeatability conditions for comparison purposes. The results can be compared in Tab. 3. They show that with an analysis of 5 elements, for Au, the counter tube is not inferior to the Si detector. Only, of course, for elements that are adjacent in the periodic system (Ni, Cu, Zn) is the better energy resolution advantageous. This is particularly significant for unknown sample compositions. The high resolution detection is preferred for qualitative analysis, while for repeated quantitative analysis for known elements, the simple (and less

Figure 4

Schematic presentation of the precision as a function of the number of elements to be analyzed. The proportional counter tube is superior to the semiconductor detector only for very few elements. The actual profile depends on the type of elements and also on the composition of the sample

Figure 5

Fluorescence spectrum of a sample with 60% Au, 8% Ag, 15% Ni, 12% Cu and 6% Zn, measured with the Fischerscope® XDVM-W (top) and the Fischerscope® XDAL (bottom)

Table 3

Repeatability precision for various detector types. The Fischerscope® XDVM-W operates using a proportional counter tube, while the Fischerscope® XDAL and XAN work with a PIN diode (Si detector) with Peltier cooling. All measurements at the same sample, meas. time 60 sec.

Element	Content (%)	u_{rep} (XDVM-W)	u_{rep} (XDAL)	u_{rep} (XAN)
Au	59.0	0.18	0.19	0.17
Ag	7.6	0.10	0.16	0.14
Ni	12.0	0.18	0.11	0.10
Cu	6.7	0.26	0.10	0.09
Zn	14.6	0.23	0.12	0.08

expensive) counter tube instruments are perfectly suitable.

In general, the repeatability can be determined with statistical means for any instrument and without any stringent conditions (contrary to the trueness, cf. Section 3.2 below). A special feature of the ED-XRFA is based on the Poisson distribution of the measurement signal, namely that the repeatability precision is inversely proportional to the root of the measurement time, or that u_{rep} is cut in half at four times the measurement time. The values of the repeatability precision for 60 sec shown in Tables 1-3 would be about four times smaller for 1000 sec.

3.1.2 Reproducibility of the method

This term covers all random error portions that are not related to the repeatability, and thus the precision of the instrument. For example, tilting of the sample (sample surface not perpendicular to the primary beam, cf. Fig. 1). Such matters are, of course, related to the types of sample and devices used. The aim is to keep such errors to a minimum, or to exclude them entirely, which is entirely possible. The total random measurement error is then reduced to the physically well-defined repeatability, which is predictable with the WinFTM® Software V.6. Detailed examinations of the reproducibility can be found in [10].

3.1.3 Inhomogeneity of the alloy

If the composition of the sample is a function of the measurement location, then the single reading defines an integral or mean value for the current measurement spot, including the uncertainties mentioned above. When making measurements at (many) different positions, one receives a distribution s_{total} of the measurement values that is composed of the repeatability distribution u_{rep} that is typical for the method and a distribution component $s_{inhomogen}$ that characterizes the inhomogeneity of the alloy composition according to

$$s_{total}^2 = s_{inhomogen}^2 + u_{rep}^2. \quad (1)$$

The uncertainty of the mean value $u_{mean\ value}$ from N single readings is

$$U_{\text{mean value},q} = S_{\text{total}} * t_{N-1,q} / \text{sqrt}(N-1), \quad (2)$$

where $t_{N-1,q}$ is the tabulated part of the t-distribution for a certain probability level as found in handbooks (e.g., [11]). Since for a large number of N, the t-distribution turns into the normal distribution, the following equation applies in approximation for the standard measurement uncertainty (confidence level of 68%, see above)

$$U_{\text{mean value}} \approx S_{\text{total}} / \text{sqrt}(N-1) \text{ (for } N \gg 1). \quad (3)$$

If N is only greater than 10..15, this approximation is entirely sufficient. One can see that the uncertainty decreases slowly with a large number N. However, the potential inhomogeneity of an alloy sample, characterized by $S_{\text{inhomogen}}$ would then dominate the measured standard deviation S_{total} according to equation (1), and thus determine the uncertainty of the mean value. As an example, a gold alloy has been measured at many (N= 25) locations, distributed over an area of 20 mm * 20 mm (30 sec measurement time):

Mean value = 74.03 % Au
 S_{total} = 0.223 % Au
 U_{rep} = 0.113 % Au (determined with a pre-test).

