

**DETERMINATION OF ARSENIC IN GERMANIUM BY THE COMBINATION  
OF ISOTOPE DILUTION AND ACTIVATION ANALYSIS**

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## DETERMINATION OF ARSENIC IN GERMANIUM BY THE COMBINATION OF ISOTOPE DILUTION AND ACTIVATION ANALYSIS

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The determination of arsenic by activation analysis in germanium may be disturbed by arsenic isotopes formed in the irradiation of the germanium matrix itself. The isotopic dilution technique will eliminate such interferences, but it requires weighing of very small masses of arsenic, after appropriate chemical separation. This weighing procedure can be avoided if the mass of the recovered arsenic is determined by activation analysis. In order to apply such a procedure, a known amount of arsenic labelled with  $^{76}\text{As}$ , whose specific activity is also known, is added to the germanium sample to be analysed. The sample is processed, the arsenic separated, and the chemical yield established. The recovered mass of arsenic is then determined by activation analysis applying the classical isotopic dilution analysis formula. The accuracy, precision and linearity of the method are discussed.

### Introduction

Direct activation analysis without separating the element to be analysed before irradiation is not always possible. This applies, for instance, to the analyses of elements with atomic numbers from 30 to 64 in a uranium matrix, since these elements are formed by fission. Another instance where direct irradiation of the sample or matrix may not be advisable is when the matrix has a very high thermal neutron absorption cross-section, such as in the case of a gold matrix.<sup>1</sup> Primary and second-order interference reactions,<sup>2</sup> or any nuclear reaction in the matrix that may give rise to radioisotopes of the element being analysed, may also hamper direct activation of the samples.

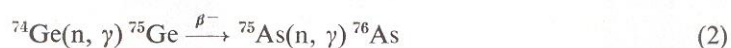
Separation of the element to be analysed before irradiation may cancel the main advantage of activation analysis, which is insensitive to accidental contamination, as observed by PAULY, SABBIONI and GIRARDI.<sup>3</sup> The loss of trace elements may also occur during separation prior to irradiation.

Application of the isotope dilution technique might by-pass the inconveniences concomitant of a direct irradiation of matrixes, such as the ones mentioned before, eliminating interferences due to fissile materials, high neutron absorption cross-section matrixes, and samples in which nuclear reactions between the matrix and bombarding particle may produce isotopes of the same element which is to be

analysed. The isotopic dilution method also takes into account and corrects for any loss of the trace element being analysed. This method has already been applied, *e.g.*, for the determination of traces of phosphorus in nuclear grade uranium.<sup>4</sup> Although in this case the element to be analysed (phosphorus) is not a fission product, direct irradiation of the matrix would require remote control processing, owing to the high activity induced in the matrix due to the formation of fission products.

In isotopic dilution it is necessary to determine the specific activity of the isolated substance being analysed, and this requires the determination of its weight. Consequently, the sensitivity of the method will be highly dependent on this weight determination (gravimetry, spectrophotometry, etc.). Frequently, the amount of substance to be determined by gravimetry or some other procedure is very small, and a very sensitive method must be used. This high sensitivity may not always be attained by the usual chemical methods. PAULY, SABBIONI and GIRARDI<sup>3</sup> have solved this problem by applying activation analysis for the determination of the weight of the recovered substance to allow the subsequent calculation of specific activity. The elements determined were lanthanum, cerium, ruthenium and molybdenum in a uranium alloy sample, for which direct irradiation is not possible since the mentioned elements would also be formed as fission products.

Conditions similar to those described above are encountered in the analysis of arsenic in germanium or germanium oxide. Germanium of high purity is required for the manufacture of diodes and transistors. The analytical methods used to check the purity of such material must have very high sensitivity. Activation analysis seems to be an extremely promising method for this purpose. In the case of arsenic, which is known to be one of the impurities that prevent such a use of germanium, activation analysis is more difficult than for the other contaminants, owing to matrix interferences. The interferences that may occur are indicated by Reactions (1) and (2).



DE SOETE, DE NEVE and HOSTE<sup>5</sup> described a method for the activation analysis of arsenic in germanium, in which the activity due to <sup>77</sup>As does not interfere with the measurement of <sup>76</sup>As; they used the first reactions to establish an internal standard for the measurement of <sup>76</sup>As. The second-order interference caused by Reaction (2) is discussed in detail by RICCI and DYER<sup>6</sup> and by SMALES and PATE.<sup>7</sup>

### Calculation

If  $x$  is the amount of the element to be determined by isotopic dilution,  $x_0$  the amount of the element present in the reagents used,  $a$  the mass of added tracer,  $A'$  its specific activity and  $B'$  denotes the specific activity of the recovered element after application of a suitable chemical procedure, we have, as it is known:

$$X = x + x_0 = a \left( \frac{A'}{B'} - 1 \right). \quad (3)$$

The mass  $a$  of the added tracer is easily determined (by using an aliquot of a solution of known concentration for instance). If the total activity added is  $A$ , and  $b$  denotes the recovered mass of the element being analysed while  $B$  is its activity, we have:  $A' = A/a$  and  $B' = B/b$ .

