INFLUENCE OF MATRIX EFFECTS ON QUANTITATIVE CHEMICAL ANALYSIS BY ESCA

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Abstract: A quantitative study of gold-silver alloys has revealed a small but significant matrix effect due to changes in the mean free path of the photoelectrons. This was shown by comparison of the sum of normalized intensities of the gold 4f and the silver 3d lines for 6 Au-Ag alloys with the line intensities of the pure metals.

INTRODUCTION

Since the development and refinement of ESCA-spectroscopy it has been shown that core level binding-energies in alloys are in good approximation determined by essentially atomic properties/1/. This seems at least in general not be true if line-intensities are concerned.
The measured line-intensity originating from a characteristic level of the atomic species i is given by /2/ :

$$I_i = I_o \eta_i \sigma_i \lambda_T(\varepsilon_i) D(\varepsilon_i) \qquad (1)$$

where I_o is the x-ray flux, $D(\varepsilon_i)$ the spectrometer function, η_i the density of atoms of type i, σ_i the photoexcitation propability and $\lambda_T(\varepsilon_i)$ the mean free path of electrons with energy ε_i.
To achieve a quantitative analysis of a sample for a given element i one has to investigate the ratio

$$\frac{I_i}{I_i'} = \frac{I_o \eta_i \sigma_i \lambda_T(\varepsilon_i) D(\varepsilon_i)}{I_o \eta_i' \sigma_i' \lambda_T'(\varepsilon_i) D(\varepsilon_i)} \qquad (2)$$

The measured intensity refer to the sample to be analyzed, the other to a standard.
Whenever the quantities determining line intensity do not change in placing atoms of type i in crystal surroundings differing frome those of the standard one gets the relation :

$$I_i / I_i' = \eta_i / \eta_i' \qquad (3)$$

Deviations from this linear behaviour, not caused by uncontrolled changes in the experimental conditions, e.g. I_o and $D(\varepsilon_i)$ are called matrix effects.

Those effects are brought about by the dependence of σ_i and $\lambda_T(\varepsilon_i)$ on crystal surrounding. It was recognized that at least for levels with high binding energy the σ_i variations could be neglected whereas the λ_T dependence has to be taken into account in most cases /3/. An experimental approach can be found by comparing intensities gained from pure elements with those from systems containing several components/4/. If there are no matrix effects the standardized sum of intensities of all components must be a constant for all possible component concentrations.
In this context it has to be guaranteed that the geometry of sample and spectrometer is fixed during the measurements.Problems may occur when the sample is heated. This leads to vaultings especially of mechanically fixed metal samples and simulates an effect. Whether this vaulting effect plays an important role for a given spectrometer and sample geometry can be tested by slightly tilting the sample holder before heating.

EXPERIMENTAL SECTION

The basis for this investigation was the question whether the demanded linearity in case of the absence of any matrix effect for a quasi-ideal system Au/Ag is fullfilled /5/.
A further interesting problem in this connection is in how far surface segregation, which is a consequence of the interaction energy between solute atoms and a free crystal surface /6/ has any

influence on λ_T. This is investigated by means of argon ion sputtering and by temperature variation.
6 Au/ag alloys (DEGUSSA) of different composition were investigated (Table 1).All samples were measured under UHV conditions ($\approx 10^{-10}$ mbar) in a Leybold-Heraeus LHS 10 ESCA-spectrometer.
The samples were prepared

- I as bought from DEGUSSA
- II after annealing for one hour at 300 °C
- III after ion sputtering for 15 min, 3 keV , 10 $\mu A/cm^2$
- IV after III and annealing for one hour at 300°C .

Fig.1 shows the standardized intensity for Au, Ag and the sum ofthe normalized intensities versus sample preparation.
It is found that the Ag concentration for the samples I is much higher in the probed sample volume than the one given by the chemical analysis of the sample material. In raising temperature we found a strong increase in intensity due to reduction of contaminations. In this connection it should be mentioned that the oxygen coverage of the surface is proportional to the Ag concentration.

Table 1 . Sample composition and sign

Au/Ag (wt %)	99/1	90/10	80/20
Au/Ag (at %)	98,2/1,8	83,1/16,9	68,7/31,3
sign	A	B	C
Au/Ag (wt %)	60/40	20/80	1/99
Au/Ag (at %)	45,1/54,9	12/88	0,6/99,4
sign	D	E	F

