DETERMINATION OF TRACE ELEMENT DIFFUSION IN QUARTZ AND IN GERMANIUM

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Les problèmes de répartition des constituants mineurs dans le quartz et le germanium très pur ont été étudiés au moyen d'analyse par activation.

Two problems have been studied. One concerns the mercury distribution in quartz mercury vapour tubes. The other concerns the arsenic and phosphorus distribution in electronically pure germanium samples.

MERCURY DISTRIBUTION IN QUARTZ TUBES

By neutron irradiation of mercury the radioisotopes ^{197}Hg ($t_{\frac{1}{2}}$ = 65 h), ^{203}Hg ($t_{\frac{1}{2}}$ = 47 d) and ^{205}Hg ($t_{\frac{1}{2}}$ = 5·5 min) are obtained. The short-lived ^{205}Hg cannot be used for a study of the radial distribution as it necessitates a chemical attack and separation procedure. In our problem a longer activation time is needed in order to determine at least 10 parts/million of mercury in 10 mg amounts of silica matrix. We can calculate that a seven-day irradiation at the neutron flux available of 10^{12} neutrons cm^{-2} sec^{-1} provides the initial activities represented in *Table 1*. The induced activities of interfering elements are also given.

As can be seen from *Table 1*, the activities of ^{197}Hg and ^{203}Hg produced are sufficient for the determination of 0·1 μg of mercury. The interferences due to ^{64}Cu, ^{42}K, ^{24}Na, ^{187}W and ^{76}As are slight after 8 days. Interferences, however, due to ^{124}Sb, ^{110m}Ag, ^{182}Ta and ^{65}Zn, increase as a function of time, which makes chemical separation necessary.

When mercury is precipitated as the sulphide in 1N hydrofluoric acid after addition of mercury carrier, good decontamination can be obtained from the isotopes ^{65}Zn, ^{187}W, ^{24}Na, ^{42}K and ^{182}Ta. On the other hand co-precipitation of antimony, arsenic, copper and silver can occur.

The activity measurement of the isolated mercury can be made in two ways:

Beta measurement is less interesting because the maximum beta energy of ^{203}Hg only amounts to 208 keV and the electron capture (E.C.) of ^{197}Hg can only be measured indirectly, and with low efficiency, by the K_x radiation.

Gamma measurement can be carried out on the 279 keV photo-peak of ^{203}Hg. The sensitivity, however, is considerably better when the 77 keV transition of ^{197}Hg is measured. Using a gamma spectrometer, impurities which occur occasionally can also be detected, and the results corrected for these.

Experimental

Two quartz samples and a mercury standard are irradiated simultaneously for 7 days at a neutron flux of 5 $\times$ 10^{11} neutrons cm^{-2} sec^{-1}.

Table 1. Interference of trace elements: 7-day irradiation; flux = 10^{12} neutrons cm^{-2} sec^{-1}

Element	*Occurrence* (parts/million)	*Isotope formed*	$t_{\frac{1}{2}}$	E_β max (MeV)	E_γ (MeV)	*Activity* at end of irradiation*
As	10^{-3}–1	^{76}As	26·4 h	β−2·97 2·41 1·76	0·555 1·210 2·06	$3{\cdot}38 \times 10^4$
Zn	0·4	^{65}Zn	245 d	β+0·324 E.C.	1·14 0·82 0·511	$4{\cdot}9 \times 10$
W	0·5	^{187}W	24·0 h	β−0·63 1·33	0·072 0·686	$3{\cdot}2 \times 10^4$
Na	0·1	^{24}Na	15 h	β−1·39	1·368 2·758	$1{\cdot}4 \times 10^4$
K	1	^{42}K	12·5 h	β−3·55 1·99	1·53 0·309	$7{\cdot}3 \times 10^4$
Ta	10	^{182}Ta	115 d	β−0·514 0·44 0·36	0·06 1·2	$3{\cdot}2 \times 10^3$
Cu	0·2	^{64}Cu	12·8 h	E.C. β+0·19 β−0·39	0·511 1·34 (0·5%)	$2{\cdot}8 \times 10^4$
Sb	1	^{122}Sb ^{124}Sb	28 h 60 d	β+/K.C. β−2·31	0·56–1·2 0·6–2·1	$3{\cdot}7 \times 10^2$ $4{\cdot}25 \times 10^2$
Ag	1	^{110m}Ag	253 d	—	0·116 1·5	$1{\cdot}7 \times 10^2$
Hg	10–100	^{203}Hg ^{197}Hg	47 d 65 h	β−0·208 E.C.	0·279 0·077	$2{\cdot}7 \times 10^2$ $1{\cdot}13 \times 10^4$