Determination of  $A$  and  $B$  involves no difficulties, but  $b$  may not be so easily obtainable, especially if it is of the order of tenths of a microgram or less. If  $b$  is determined by activation analysis, sensitivity will be enhanced, and it will not be limited, *e.g.* by the balance, as in the case of gravimetric analysis.

If the element used as the tracer has a short half-life, its activity will be zero or negligible by the time of the irradiation of the mass  $b$ ; however, if an isotope with long half-life is used, the remaining activity of  $b$  will have to be subtracted from the total activity. Therefore, whenever possible, an isotope with short half-life should be used in the determination of  $b$ . For instance, in the analysis for silver,  $^{110m}\text{Ag}$  ( $T = 250$  d) may be used as the tracer, and  $^{110}\text{Ag}$  ( $T = 24$  sec) for the activation analysis of the mass  $b$ .

Considering that  $X$  represents in Eq. (3) the amount of arsenic in the sample ( $x$ ) plus the amount of arsenic introduced with the reagents ( $x_0$ ), we may write:

$$X = x + x_0 = a \left( \frac{A/a}{B/b} - 1 \right). \quad (4)$$

The chemical yield  $r$  is equal to  $B/A$ , thus Eq. (4) can be written as

$$X + a = b/r. \quad (5)$$

If the mass  $b$  is irradiated together with a standard of mass  $M_s$ , and if  $B_1$  and  $A_s$  are the activities of  $b$  and  $M_s$ , respectively, after irradiation we have:

$$b/M_s = (B_1 - B_t)/A_s.$$

$B_t$  is the remaining activity of the tracer corrected for a decay time up to the end of the irradiation  $b$ ; it can be calculated by measuring the activity  $A_t$  of the tracer solution, used at the beginning of the process, at the end of the irradiation of  $b$ . As the relation  $B/A$  is always equal to  $r$ ,  $B_t = rA_t$ . In this way  $b$  can be calculated and substituted into Eq. (5) and we shall have:

$$x + x_0 + a = (B_1 - B_t)M_s/rA_s. \quad (6)$$

In the same way,  $x_0$ , the amount of arsenic in the reagents or blanks, may be determined by running a blank analysis:

$$x_0 + a = (B_{01} - B_{0t})M_s/r_0A_s. \quad (7)$$

The final formula for  $x$  is obtained by subtraction of Eqs (6) and (7). One gets:

$$x = [(B_1 - B_t)/r - (B_{01} - B_{0t})/r_0] M_s/A_s. \quad (8)$$

It is supposed that the same amount  $a$  of the tracer has been added to the samples and blanks. If the amounts of tracer added to the samples and blanks are  $a$  and  $a_0$ , respectively, the difference  $(a - a_0)$  has to be subtracted from the right-hand side of Eq. (8).

### Experimental

The procedure consists of two parts:

1. Isotopic dilution including determination of the activity of the recovered tracer, *i.e.*, determination of the chemical yield  $r = B/A$ .
2. Determination of the mass  $b$  of the recovered tracer by activation analysis.

#### Reagents

Nitric acid, analytical grade, 65%.

Hydrochloric acid, analytical grade, 37%.

Lead nitrate solution, analytical grade, 10 mg Pb/ml.

Ammonium hydroxide solution made by introducing pure gaseous ammonia into water to attain a concentration of about 23%  $\text{NH}_3$ .

Water: deionized.

$^{76}\text{As}$  tracer solution: 1 mg of  $\text{As}_2\text{O}_3$  is irradiated with a thermal neutron flux of  $10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$  for about 8 hrs. The  $\text{As}_2\text{O}_3$  is dissolved with drops of aqua regia, and diluted with water to obtain a concentration of 0.1  $\mu\text{g}$  of labelled arsenic, per milliliter of solution.

#### Procedure

Germanium samples (300 mg–2000 mg, depending on the proportion of arsenic present) are placed in 50-ml beakers. Another set of six 50-ml beakers is used for a parallel blank analysis of the reagents. To each beaker a volume of 500  $\lambda$  of tracer solution is added. Another volume of 500  $\lambda$  of the tracer solution is kept for counting at the end of the whole process, to correct in this way for the decay of the activities (calculation of  $A$ ,  $A_0$ ,  $B$  and  $B_0$ , in order to apply Eq. (8)).