$U_{\text{mean value}}$ = 0.05 % or : 74.03 ± 0.10 % Au (95% confidence level)
 $S_{\text{inhomogen}}$ = 0.19 %

Using equation (3) results in an uncertainty of the mean value of 0.05 %, such that for a confidence level of 95%, the “true value” is within (74.03 ± 0.10) % Au. This would approximately correspond to the required accuracy.

However, for an ideally homogenous sample, the accuracy of the mean value would be better by a factor of two: $U_{\text{mean value}} = 0.022 \%$ (± 0.05 % Au) – or the measurement could be significantly shorter, instead of 750 sec only 150 sec. Of course, additional information about the uniformity of the Au concentration can be obtained from the 25 single readings. Using equation (1), one can estimate the distribution of the Au content with $S_{\text{inhomogen}} \approx 0.19 \%$. This numeric value characterizes the inhomogeneous Au distribution. A visual presentation of the distribution is much more descriptive. Fig. 6 shows the result for the distribution discussed here. One can clearly see the inhomogeneous Au structure and the significant lower Au concentration at the upper edge. The aforementioned mean value is representative for the entire area and corresponds to a virtual fire assay of the entire sample. However, most often in practical applications, only small areas of a sample are assayed such that the same observations apply that have been presented here.

Figure 6

Lateral distribution of the Au concentration within an area of 20 mm * 20 mm for sample P12 (see below), measured using the Fischerscope® XDVM-W. The variations are statistically significant because the repeatability distribution U_{rep} is only 0.11%. Range = 1.27%, S_{total} = 0.224% (N=441)

3.2 Trueness

The systematic deviations of the displayed value from the “true” value can be corrected with a calibration of the instrument. It is carried out by measuring samples with known contents, so-called standards that are combined in a “calibration standard set”. The calibration can be viewed as fine-tuning because WinFTM® provides already near correct results without standards based on building realistic fundamental parameter models [7,12]. Each calibration (Fig. 9) depicts both the non-corrected or theoretical and the corrected readings for each standard. The mean difference between nominal value and theoretical value is at about 0.5 mass-% for the gold analysis with WinFTM. Of course, this value may fluctuate slightly from one instrument to the next. To obtain an overview analysis, often no calibration is required, however, it is required for traceable analyses. The term traceability [13] includes a complete error calculation, or more precisely, a quantitative determination of the entire measurement uncertainty. This is ensured with WinFTM; cf. Section 3.3.4. It is important that the uncertainty (error, tolerance) must be provided to the program for each standard (Fig. 7). As a rule, the uncertainties are smaller for the precious metals than for the accompanying elements.

3.3 Calibration

3.3.1 Availability of standards

In addition to commercially available standards, samples can also be used that have been analyzed in-house using cupellation or other methods. Since, normally, only the

Dialogue		
Element	Value	Error +/-
Au 1 [%]	74.950	0.100
Ag 1 [%]	0.000	1.000
Cu 1 [%]	0.000	1.000
Pd 1 [%]	10.000	1.000
Zn 1 [%]	0.000	1.000
Ni 1 [%]	15.050	1.000

Figure 7

When entering the standard samples of the so-called "calibration standard set", the uncertainties (errors) must be entered in addition to the actual nominal values, in dimension of mass-%. WinFTM® V.6 also accepts skipping these inputs and will automatically enter default values (1%). Shown here as an example for the entry dialog is a gold alloy for the calibration of the measurement application Au-Ni-Cu-Zn-Pd-Ag

interesting precious metal content is known for such parts, but to make a measurement all accompanying elements must be entered into the calibration standard set, the standard-free analysis mode may simply be used for such applications – and a greater uncertainty, e.g., 2 mass-%) can be assigned to it. One should ensure that the samples are sufficiently homogeneous (see above).

