

# ADSORPTION PHENOMENA IN THE DETERMINATION OF TRACE IMPURITIES OF GERMANIUM AND SILICON BY ACTIVATION ANALYSIS

by

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## Introduction

The primary object of our work was the determination of the degree of copper and gold impurities in germanium of semiconductor purity by neutron activation analysis. The exceedingly high scattering (1–2 orders of magnitude) of the results of parallel measurements prompted us to elucidate the factors causing this scattering, with the aim of reducing their effect, so that the scattering (standard deviation) of results, obtained for simultaneously activated identical samples within the concentration range between  $10^{-7}$  to  $10^{-9}$  g of Cu/g of Ge and  $10^{-9}$  to  $10^{-11}$  g of Au/g of Ge,

$$(sd) = \sqrt{\frac{\sum \Delta_i^2}{z - 1}}$$

(where  $z$  is the number of measurements,  $\Delta_i$  is the deviation of the individual measuring results from the average value:  $X_i - \bar{X}$ ) shall not exceed a maximum of  $\pm 20$  per cent.

## Factors influencing reproducibility in the determination of the copper content of germanium

Copper in germanium, activated in a reactor of a neutron flux of  $10^{13}$   $n/cm^2 \cdot s$  (time of activation 64 h), was determined with the following methods [1].

1. Distillation—precipitation method: activated germanium and a weighed amount (20–40 mg) of copper carrier were dissolved in nitrohydrochloric acid, germanium tetrachloride was distilled (twice, in the presence of inactive

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germanium tetrachloride hold back carrier, in a modified Othmer apparatus), and copper was precipitated in the form of copper(I) thiocyanate or copper(I) iodide [1].

From the point of view of selectivity — radiochemical purity — cuprous iodide was found to be superior, however, according to our experiences, the reproducibility of both precipitation methods is satisfactory, that is to say, on performing with standard active substances the determination of copper, the scattering is less than  $\pm 20$  per cent. Precipitation with thiocyanate or iodide after distillation has the advantage that gold, not enriched by the carrier, precipitates together with copper, also quantitatively. Cu-64 and Au-198 can be determined side by side, without further separation, by gamma spectroscopy.

The scattering of the results of precipitative copper determination, carried out on a mixture of a weighed quantity of active copper and active germanium ( $10^{-7}$  g Cu/g Ge), was less than  $\pm 20$  per cent, with a deviation of  $+20-35$  per cent from the weighed in quantity of copper, measured in the area of the 0.51 MeV photopeak with a single channel analyser according to the simplified method of COVELL.

2. Distillation—ion exchange—precipitation method: before the precipitation with cuprous iodide, the solution of the distillation residue in 0.2 n hydrochloric acid was passed through a cation exchange column, washing the column for the purification of copper, first with 0.4 n hydrochloric acid, then with hydrochloric acid diluted to 1:1.

Also here, the scattering of results of experiments with model systems was less than 20 per cent, and moreover, the method is of considerably higher accuracy than the simple distillation—precipitation method (yielding a value by 10 per cent higher than the true copper content, while the simple Cu(I) SCN precipitation method resulted a copper content higher by 25 to 30 per cent, and the simple Cu(I) precipitation method a value higher by 20 per cent).

3. Extractive-substoichiometric method [2]: the reproducibility and the accuracy of this method, developed by RUIČKA et al., are the same as those of the distillation—ion exchange—precipitation method, described in paragraph 2.

The investigations of the conditions of Cu-64 detection showed substantial sources of error in the measurements undertaken with the scintillation single-channel amplitude analyser, tuned into the 0.51 MeV annihilation gamma energy of Cu-64. Thus, for example, measured intensity is increased by the presence of active germanium. To eliminate this error, the  $\gamma\text{-}\gamma$  coincidence method with two detectors was used. This increased accuracy, however, at the cost of reproducibility (scattering is greater).

These investigations showed that:

1. our set task (a scattering of about  $\pm 20$  per cent and an accuracy within 10 per cent) can be realized;

2. the scattering by order of magnitude cannot be ascribed to random errors of the methods of determination,

3. but to the inadequate treatment of the germanium samples before activation, probably from surface contamination.

The importance of the treatment before and after activation and of surface effects was indicated, among others, by the results of experiments, involving essentially the studying of identical quantities of the same germanium, prepared in form of test samples of various geometrical form (prism, sheet) and of various specific surface areas.

