

DETERMINATION OF COPPER AND GOLD TRACE IMPURITIES IN HIGH PURITY GALLIUM BY ACTIVATION ANALYSIS WITH PRETREATMENT*

By

L. G. NAGY*, G. TÖRÖK*, J. GIBER** and L. SZOKOLYI***

**Department of Physical Chemistry, Technical University, Budapest,*

****Tungsram" Electric Corporation, Budapest and*

***National Office of Measures, Budapest*

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Introduction

The selection of investigative techniques suitable for gallium is subject to limitations imposed by its nuclear half life. The half life of ^{72}Ga is 14.3 h, it being of the same order of magnitude as that of ^{64}Cu , among others. After 1—2 days of activation its activity may reach the 10 C/g level ($\varnothing = 10^{13}$ n $\text{cm}^{-2} \text{sec}^{-1}$).

The determination of isotopes with half lives of 0.1 to 10 days definitely requires destructive separation [1, 2] since more than 20 peaks have been identified in the 0.12 to 3.3 MeV range of the irradiated gallium gamma spectrum. On the other hand the determination of trace impurities in the parts per million to parts per billion range (ppm-ppb) requires 0.1 to 1.0 g gallium samples. As a consequence, samples with an activity of 1 to 10 C should be radiochemically processed, this being only possible in a hot laboratory.

Our objective was to develop a method suitable for destructive activation analysis of gallium in laboratories for medium activity levels. Therefore, we had to decrease the activity of the gallium matrix by at least 2 orders of magnitude. This can be achieved by *pretreating the sample before activation*.

The essential feature of the method is that the concentration of the trace impurity is increased relative to that of gallium. In principle, this can be accomplished in two ways: (1) the trace impurities are separated from the material (e.g. by electrochemical or chromatographic techniques); (2) the basic material is removed or its concentration decreased. Both possibilities have been tested in preliminary experiments.

Ion exchange and paper chromatography have been employed as possible means of using approach (1). The results were not satisfactory, thus supporting the assumption that the chemical properties of gallium would make (2) more suitable.

* Dedicated to Prof. Erdey on the occasion of his 60th birthday

Utilizing the significant differences in volatility between gallium chloride and the chlorides of possible trace impurities, a distillation method has been developed for the removal of gallium.

Experimental

Apparatus and reagents

Gallium was chlorinated in the apparatus (with block diagram shown in Fig. 1). The attachment is shown in Fig. 2. Chlorine was prepared by oxidizing hydrochloric acid with potassium permanganate. In order to maintain the

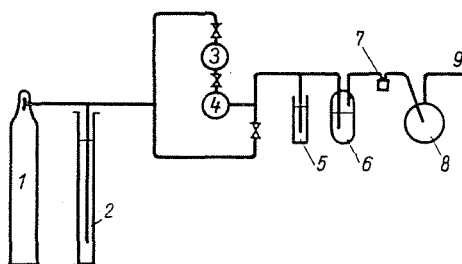


Fig. 1. Block diagram of the distilling apparatus 1. gas cylinder 2. pressure regulator, 3. hydrochloric acid container, 4. potassium permanganate container, 5. pressure regulator, 6. gas washing bottle, 7. reactor vessel, 8. absorption flask, 9. gas outlet

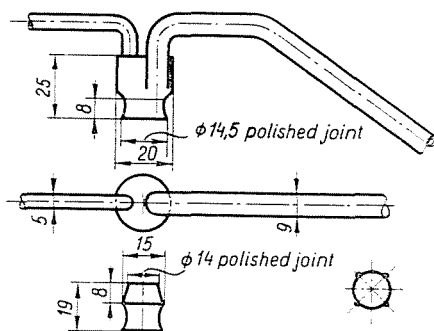


Fig. 2. Reactor vessel

necessary flow-rate, nitrogen was introduced to raise the pressure by 500 to 1000 mm of Hg above atmospheric pressure. After pressure regulation, crude chlorine was bubbled through concentrated sulphuric acid (analytical grade purity — p.a. — and led into the reactor. Potassium permanganate and hydrochloric acid (p.a., manufactured by Reanal) were used for the preparation of chlorine. The tubing that led the gas mixture in and out of the reactor was surrounded by heating coil, the distillation vial was heated by an elec-

tric hot plate. In order to avoid contamination, the distillation was carried out using the same vial in which activation was performed. The samples were activated in the reactor of the Central Research Institute for Physics, Hungarian Academy of Sciences (KFKI) with a neutron flux of $(2 \text{ to } 3) \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ (irradiation time 12 to 24 h).