For the present investigation, two sets of such calibration samples were available. The set consisting of

16 parts each with 6 elements (Au-Ni-Cu-Zn-Ag-Pd) /14/, which is distributed by the Polish Mint (samples P1, P2, ..) and the set consisting of only 5 samples and 4 elements (Au-Cu-Zn-Ag) from Fischer, which uses Degussa source materials (samples D1, D2, ..). Both sets are well traceable to cupellation tests as well as AAS. Investigations about the homogeneity of the samples are reported in Section 4 (Micro analysis). Here, it shall be investigated whether both sets are consistent with one another (within the scope of the certified uncertainties). At the same time, the methodology is tested using well-defined samples.

Looking at the differences between the "nominal values" and the measurement results in Tabs. 4 and 5, one can see that these are at only a few tenths of a percent. For most test samples, this is within the total standard measurement uncertainty of the results. However, there are exceptions where the difference is too great.

In Tab. 4, samples that are alloys of the elements Au (33%-75%), Ag (3%-30%), Cu (10%-40%) and Zn (0%-16%) have been used for the calibration. However, the test samples P1-P15 also contain Ni and Pd, and they have other concentration ranges, for example, Au up to 98.6% (P15). The effect of the smaller number of calibration samples can be seen primarily in the systematic measurement uncertainty (calibration error). One can also observe this in a comparison with Tab. 5, where partially the same test samples (P2, P4, .. P14) are used. Consequently, the sometimes excessive differences in Tab. 4 could be caused by non-compatible

Table 4

Measurement of the samples P1-P15 using a calibration with D1-D5. Instrument Fischerscope® X-Ray XDAL. Mean value of 10 measurements each (60 sec) at different positions

Sample	Nominal (%)	Measured (%)	Meas. uncertainty (%)			Difference (Nominal - Measured) (%)
			statistical	systematic (calibration error)	total	
P1	33.32	33.44	0.07	0.51	0.51	-0.12
P2	33.35	33.26	0.09	0.63	0.63	0.09
P3	37.07	37.61	0.16	0.57	0.59	-0.54
P4	37.06	37.79	0.17	0.13	0.21	-0.73
P5	37.14	36.98	0.08	0.68	0.68	0.16
P6	49.99	50.89	0.12	0.45	0.47	-0.90
P7	57.88	59.33	0.09	0.33	0.34	-1.53
P8	59.01	58.93	0.08	0.51	0.52	0.08
P9	57.81	57.38	0.20	0.56	0.59	0.43
P10	74.83	75.12	0.05	0.34	0.34	-0.29
P11	74.95	75.60	0.28	0.31	0.42	-0.65
P12	74.98	74.23	0.08	0.37	0.39	0.75
P13	91.67	92.48	0.07	0.09	0.12	-0.81
P14	96.00	96.45	0.04	0.06	0.07	-0.45
P15	98.60	98.93	0.05	0.025	0.051	-0.33

Table 5

Measurement of the samples P2, P4, .. P14 (even numbers) and D1-D5 using a calibration with P1, P3, .. P15 (uneven numbers). Instrument Fischerscope® X-Ray XDAL. Mean value of 10 measurements (60 sec) each at different positions