* Disintegrations per second per microgram of element.

The quartz tubes with unknown mercury content are coated on the outside with paraffin, so that only the inside can be dissolved away.

The samples are successively weighed, treated with 38 per cent hydrofluoric acid containing one drop of concentrated nitric acid and washed twice with distilled water. This series of operations is repeated several times.

The hydrofluoric acid and washing solutions are combined in polythene centrifuge tubes. To each of these mercury-containing solutions 2 ml of mercuric nitrate solution (0·9 mg Hg/ml) is added as a mercury carrier. The solutions are mixed homogeneously and further acidified with nitric acid ($d = 1{\cdot}40$) in order to minimize co-precipitation of copper, antimony and arsenic sulphides.

The mercury is precipitated as sulphide, the supernatant solution is decanted after centrifugation. The mercuric sulphide residue is washed twice with a dilute solution of hydrofluoric (1N) and nitric (0·1N) acids and once with distilled water. Filtration is finally done on SS 589[3] filter paper or on porcelain filtering discs. The standard is treated in the same way.

Activity measurements—The low gamma and beta energy of the mercury isotopes formed permit easy purity control. Measurements have been done by means of the multichannel RCL 256 gamma-ray spectrometer of

the Physics Department. As a result only ^{122}Sb seemed to be a source of interference, particularly when measuring gamma radiation above 200 keV. The disintegration ratio of ^{122}Sb and ^{203}Hg has been derived from the surface ratio of the respective photo-peaks and amounts to 19 per cent in the worst cases—two days after the end of irradiation.

From this statement it seems that further purification of the isolated mercuric sulphide is necessary. However, in gamma-ray measurements between the limits of 60 and 85 keV interference by ^{122}Sb is negligible. Under these measuring conditions no further purification is needed.

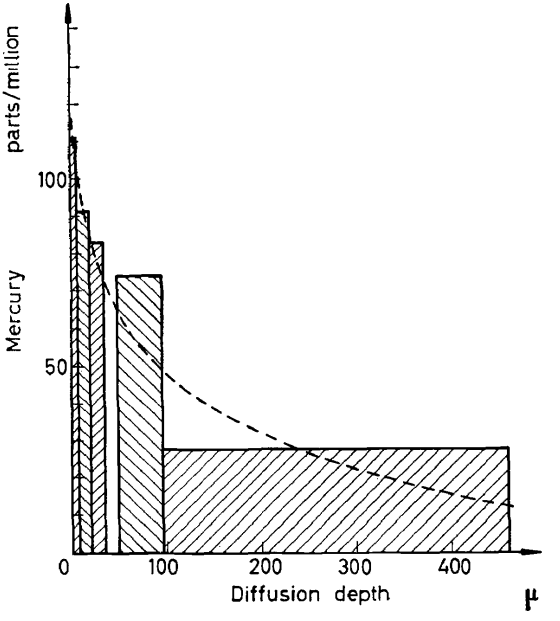

Figure 1. Diffusion of mercury in quartz tubes (N. V. Philips Monster 5)

Results

The radial distribution of mercury as found by activation analysis is represented in *Figure 1.* The mercury content decreases noticeably with increasing depth. The results allow the determination of the total energy from the diffusion depth of the activated mercury atoms to be made.