At the same time, it became evident from data in literature and results of our own investigations that germanium cements among others copper, gold and silver from various solutions with high efficiency and within a relatively short time. Therefore, it was reasonable to assume that during the treatment preceding activation germanium binds from various solutions relatively important amounts of copper, gold and silver, and in the further procedure, this quantity is determined together with the impurities originally present. Presumably, the changing copper, gold and silver content of various chemicals used in the pretreatment, as well as the variation in the duration of pretreatment processes substantially influence the magnitude of surface concentration. To verify this assumption, the following experiments in activation analysis were undertaken with germanium:

1. analysis without any pretreatment;
2. etching after activation with a mixture of nitric and hydrochloric acids (up to a loss in weight of 5, 10, 20 and 40 per cent, respectively, of the sample);
3. etching after activation with alkali (up to a loss in weight of 10 and 20 per cent, respectively, of the sample);
4. etching before activation with a mixture of nitric and hydrochloric acids (up to a loss in weight of 20 per cent of the sample) and subsequent washing with water purified by various methods;
5. etching before activation with alkali, and subsequent washing with water purified by various methods;
6. treatment before and after activation with a mixture of nitric and hydrochloric acids, and washing with water purified by various methods.

Measuring results are summarized in Table I. These data clearly show that measuring results of relatively good reproducibility and accuracy are to be expected only in case of a pretreatment and after-treatment with a mixture of nitric and hydrochloric acids and with water "de-coppered with germanium".

500 ml portions of alkali, distilled water, 0.1 n and concentrated hydrochloric acids, and mixture of hydrochloric and nitric acid, respectively, each containing active copper impurity, were shaken for 1 hour with 1 g of pulverized

Table I

The copper content of germanium pretreated by various methods  
(determined as Cu—I—SCN)

Pretreatment	Prism	Sheet	Flitter
	Cu $10^{-6}$ g/g Ge		
Without pretreatment	124	179	1020
	220	151	—
	113	600	—
Etching after activation with nitrohydrochloric acid (m = 5%)	90	200	980
	130	78	—
	73	180	—
Etching after activation with nitrohydrochloric acid (m = 20%)	68	180	1900
	45	115	—
	80	340	—
Etching after activation with alkali (m = 20%)	148	290	—
Etching before activation with nitrohydrochloric acid, and washing with: ion exchanged water	73	90	700
	90	130	—
	109	120	—
water treated with germanium	45	61	380
	38	70	—
	70	61	—
Etching with alkali and washing with water treated with germanium, before activation	145	350	1450
	190	220	—
	92	400	—
Treatment before and after activation with nitrohydrochloric acid and water purified with germanium	24	11	364
	28	8	—
	22	1	—

germanium. The concentration of the copper was  $10^{-6}$  g/g. From the alkali, the distilled water and the dilute hydrochloric acid, copper was cemented out almost quantitatively by the germanium, while the copper content of the concentrated acids remained practically unchanged.

### Investigation of silicon of semi-conductor purity

The investigation of the copper, gold and silver content of silicon of semi-conductor purity yielded similar results [3]. With silicon, the etching agent was a HF—HNO<sub>3</sub>-mixture. Results are shown in Table II.

Table II

Au, Cu and Ag contents of differently pretreated silicon of 5 $\Omega$  cm resistivity

Pretreatment before activation	Original		Polishing-etching 10 : 1 = HNO <sub>3</sub> : HF		Polishing-etching HF	
	—	Etching	—	Etching	—	Etching
<sup>197</sup> Au (g/g Si)	1.5 · 10 <sup>-9</sup>	5.2 · 10 <sup>-11</sup>	2.6 · 10 <sup>-10</sup>	7.8 · 10 <sup>-11</sup>	7.4 · 10 <sup>-9</sup>	3.5 · 10 <sup>-10</sup>
<sup>63</sup> Cu (g/g Si)	9.7 · 10 <sup>-8</sup>	3.6 · 10 <sup>-9</sup>	5.2 · 10 <sup>-9</sup>	2.7 · 10 <sup>-9</sup>	1.0 · 10 <sup>-9</sup>	7.2 · 10 <sup>-9</sup>
<sup>107</sup> Ag (g/g Si)	4.8 · 10 <sup>-8</sup>	3.8 · 10 <sup>-8</sup>	1.0 · 10 <sup>-7</sup>	4.10 <sup>-8</sup>	4 · 10 <sup>-8</sup>	—

### Summary

Factors influencing the reproducibility and the accuracy of the determination of the copper, gold and silver content of high purity germanium and silicon by activation analysis were studied.

Experimental results showed the contamination of the surface, and consequently the specific surface area and the mode of treatment before activation to be one of the most important factors.

When purification before activation is undertaken with concentrated acids and de-copperized water, copper, gold and silver, cemented out on the surface, can be removed to such an extent that surface impurities do not practically influence measuring results, except in the case of samples of relatively great specific surface area.

### References

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