Sample	Nominal (%)	Measured (%)	Meas. uncertainty (%)			Difference (Nominal - Measured) (%)
			statistical	systematic (calibration error)	total	
P2	33.35	33.38	0.10	0.25	0.27	-0.03
P4	37.06	37.71	0.18	0.24	0.31	-0.65
P6	49.99	50.37	0.12	0.24	0.27	-0.38
P8	59.01	58.70	0.07	0.22	0.23	0.31
P10	74.83	74.94	0.04	0.16	0.16	-0.11
P12	74.98	74.04	0.08	0.25	0.28	0.94
P14	96.00	96.02	0.04	0.05	0.06	-0.02
D1	33.30	34.46	0.14	0.19	0.24	-1.16
D2	58.60	58.56	0.12	0.29	0.31	0.24
D3	58.60	58.73	0.17	0.24	0.29	-0.13
D4	75.10	75.31	0.06	0.18	0.19	-0.21
D5	75.10	75.23	0.09	0.20	0.22	-0.13

concentrations between standards and specimens. For example, the samples with higher than 90% Au are not covered by the calibration. Hence, the estimation of the calibration error that is based on the “experience” with the measured standards does not fit outside the concentration range of the standard. Tab. 5 points to another cause for possible discrepancies. In this case the calibration samples cover essentially the entire concentration range. But here also we find differences between measured and specified values that are too large. With samples P12 and D1, they exceed 3 to 5 times the uncertainty of the measurement value – which is highly unlikely. For such nominal/actual value comparisons, we also need to take the uncertainty of the nominal value into account. Yet, according to [14], it is at the most 0.1%.

Clarifying this contradiction is essential for the measurement application under consideration. It is known that precious metal alloys exhibit a more or less pronounced inhomogeneity, stemming from the manufacturing process (liquation). For gold alloys this is true particularly for samples of a lower Au content. Based on this suspicion, samples P12 and D1 were investigated with regard to their lateral concentration distribution. The result was surprising. Both samples showed inhomogeneous element distribution: for P12, the difference of the Au concentration across an area of 20 mm * 20 mm is a substantial 1 % (Details see Fig. 6 in Section 3.1), for D1 across an area of 6 mm * 6 mm even 3 % (Fig. 8). Therefore, the uncertainties of the nominal value of 0.1% (Fig. 7) specified in the calibration standard set can not be maintained for these samples. They must be increased significantly for these samples. Hereby the objectionable differences in Tab. 5 have been clarified.

The manufacturer of standards should avoid such serious inhomogeneities; however, a fully homogeneous alloy will generally not be attainable. Since an analysis is interested in a representative mean value, the calibration as well as the measurement must be designed such that (small) inhomogeneities are averaged. This is accomplished by measuring at different positions. We recommend 5 – 10 measurements. This will provide a good mean value.

3.3.2 Performing the calibration

The calibration determines a theoretical mean value for each standard ideally with a small statistical error. The measurement time used should be adjusted to the smallest

Figure 8

Lateral distribution of the Au concentration within an area of 5 mm * 5 mm for the sample D1, measured with the Fischerscope® XDVM-W. The differences are statistically significant, because the repeatability distribution u_{rep} is only 0.12%. Range = 4.2%, S_{total} = 0.75%

tolerance (error) of the nominal values. If this tolerance is about 0.1% for Au, then the random measurement uncertainty should be slightly smaller. On the other hand, there is no purpose in unnecessarily prolonging the measurement time, because the effective calibration error is determined by the square sum of both portions. In the above example of Fig. 9 (samples P1-P15), each standard sample has been measured at 10 different positions, each with a measurement time of one minute. When using instruments with a programmable measuring stage, the relatively time-consuming calibration (here 2.5 hours) can run automatically.

Due to the aforementioned problems, in practical applications, certain standards are frequently eliminated or replaced by others, or more standards are added. When using WinFTM®, it is not necessary to repeat all measurements. It is sufficient to only measure the new standards; the measurement of the unmodified existing standards can be skipped.

A total of 15 standards /14/ have been used. The presented dialog shows the nominal values, the un-corrected (theoretical) measurement values, as well as the corrected values for each standard. The input of the standards (-> Dialog according to Fig. 7), the setting of the type of error display (here “Systematic part”), among others, is carried out in this window. For documentation purposes, this table can be printed.