Chemicals (p.a. Reanal products) were used in processing the activated samples. The cation exchange resin was of the Varion KS type (Hungarian product, H⁺-form, column length 200 to 300 mm, diameter 8 mm, capacity 12 to 18 milli-equivalents).

10 to 20 mg of copper(II) oxide standard (spectroscopic purity) was activated with the sample in all cases. Intensities were measured with a single-channel amplitude analyzer (System GAMMA Works).

Procedure

The activation analysis of copper and gold impurities in gallium included the following steps:

- 1) distillation with chlorine gas prior to activation,
- 2) irradiation,
- 3) decomposition of the activated sample,
- 4) separation of the elements to be analyzed,
- 5) preparation of samples suitable for quantitative analysis,
- 6) intensity measurements and check of radiochemical purity,
- 7) preparation of a copper monitor sample and its analysis.

The apparatus was first deoxygenated by flushing with nitrogen and cold chlorine gases, for 5 minutes each. The deoxygenation determines the efficiency of the distillation procedure. Chlorination starts after the heating is begun. (Gallium trichloride boils at 201.3° C.) The reaction is exothermic, heating is only necessary to compensate for losses of heat. Gallium trichloride distills as a white smoke. (The optimum time for distillation is 20 to 30 min, the optimum sample weight about 100 mg.)

The distillation residue (1—2 mg) had to be decomposed in the vial after activation. A suitable attachment was used during the operation. The procedure was as follows. Weighed samples (10 to 40 mg) of inactive copper and gold carrier solutions were added to the vial and evaporated to dryness. The dry residue was decomposed with aqua regia. After boiling off the fumes, the residue is dissolved by adding 0.1 N hydrochloric acid. The solution is diluted to a given volume, and aliquots are transferred to an ion exchange column. Elution with 0.1 N hydrochloric acid yields the gold while the copper is obtained by elution with 1.1 N HCl. Gold is precipitated by reduction with zinc powder [3] (in 1 : 1 hydrochloric acid, yield 90 to 95%). Copper is precipitated as copper(I) iodide [4] in a slightly acidic medium (yield 80 to 90%).

The copper and gold contents were determined by the modified Covell-method [5], measuring the intensities in the ranges of 0.5 and 0.4 MeV, respectively.

Results

In order to establish the random and systematic errors of the method, the distillation and decomposition steps had to be subjected to a more thorough study since the losses in subsequent steps can be taken into account on the basis of the yields.

It has been observed that no contamination occurred when empty quartz vials were chlorinated under the described conditions, indicating that the chlorine did not contain impurities which would condense and become radioactive in the vial.

The efficiency of the distillation was characterized by the percentages of the ^{64}Cu standard (η_a) and the gallium sample (η_s) in the residue.

The values of η_s and η_a were determined by weighing, and from the number of counts, respectively. The minimum number of counts was 10^3 , usually being above 10^4 . The standard deviation of the intensity measurements was less than 3%, but usually did not exceed 1%.

Since copper is one of the most harmful impurities in semiconductor materials, the objective was, among others, the determination of copper.

The efficiency of distillation was studied also with ^{64}Cu because of its favorable chemical and nuclear properties.

The relatively high vapor pressure of copper halides supports the assumption that if no copper losses are observed, no losses due to evaporation of less volatile metal halides are to be expected. This has been experimentally demonstrated on the model of ^{198}Au . Since the vapor pressure of copper(II) chloride is less than 0.1 mm of Hg even at 500°C , there is no danger of losses due to evaporation around 100°C . (Some references quote a high value for the vapor pressure but this is the equilibrium pressure of chlorine formed in the decomposition.)