PHOSPHORUS AND ARSENIC DISTRIBUTION IN GERMANIUM SAMPLES

The determination of arsenic impurities and other trace elements in germanium by means of activation analysis has been worked out by several authors. Smales and Pate[1] were the first to determine submicrogram amounts of arsenic in a germanium matrix. Their method involves a chemical separation procedure based on the distillation of germanium as germanium tetrachloride, followed by distillation of arsenic as arsenic tribromide, in a second fraction. In 1956 Morrison and Cosgrove[2] and

J. V. Jakovlev[3] published their results on the activation analysis of impurities in germanium obtained by using γ-spectrometry as a tool to simplify or to eliminate chemical procedures.

No results have been found in the literature about the determination of phosphorus in high-purity germanium.

For the determination of phosphorus and arsenic distribution gradual dissolution of the germanium sample is necessary, followed by the analysis of the respective fractions. The distillation procedure according to Smales and Pate is rather tedious for the simultaneous analysis of six to eight fractions. Solvent extraction procedures[4, 5] also have been described which provide an enrichment factor for ^{76}As of between 10^4 and 10^5. However, they do not permit simultaneous analysis of the different fractions by one operator. The most promising enrichment method seems to be an ion-exchange procedure. Indeed, interesting work has been done in that field: Irvine and co-workers[6] prepared carrier-free ^{74}As by eluting the As^{3+} from Dowex I by means of 0·5–2·5N hydrofluoric acid solution. Further Kraus and co-workers[7, 8] published distribution data on germanium and arsenic in hydrochloric and hydrochloric–hydrofluoric acid media. As the chief contaminant apart from ^{77}As seems to be ^{32}P, we required conditions under which arsenic is selectively eluted. Batch experiments in ammonium fluoride–hydrofluoric acid media indicated great differences

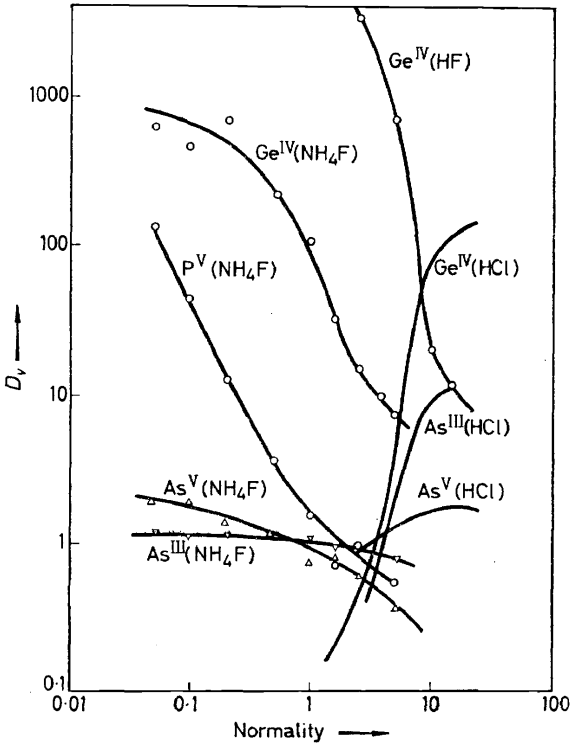

Figure 2. Distribution coefficients (D_v values) as functions of HF, HCl and NH_4F concentrations

in the distribution coefficients (D_v values) of Ge^{IV}, P^V and As^V, as is shown in *Figure 2*. However, column experiments did not agree with the values under batch conditions. Eventually elution in hydrofluoric acid medium was applied, followed by a chemical separation of arsenic and phosphorus.

Experimental

For analysis of the radial distribution of arsenic and phosphorus, a cylindrical germanium sample weighing about 4 g is irradiated for 24 h in a neutron flux of 10^{12} neutrons cm^{-2} sec^{-1}. Standard samples containing ammonium dihydrogen phosphate, ammonium sulphate and arsenious oxide and a small piece of germanium are added.