3.3.3 Verifying the calibration

After calibration, the measurement application is ready for the analysis of samples. For the measurement to be valid it must be ensured that the conditions of the instrument are the same as they were at the time of the calibration. In /10/ the long-term stability is being checked, which verifies the general suitability of a certain instrument. However, since this

does not provide any information about the situation in a particular laboratory, clear specification for the so-called monitoring of the measurement equipment must be established when setting up the methodology. Our recommendation is to regularly verify a typical sample in a separate “product”. If the statistically secured mean value is within pre-specified tolerances, then the measurement, or the calibration, is still valid, and it can be used to make measurements. If not it must be corrected. The frequency of monitoring the instrument can be derived from the history of the equipment. Typically, these periods range from a few days to weeks, partially also dependent on the measurement application.

3.3.4 Uncertainty of the calibration

When measuring standards, a statistically secure measurement value is the aim, but a certain residual statistical uncertainty u_{exp} remains. This uncertainty and the tolerance of the “Nominal value” u_{std} determine the uncertainty of the calibration (calibration error) u_{corr} . u_{std} is an input value for the calibration, (Fig. 7). The manufacturer of the standard must provide this information. To keep u_{exp} as small as possible, a sufficient measurement time must be used for the calibration. This requires a relatively long time. Since the total uncertainty u for a standard is comprised of the square sum of both portions ($u^2 = u_{exp}^2 + u_{std}^2$), it is of no use to keep only one amount small. A bad, i.e., inaccurate standard does not become better through infinitely long measurements. Conversely, a standard with very narrow tolerances, i.e., an accurate standard, should also be measured with good precision. With WinFTM® V.6, each standard functions independently of the other standards, each one also contributes to the security of the correction. Of course, it must be known how good or how secure the nominal values are. After all, these uncertainties determine the weight of each calibration standard. In the end, the result of the ensemble of all calibration measurements, that is, of all standards, will be a residual systematic measurement uncertainty u_{corr} . It depends on the number of used standards, on the tolerances u_{std} and on the statistical measurement uncertainty u_{exp} , but also on the difference of the actual measured values to the certified (nominal) values. It is a known experiential fact that further away from standards, greater systematic uncertainties can be expected than when measuring in close proximity to a standard. WinFTM® V.6, therefore, offers the capability of filling such gaps by adding one or more standards to the calibration without the need of re-measuring all previously measured standards. WinFTM® V.6 can display this systematic uncertainty of the calibration (correction of the standard-free measured value) directly /15/. It is also possible to display only the random portion of the measurement uncertainty – or the square sum of the two.

No	Elements	Au 1[%] S	Au 1[%] T	Au 1[%] C	Ag 1[%] S	Ag 1[%] T	Ag 1[%] C	Cu 1
1	Au-Ag-Cu-Pd...	33.32	33.74	33.32	66.59	66.25	66.59	
2	Au-Ag-Cu-Pd...	33.35	33.78	33.35	44.65	45.27	44.65	
3	Au-Ag-Cu-Pd...	37.07	37.96	37.07	10.57	10.53	10.55	
4	Au-Ag-Cu-Pd...	37.06	37.92	37.06	20.00	19.91	20.00	
5	Au-Ag-Cu-Pd...	37.14	37.29	37.14	25.09	25.86	25.10	
6	Au-Ag-Cu-Pd...	49.99	51.24	49.99	12.54	12.56	12.54	
7	Au-Ag-Cu-Pd...	57.88	59.26	57.88	27.68	27.45	27.68	
8	Au-Ag-Cu-Pd...	59.01	59.16	59.01	7.640	7.443	7.652	
9	Au-Ag-Cu-Pd...	57.81	58.40	57.82	0.000	-0.029	0.053	
10	Au-Ag-Cu-Pd...	74.83	75.30	74.83	0.000	0.028	0.008	
11	Au-Ag-Cu-Pd...	74.95	75.65	74.95	0.000	-0.134	-0.000	
12	Au-Ag-Cu-Pd...	74.98	74.21	74.98	0.000	-0.008	0.019	
13	Au-Ag-Cu-Pd...	91.67	92.22	91.68	2.760	2.831	2.817	
14	Au-Ag-Cu-Pd...	96.00	96.17	96.00	0.000	-0.028	-0.005	
15	Au-Ag-Cu-Pd...	98.60	98.67	98.60	0.000	-0.006	0.000	