The results are shown in Figs 3 and 4 as distribution curves (histograms). Fig. 3 shows the results of a series where the volume of the distillation vial was around 3 ml. The diagram indicates normal distribution: $\eta_s = (80 \pm 20)\%$, and $(80 \pm 10)\%$, with 80 and 60% statistical occurrence, respectively.

Similar histograms can be constructed from the η_s data. The distillation residue is $(2 \pm 2)\%$ with 84% probability.

Since the weight of the sample before and after distillation can be determined, samples with high errors can be discarded. Therefore, this value only serves the purpose of comparison.

Similar tests were carried out using vials of 1 ml volume, Fig. 4. It can be seen that the volume reduction of the vial modified the shape of the curve,

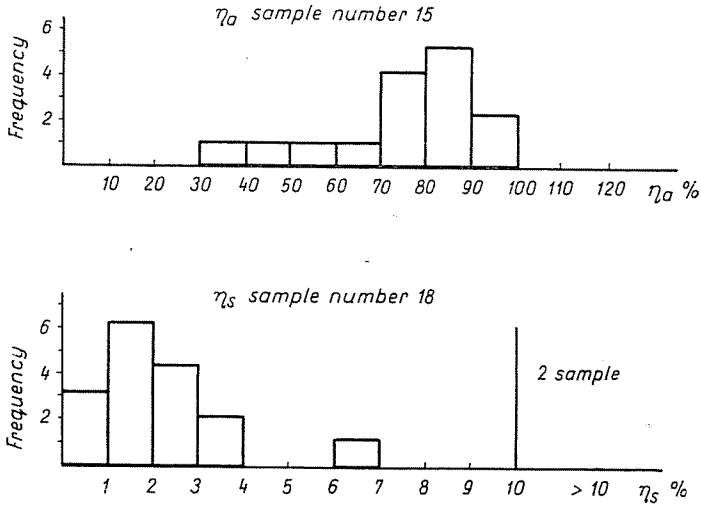


Fig. 3. Frequency distribution of the first series

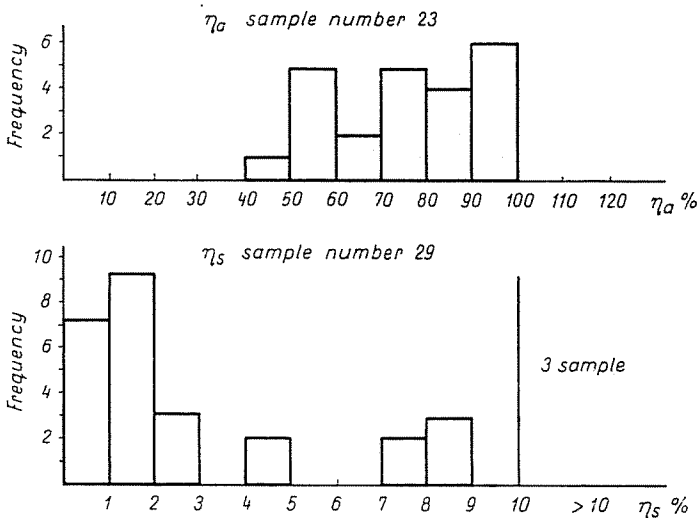


Fig. 4. Frequency distribution of the second series

altered the deviation. On the basis of the histogram, an accurate distribution cannot be determined, but at the same time the most probable value, the limit of error and the statistical confidence level can easily be established: $(75 \pm 25)\%$ (96%) and $(80 \pm 20)\%$ (74%), respectively.

In order to clarify the reasons for results at variance with the theory, intensities have been measured for a number of samples before and after chlorination, at half hour intervals at constant temperature and chlorine flow.

The maximum total time of chlorination was 3 h. No significant intensity changes were observed after the initial decrease at the given conditions for distillation.

Accordingly, the copper losses are due to *technological* factors such as carry-over, local overheating, etc. The characteristics and operation of the apparatus are, therefore, of fundamental importance with respect to reproducibility.