One hour after irradiation the samples are dissolved gradually in a mixture of 3 ml of concentrated hydrofluoric acid and 0·5 ml of nitric acid ($d = 1{\cdot}40$). To the fractions obtained 5 mg of arsenic and 5 mg of phosphorus carrier are added, after which the solutions are diluted with distilled water until 0·5N with respect to hydrofluoric acid.

The solutions are poured onto Dowex I (8 columns 12 cm high, 1·2 cm diameter). As^V and P^V are then eluted with 100 ml of 0·5N hydrofluoric acid. To the eluate are added immediately 0·5 g of boron trioxide and 3 drops of a 10 per cent solution of potassium iodide, after which arsenic trisulphide is precipitated by means of hydrogen sulphide. The solution is kept for 2 h at 80°C, and saturated again with hydrogen sulphide. The precipitate is filtered off on SS 589³ filter paper and washed with 20 ml of 0·5N hydrofluoric acid.

The filtrate containing ^{32}P is further acidified by means of nitric acid ($d = 1{\cdot}40$) until a 2N nitric acid solution is obtained. Since fluoride ions are masked by the boric oxide, phosphorus can be precipitated as ammonium phosphomolybdate. The precipitate is filtered off on SS 589³ filter.

Measurements of ^{76}As in the ^{76}As–^{77}As mixture are made by means of an anthracene detector beta spectrometer. The ^{32}P is measured by means of a Geiger–Müller detector. Purity is checked by gamma spectrometry and decay control.

Discussion of results

The results obtained indicate the presence of 0·10–0·15 parts/million of arsenic throughout the germanium sample. Phosphorus content, on the other hand, is lower than 10 parts/million, and seems to be slightly enriched on the outer side of the sample.

The formation of ^{32}P from $^{32}S(n,p)^{32}P$ cannot be regarded as an important source of error under the irradiation conditions. This has been proved by the specific activities of ^{32}P formed by (n,γ) and (n,p) reactions. The absence of chlorine has also been demonstrated.

Difficulties arise from the necessity of dissolving the germanium sample gradually. In order to avoid errors due to neutron shadow, the germanium sample is weighed after each dissolution process. Two days after irradiation of the germanium samples the ^{77}As is milked off again. The specific activity due to ^{77}As is compared for each fraction and with that of a small germanium monitor sample.

References

[1] A. A. Smales and B. D. Pate. *Anal. Chem.*, **24**, 717 (1952)
[2] G. H. Morrison and J. F. Cosgrove. *Anal. Chem.*, **28**, 320 (1956)
[3] J. V. Jakovlev. *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955*, **15**, 54–9
[4] Mino Green. *J. Chem. Soc.*, **1955**, 1604–7
[5] Mino Green. *J. Chem. Phys.*, **22**, 760 (1954)
[6] J. W. Irvine and U. Schindewolf. *Anal. Chem.*, **30**, 906 (1958)
[7] K. A. Kraus and F. Nelson. *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva 1955*, P/837 (U.S.A.)
[8] K. A. Kraus and co-workers. *Chemistry Progress Report O.R.N.L.*-2386

DISCUSSION

K. LJUNGGREN (*Sweden*): Metallurgy seems to be a field in which it is very appropriate to use an inactive tracer which is then determined by radioactivation analysis. In some recent work carried out in Sweden gold has been used as a tracer for determining the refractory wear of an electric steel furnace. Suitable amounts of gold were added to the refractory bricks in the bottom of the furnace. In a series of runs samples were taken of consecutive steel melts and analysed for gold by radioactivation. A rapid chemical separation was used because of an interfering chromium activity in the stainless steel. Concentrations of gold down to 0·01 parts/million were easily detected. We have also used lanthanum and dysprosium for the labelling of slag, both in order to determine the total amount of slag, and also to investigate the origin of non-metallic inclusions.