Figure 9
Calibration results

Figure 10

Distribution of the Au concentration for sample D5 along a distance of 10 mm. The measurements were performed using the Fischerscope® XDVM-W, Collimator 3 (measurement spot size = 90 µm) /10/

4 Micro analysis

Finding an inhomogeneous standard sample when verifying the calibration supports a more thorough investigation of the lateral element distribution. The x-ray fluorescence analysis offers an excellent capability of investigating such questions in a non-destructive manner. Using a fine primary beam, a defined area of the surface can be scanned to obtain the local concentration distribution. This applies to any type of sample, not only Au alloys.

Samples are shown in Figs. 10 and 11. While a line scan (Fig. 10) measures only individual random peaks or dips, a true area scan (Fig. 11) clearly provides the spatial distribution with good local resolution. An area with a side length of only 0.5 mm is scanned that otherwise corresponds to the size of the measurement spot. The visible distributions should correspond to the metallographically measurable structural regions. Additional detailed studies can be imagined in this field. It should be emphasized that these microstructures generally do not influence the measurement uncertainty – in contrast to the macroscopic inhomogeneities (see above).

5 Invalid premises

Thus far, we implied that the assumptions about the composition of the alloy were correct. This affects the selection of the appropriate measurement application. With

ED-XRFA, the elements, for which concentrations are to be measured, must be known. The same applies to the structure of the sample. We have always implied that we have a solid (almost) homogeneous alloy.

5.1 Other elements

While the manufacturer knows the composition qualitatively, well founded doubts may arise during receiving inspections. Of course, the ED-XRFA also allows for a qualitative analysis, in particular when an instrument with a Si-detector (cf. Section 3.1.1) is available. WinFTM® even provides an automatic element search. The situation becomes critical when a different, non-defined element composition occurs during a routine analysis. Most ED-XRFA evaluation programs react rather helplessly and still display a result, which is, of course, wrong. For this reason, WinFTM® features an internal test, checking if results are reasonable and reacts very sensitively to any changes. This functions so well, even with instruments using a proportional counter tube, that samples that contain other elements are eliminated. The following example is taken from /10/.

An application Au-Ag-Cu-Zn is defined, without Pd and without Ni. Should these elements occur nonetheless, the test value “mq” becomes significantly greater. The regular threshold is set to $mq = 5$. For samples containing Pd and/or Ni, a warning would appear on the screen, and no result would be displayed.

Measurement conditions: XDVM-W, Coll. 2, Measurement time 60 sec.

Figure 11

Microanalysis of the Degussa white gold alloy (sample D1). Only an area of 0.5 mm * 0.5 mm with 30 * 30 points has been scanned. The instrument used (Fischerscope® XDVM +XOS polycapillary optic) is described in /16/. The local resolution is about 20 µm

5.2 Coating instead of solid alloy

The same basic idea of subjecting a measured spectrum to a viability test and to display and evaluate the result as a numeric value, mq, also functions for the differentiation between solid Au alloys and Au-containing coatings. Tab. 9 shows examples.

The values have been determined using an XDAL (Si-Detector) and an XUL (Proportional counter tube). Measurement time = 100 sec. The application for a solid alloy of Ni, Cu, Zn, Pd, Ag and Au according to /17/ has been employed.

The enrichment of noble metals after a corrosive acid treatment (to remove oxide layers after heating) builds something like a pure Au coating on the surface over the alloy material – which influences ED-XRFA. An artificially high Au concentration is obtained. Firstly, the “mq-test” would reflect such a situation and secondly, these coatings can be removed quite easily, e.g. by polishing or even using an eraser.