The efficiency of decomposition has also been studied with ^{64}Cu . (A sample contaminated with copper of known activity was decomposed.) In the presence of 20–80 mg of copper carried, 90% of the total amount of copper has been recovered from the original vessel, the largest deviation being $\pm 8\%$.

After the above data had been determined, a pure (B) and an impure (A) gallium sample were subjected to activation.

The results are shown in Table 1. The average copper contents are $2.1 \times 10^{-6} \text{ g} \pm 40\%$, and $6.3 \times 10^{-7} \text{ g} \pm 45\%$, while the average gold contents equal $4.3 \times 10^{-8} \text{ g} \pm 50\%$, and $3.7 \times 10^{-9} \text{ g} \pm 45\%$, respectively.

Discussion

It can be established from the distillation results that the method is suitable for purposes of activation analysis because the gallium content can be decreased by 2 orders of magnitude. However, a certain percentage of the impurities to be analyzed remains in the residue. The pretreatment does not contaminate the samples.

Although, in principle, 100% of the impurities should be in the residue, the experimentally observed efficiency was significantly less than 100%. According to the experimental results, the amount of copper in the residue is governed by „technological” factors.

In view of the fact that the dimensions of the irradiation channel determine the vial dimensions, the deviation can only be decreased by *careful stabilization of the distillation parameters*.

This statement receives support from the data in Figs 4 and 5, indicating that the efficiency is decreased and the deviation increased when the cell dimensions are decreased.

The enrichment factor $\eta_a/\eta_s = 50$ for the distillation process, i.e. there is no way to simplify the operations subsequent to activation. However, the original objective was not this but to *decrease the activity level* which has been achieved, the residual activity being 10 to 20 mCi. (The enrichment factor can only be increased by improving the distillation procedure and by a more complete deoxygenation of the system and the chlorine gas.)

Since the enrichment factor for the ion exchange operation is 11 ± 3 , the total *radiochemical purity ratio* is 1 : 550. (A cation exchange resin has been

used because the separation of copper and gallium chloride complexes is difficult on an anion exchange resin.) In agreement with the conclusions drawn from gamma spectra, this indicates the necessity to separate the impurities under consideration when a quantitative analysis is to be performed.

According to the results, the error of copper determination is $\pm 40\%$ in the range of 10^{-6} to 10^{-7} g/g. In the case of gold the error is $\pm 50\%$ in the range of 10^{-8} to 10^{-9} g/g (cf. Table 1). This indicates that the deviation of the results is practically determined by the deviation characteristic for the distillation. The latter does not exceed the error limits for activation analysis.

Table 1

Copper and gold contents of some gallium samples

No.	Sample designation	Copper content (g/g)	Gold content (g/g)
1	A ^a	3.1×10^{-6}	
2	A	1.5×10^{-6}	6.5×10^{-8}
3	A	2.6×10^{-6}	4.5×10^{-8}
4	A	1.3×10^{-6}	2.1×10^{-8}
5	B ^b	5.2×10^{-7}	2.2×10^{-9}
6	B	9.8×10^{-7}	4.6×10^{-9}
7	B	4.0×10^{-7}	6.1×10^{-9}

^aA = impure

^bB = pure

Summary

A distillation method has been worked out to remove the gallium matrix, utilizing the significant vapor tension differences between the gallium trichloride and the chlorides of the investigated impurities.

The main point of the method is the reaction between the metallic gallium sample and dry chlorine gas. In this way 99% of the gallium matrix can be removed, and thus the total activity of the initially 100 mg gallium is reduced to below 20 mCi.

After the distillation process a well defined portion of the investigated impurities is retained, and the distillation efficiency is governed by technological factors.

According to our data it was possible to determine the copper content at a concentration range of 10^{-6} to 10^{-7} g/g with $\pm 40\%$ deviation, and the gold content at a concentration range of 10^{-8} to 10^{-9} g/g with $\pm 50\%$ deviation.

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dr. Lajos G. NAGY }
dr. Gábor TÖRÖK } Budapest XI., Budafoki u. 8. Hungary
dr. János GIBER } Budapest IV., Váci u. 77. Hungary
László SZOKOLYI } Budapest XII., Németvölgyi u. 37. Hungary