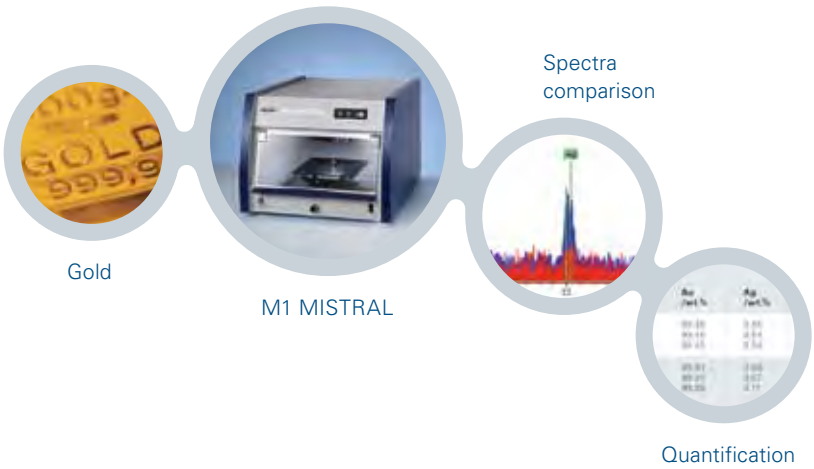

Lab Report XRF 448

Analysis of pure gold containing traces of other metals

It is a common task in precious metals analysis to distinguish different levels of purity of gold. In particular the separation between 99.5 wt.% and 99.9 wt.% is important for different applications: the effort in refining gold to the higher purity is bigger although the material value is not that different. For economic reasons it can therefore be important to know which caratage is at hand.

Because gold is very often used in the manufacture of jewelry and pieces of jewelry are small and intricate, it can be necessary to analyze only a small area of the specimen. If the analysis is to be performed non-destructively with XRF a µ-XRF instrument is required that concentrates the excitation radiation to areas down to 0.3 mm in diameter. In this lab report the influence of different measurement parameters and different models of data evaluation on the analytical result are considered to determine gold concentrations in the high caratage range with high accuracy.

Instrumentation

A M1 MISTRAL was used for measurement. This instrument has an high resolution silicon drift detector (SDD) and a collimator changer. Here a collimator with 0.7 mm diameter was used. Measurements were performed with 40 kV and 800 µA, measurement times were 30 s and 100 s. Different models were used for quantification:

- Standard-based quantification,
- Standardless quantification based on a Fundamental Parameter model and
- Determination of gold concentration per difference of the trace concentration to 100 %.