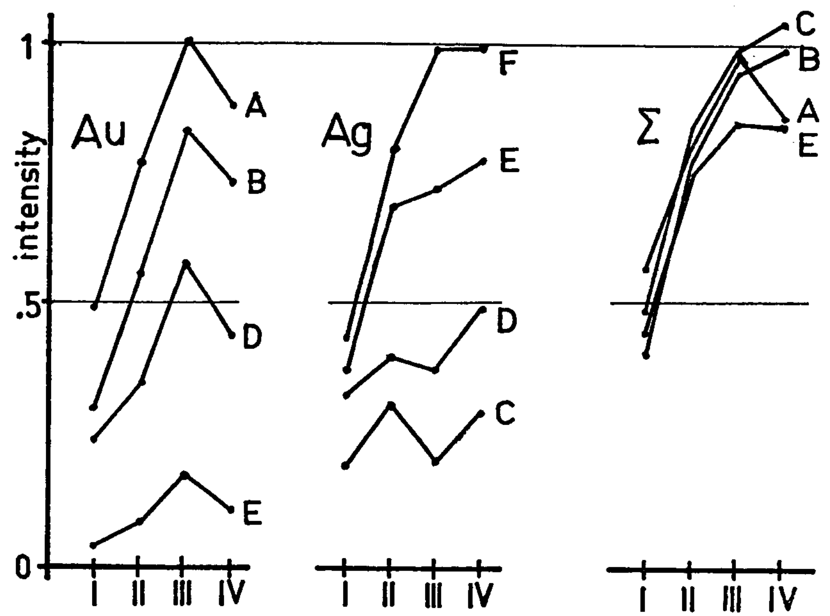

Fig. 1. Standardized intensity for Au and Ag and sum of normalized intensities vs. sample preparation

After sputtering one realizes the known effect /7/ that the Ag concentration is selectively reduced accompanied by a complete removal of oxygen from the surface. After having tempered the sputtered sample at 300°C for 1 hour the composition of the sample surface heals off again.
In fig.2 the bulk composition as given by DEGUSSA is plotted vs. the found not standardized sample composition as a function of sample preparation. The claimed linear curve for sputtered samples /5/ was not reproduced. The curves for the annealed samples show linear dependence.
As a summary of our measurements fig.3 shows the standardized sum of intensities for all studied Au/Ag alloys. Linear interpolation between the measured values indicates that only in the region of 60 % Au equation (3) is fulfilled. The other standardized sum intensities range in the region 100 ± 10 % and show a systematic curve which is above 100 % for alloys with low Ag concentration and below 100 % for those with high Ag concentration.

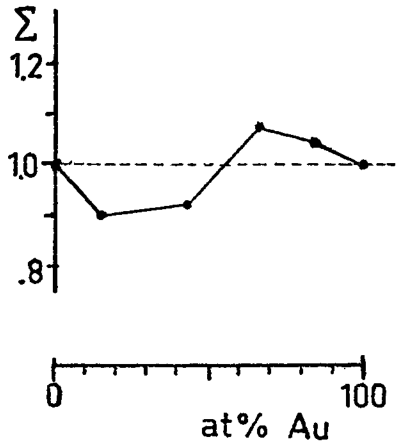

Fig. 3. Sum of normalized intensities vs. alloy composition

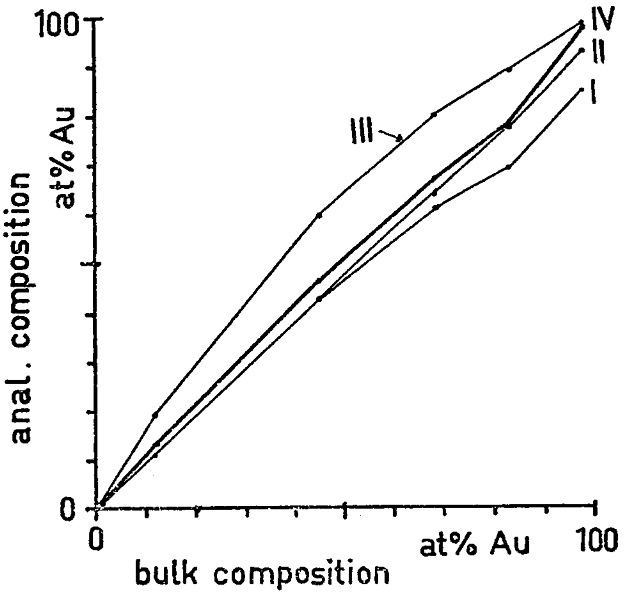

Fig. 2. Bulk composition vs. analyzed composition as function of sample preparation

DISCUSSION and CONCLUSION

Annealing of Au/Ag alloys to 300°C leads to a drastic reduction of contamination and enhancing of intensity to approximate 80 - 90 % of the intensity for clean surfaces, as seen from fig.1 . As seen from fig.2 the unprepared samples show an enhancement of silver increasing with decreasing silver content.

Fig.3 shows a small but significant matrix effect in the gold-silver system.

It was shown that good quantitative results for gold-silver alloys can be obtained for samples annealed to 300°C for approximate one hour. Deviations are smaller 5 % . Best results (+/- 2 %) were obtained by sputtering with Ar_2 ions of 3 keV (dose : 10mCb/cm^2) followed by annealing to 300°C for more than 15 minutes.

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