Conclusions and Outlook

Compared to cupellation, ED-XRFA is still in its infancy as a method for gold analysis and its specific performance features have only partially been investigated. Its essential advantages are its speed and the fact that it operates in a non-destructive manner. Thus, it is an ideal complement to cupellation for statistical quality control for multiple samples. Cupellation continues to be prudent for tests on a few random specimens.

The influence of an inhomogeneous alloy on the analysis result must be reduced or eliminated by measuring at various positions. Here, ED-XRFA is clearly superior to cupellation, because cupellation means melting of the entire part in order to obtain a representative value.

The hardware will improve in the very near future to obtain a higher precision and/or lower measurement times. The method itself is also expected to fulfill better the specific

Table 8

The *mq* value is a sensitive characteristic quantity to determine whether the measured sample corresponds to the assumed (defined) alloy type

Sample	%Au	%Ag	%Cu	%Pd	%Zn	%Ni	mq-value
P1	33.32	66.59					1.2
P2	33.35	44.65	21.98				1.2
P3	37.07	10.57	20.1	32.44			8.3 !!
P4	37.06	20.00	10.53			32.43	15.1 !!
P5	37.14	25.09	23.83		4.92	8.96	5.4 !!
P6	49.99	12.54	12.53	24.96			7.7 !!
P7	57.88	27.68		14.43			5.6 !!
P8	59.01	7.64	11.98		6.74	14.57	7.0 !!
P9	57.81		15.31		9.74	16.87	7.3 !!
P10	74.83		9.64		2.60	12.89	7.0 !!
P11	74.95			10.00		15.05	10.4 !!
P12	74.98					24.94	13.9 !!
P13	91.67	2.67	5.28				1.1
P14	96.00		4.02				1.0
P15	98.6		1.40				1.0
P16	99.99						1.0

Table 9

The *mq* value for solid alloy samples and coating systems with a top coating made of an Au alloy

Sample	mq XDAL	mq XUL
Solid alloys		
S1 (18 carat)	1.9	2.1
S2 (14 carat)	1.9	1.6
S3 (8 carat)	2.0	2.6
S4 (14 carat)	1.8	1.7
S5 (18 carat)	1.9	1.4

Au alloy coatings on brass, A-E approx. 11 µm Ni intermediate, f1-f4 no Ni

A (4 µm, 18 carat)	3.2	4.3
B (5 µm, 16 carat)	3.0	4.3
C (6 µm, 14 carat)	3.0	4.5
D (7 µm, 12 carat)	2.9	4.6
E (8 µm, 11 carat)	3.1	4.7
f1 (10 µm, 18 carat)	3.1	5.1
f2 (8 µm, 18 carat)	2.8	5.5
f3 (5 µm, 18 carat)	2.8	4.2
f4 (2 µm, 18 carat)	2.6	4.7

Au alloy coatings on steel, about 4 µm Ni in-between

041 (8 µm, 18 carat)	3.4	5.8
075 (9 µm, 17 carat)	3.4	5.6
078 (9 µm, 16 carat)	3.4	5.8
106 (5 µm, 18 carat)	6.9	10.3
116 (9.5 µm, 16 carat)	3.5	5.7
144 (2.5 µm, 18 carat)	9.3	14.2

needs of this field The ability to achieve sophisticated investigations (e.g. on microstructure) and a more user-friendly test routine (e.g. improved self-check of calibration integrated in a monitoring procedure) are under preparation. An important point is the reliability of the analytical method itself. Intelligent internal checks must avoid incorrect results automatically – as far as is possible.

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V.Roessinger studied physics at Leipzig University and finished in 1973 with a PhD on nuclear magnetic resonance (NMR). In the German Academy of Science he worked on different analytical techniques including PIXE, RBS, and XRF. Since 1992 he is employed at the Helmut Fischer GmbH + Co. KG in Sindelfingen (Germany) where he is responsible for the development and application of the XRF instrumentation.

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 - 17 Fischer Application Note vr0227 "The "mq" number discriminates layered samples from jewelry alloys"
- ¹ In general in this paper, the composition is given in mass-% (1 % = 1 g / 100 g)