Spectra with different acquisition times

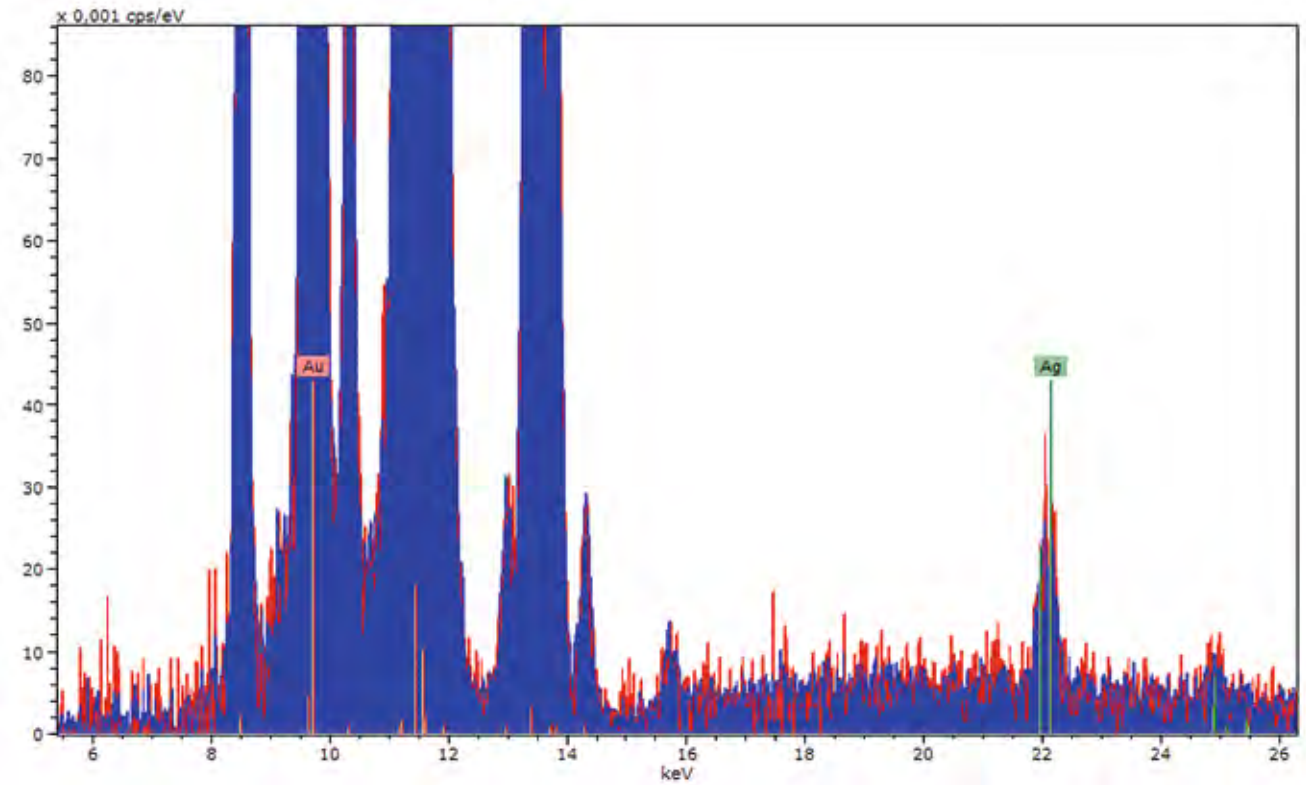

Fig. 1: Spectra of an Au-alloy with approx. 0.5 wt.% Ag acquired for 30 s (red) and 100 s (blue).

Results

Influence of measurement time

The influence of measurement time is demonstrated in Fig. 1. Here spectra of the same sample with approx. 0.5 wt.% Ag, measured with 30 and 100 s, are superimposed. The figure shows the high energy part of the spectra to demonstrate the changes related to the different measurement times. For the longer measurement time the fluctuations are – as expected – reduced, because the statistical error is smaller. From this examination it can be concluded that a longer measurement time will result in a better sensitivity for small concentrations but also in improved accuracy. On the other hand it can be seen that already the relatively short measurement time of 30 s provides acceptable statistics for the analysis of the low Ag concentration.

Determination of limits of detection in Au-alloys

Fig. 2 shows spectra with same measurement time of 30 s but with differences in Ag concentration. It can be seen that the blue spectrum with 0.5 wt.% Ag has a significantly higher peak than the other one containing only 0.1 wt.%. All other peaks in the spectrum are part of the Au-L-series with one exception, the peak at 15.6 keV is the Zr-K-line generated by the detector collimator.
From these spectra the limit of detection (LOD) with the 3 Sigma criterion can be calculated for Ag for the described measurement conditions. It is listed together with LOD for other typical alloy elements of gold in Table 1. The differences are a result of excitation probability (difference between Cu and Cd) and of peak overlaps (Zn, Pt).

Table 1 Limits of detection for Au-alloys with 30 s measurement time.

Limits of detection

Element	Ni	Cu	Zn	Pd	Ag	Cd	Pt	Pd
LOD /wt.%	0.015	0.028	0.035	0.033	0.040	0.045	0.040	0.050

