

Lab Report XRF 433

Accuracy in the analysis of jewelry alloys

The monetary value of jewelry is largely determined by the content of precious metals in the alloy and the type and quality of gems. Design and workmanship play a less important role.

There are several methods for alloy analysis, the oldest and most accurate one is fire assay. This method uses the high accuracy and precision of balances to weigh a small piece of the original metal. Then, the non-precious metals in it are removed by different procedures (oxidation and dissolution) and the residue is weighed again. This is a destructive analysis that damages the jewelry though. Furthermore, this method is time consuming, generates environmental waste and cannot distinguish between the different elements in the sample, what could lead to misinterpretations of the analytical results.

However, the X-ray fluorescence (XRF) analytical method discussed here offers a contact-free and non-destructive analysis with good accuracy. Since jewelry pieces are often small and intricate or even non-homogeneous, it is also very important to analyze only a small area. This is possible due to the strong collimation of the excitation beam provided by the instrument used here.

Instrumentation

All measurements were performed using the M1 MISTRAL spectrometer equipped with a large area proportional counter. It features following technical parameters:

Excitation	W-tube (max. 40 kV, 40 W) glass side window
Detection	prop-counter with 1100 mm ² sensitive area approx. 900 eV energy resolution (Mn K α) 30,000 cps maximum count rate
Dimensions	size (WxDxH): 450x550x420 mm, 46 kg

Analysis

The measurements were performed on a large series of gold alloys that was carefully analyzed with fire assay (for Au and Ag) and with ICP (Inductively Coupled Plasma) for non-precious metals like Cu, Zn, Cd, Pd, etc. The concentrations ranged from 35 wt.% Au (approx. 8 karat) to 100 wt.% Au (24 karat). The measurement time was 100 seconds.

Working principle

When excited by the radiation of an X-ray tube, the sample emits characteristic radiation. This radiation is detected by a proportional counter that delivers energy-dispersive signals. The energy distribution of the emitted radiation is determined by a pulse height analysis. It contains information about the qualitative and quantitative composition of the sample. Special quantification models are necessary to calculate the concentration of different elements in the sample. The complete instrument is controlled by a special software package that runs on a notebook that is connected to the device only via a single USB cable.

Quantification

A standardless model was used to determine appropriate concentrations. Additionally, a standard-based model was used to improve accuracy. In this case, separate calibrations for limited concentration ranges were necessary to guarantee satisfying accuracy. Furthermore, a comprehensive set of standards was required for every concentration range.

Results

The results of both quantification models are shown in Figure 1. The standard-based model offers better results.

The reliability coefficient shows some differences:

Standardless analysis: 0.9958

Standard-based analysis: 0.9998

The differences between both quantification models become clearer, when the deviations from the given value are displayed (see Fig. 2). The average deviation for Au in the given concentration ranges is shown in Table 1.

Conclusion

Quantification can be performed both with standardless and with standard-based models. Standardless models have the advantage that they can be used for a wide range of sample qualities but offer only limited accuracy. In the case of standard-based models, the expected accuracy is better, but they require a large set of standards that are valid only for a limited range of concentrations.

The statistical error is in the range of the deviations in standard-based analyses. That means that the accuracy can be improved with longer measurement times. In standardless analyses, the statistical error is smaller than deviation i.e. an improvement of accuracy is not possible with longer measurement times but only with improved quantification models or more accurate fundamental-parameters.

Calibration results for Au

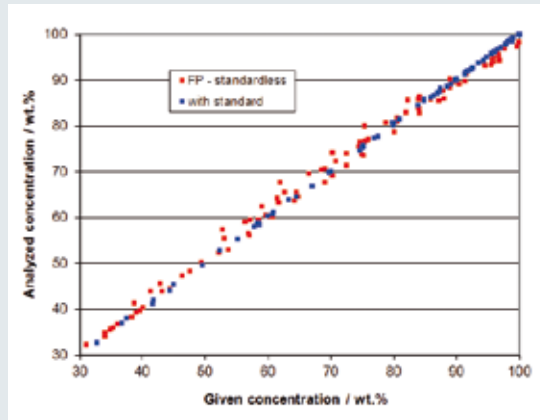


Fig. 1 Diagram showing the calibration results for Au

Deviations on the concentration of Au

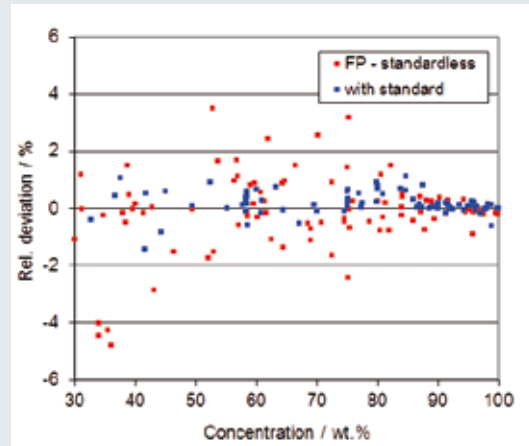


Fig. 2 Diagram showing the deviations from the given value

Average deviation

Au / wt.%	Karatage	Deviation FP	Dev. Stand.
33 - 45	8 - 12	0.91	0.31
45 - 60	12 - 14	1.27	0.25
60 - 85	14 - 20	1.68	0.21
85 - 100	20 - 24	1.35	0.18

Tab. 1 Average deviation for Au

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