Spectra of Au alloys with different Ag content

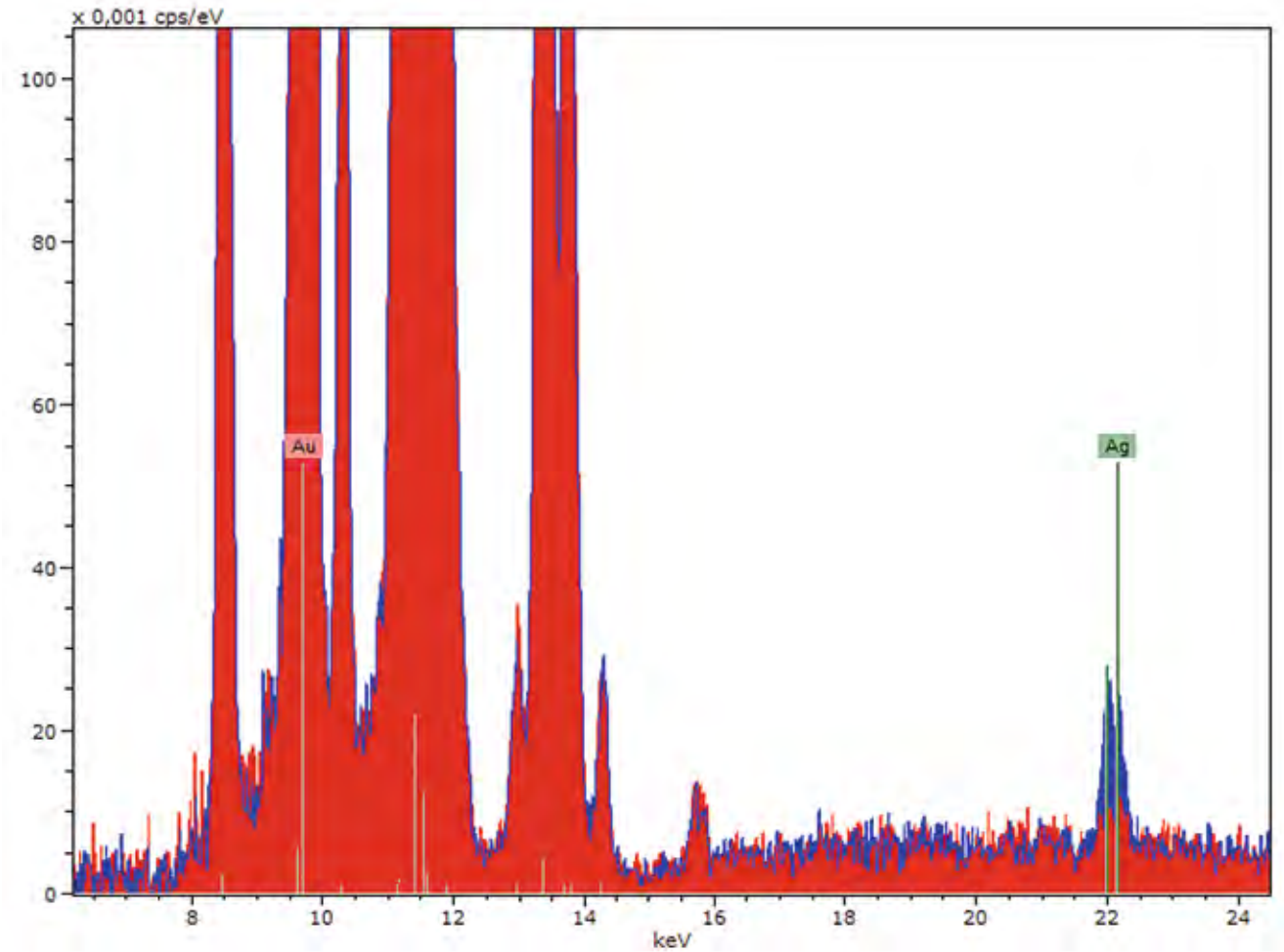

Fig. 2: Spectra of Au-alloys with 0.5 wt.% (blue) and 0.1 wt.% Ag (red).

For longer measurement times LOD will be improved. The reduction in LOD is by the square root of the factor of acquisition time prolongation, i.e. for a measurement time of 100 s the LOD are improved by a factor of approx. 2.

Quantification results

These spectra were quantified with three different models:

- The standard-based model uses standards and compares measured intensities of the unknown sample with those of standards.
- The standardless model calculates the concentration without standard with the help of the known description of radiation interaction with the sample. This quantification method is normally less accurate.
- The quantification per difference model determines the concentrations of traces and substracts these concentrations from 100 %. The expected analytical error of traces is in the range of 10 % relative, i.e. the absolute error for 0.5 % would be approximately 0.05 wt.%. For the high concentrations the analytical error is determined by the statistics. For the example discussed here it will be in the range of 0.4 % for gold. That means this error is approx. 8 times larger than that for the traces. The accuracy for the major element can therefore be improved by this difference method.

Results of these three methods and for two different samples – all measured for 30 s are displayed in Table 2. As can be seen, results are already comparable in case of a relatively short measurement time.

Table 2 Quantification results for pure Au-alloys at 30 s acquisition time

Comparing quantification methods using spectra with different trace concentrations

Element	Quantification method	Au /wt.%	Ag /wt.%	Cu /wt.%	Zn /wt.%
Sample 1 (Fig. 2, red spectrum)	Standard-based	99.45	0.55	0.00	0.00
	Standardless	99.45	0.54	0.01	0.00
	Per difference	99.45	0.54	0.01	0.00
Sample 2 (Fig. 2, blue spectrum)	Standard-based	99.93	0.09	0.00	0.00
	Standardless	99.91	0.07	0.01	0.00
	Per difference	99.89	0.11	0.00	0.00

Conclusion

The measurements show that it is possible to distinguish between 99.5 wt.% and 99.9 wt.% Au. In case of 99.5 wt.% Au the peaks of traces can easily detected and used for quantification. Even in case of 99.9 wt.% Au the peaks of the traces can be identified and provide sufficient statistics for concentration determination. The measured samples have concentrations of approx. 0.5 wt.% and 0.1 wt.% Ag, respectively. Both peaks can be detected with sufficient accuracy. With help of a longer measurement time it is possible to reduce the statistical error, but the final results are not influenced significantly.
Other trace elements (for example Cu, Ni, Zn, Pd) have even a better limit of detection due to their higher excitation efficiency.

It can be concluded that it is possible to identify and quantify elements with a concentration lower than 0.04 % to 0.01 %. The intensity and the peak-to-background ratio of these peaks are large enough for detection.

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