2.5 ml of concentrated nitric acid followed by 7.5 ml of hydrochloric acid are added to each sample and blanks, and the beakers are let to stand for about

1 hr at room temperature, in order to allow time for the dissolution of germanium. The solutions are then carefully heated to remove excess aqua regia; evaporation should proceed almost to dryness. About 20 ml of water is added, the solutions are neutralized, and made alkaline by adding 3 ml of ammonium hydroxide. 2 ml of lead nitrate solution is then added; the resulting lead hydroxide precipitates, with the arsenic entrained as lead hydroarsenate.<sup>8</sup> The precipitates are aged for about 2 hrs, then filtered with suction, using small filter papers of medium porosity, in a chimney funnel apparatus. The precipitates are dried under an infra lamp, placed (together with the filter paper) in small polyethylene envelopes and counted in a 400-channel gamma spectrometer coupled to a 3" × 3" NaI(Tl) well-type scintillator. Area  $B$  under the peak of 1.20 MeV or 0.56 MeV of <sup>76</sup>As is determined and compared with the same area  $A$  obtained by counting 500 lambdas of the <sup>76</sup>As tracer solution. In this way the relations  $r = B/A$  and  $r_0 = B_0/A_0$  (chemical yield) of the recovered activities for samples and blanks, respectively, are determined.

The lead hydroxide precipitates in the polyethylene envelopes and the standards of As<sub>2</sub>O<sub>3</sub> are then irradiated for 8 hrs with a thermal neutron flux of 10<sup>12</sup> n · cm<sup>-2</sup> · sec<sup>-1</sup>. After irradiation, the samples and standards are processed by a radiochemical-Gutzeit method,<sup>9</sup> and counted as before. In this way the values  $B_s$ ,  $B_{0s}$ ,  $M_s$  and  $A_s$  for the samples, blanks and standards are obtained.  $B_t$  and  $B_{0t}$  (Eq. 8) are obtained, as shown, from the relations:

$$B_t = rA_t \quad \text{and} \quad B_{0t} = r_0A_{0t}$$

$A_t$  and  $A_{0t}$  are the activities of the amount of tracer equal to the one added to the samples and blanks at the beginning of the process (zero hour), measured after the time elapsed from zero hour to the end of the irradiation of  $b$ .

### Results

In order to check the method, three sets of sodium arsenite solutions containing 0.25 μg, 0.50 μg and 1.00 μg of arsenic were prepared. Several samples, for each set, were analysed according to the method proposed. The results are presented in Table 1.

The determination of the confidence limits for the results presented in Table 1, at 0.05 level, gives, using FISCHER and YATES' tables:<sup>10</sup>

$$\begin{array}{lll} P = 0.05 & N_1 = n_1 - 1 = 9 & t_1 = 2.262 \\ P = 0.05 & N_2 = n_2 - 1 = 8 & t_2 = 2.306 \\ P = 0.05 & N_3 = n_3 - 1 = 7 & t_3 = 2.365. \end{array}$$

Hence, every single result has 95% probability of having the value  $\bar{x} \pm s_x t$ ; and the mean  $\bar{x} \pm s_m t$ . Table 2 presents the results.



Table 1  
 Added and recovered arsenic  
 (sodium arsenite solutions)

	Added, $\mu\text{g}$		
	0.25	0.50	1.00
	Recovered		
	0.27	0.58	0.98
	0.28	0.44	0.97
	0.24	0.53	1.09
	0.28	0.42	1.13
	0.26	0.60	1.00
	0.22	0.46	1.05
	0.23	0.50	1.12
	0.23	0.47	1.10
	0.21	0.45	—
	0.24	—	—
Mean $\bar{x}$	0.25	0.49	1.05
$s_x^*$	0.02	0.06	0.06
$s_m^{**}$	0.01	0.02	0.02

\* Standard deviation of a single result  
 \*\* Standard deviation of mean

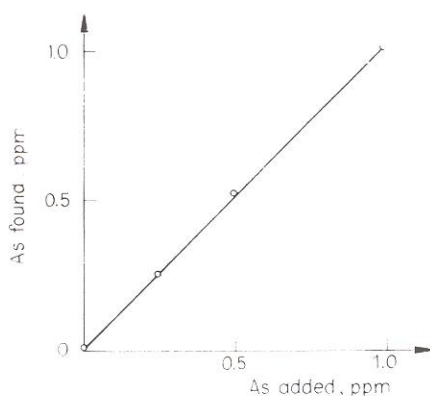


Fig. 1. Check of the linearity of the method

The method was next applied to a 99.999% pure germanium sample. Amounts from 220 to 424 milligrams were used, and nine samples were taken from the same batch of germanium (granules). The results are presented in Table 3.

The linearity of the proposed method was checked by the addition of known amounts of arsenic to a high purity germanium sample (400-mg samples), in the range from 0 to 1.0 ppm. The results are shown in Table 4 and Fig. 1.

Table 2

Confidence limits (0.05 level) for the results with the samples in Table 1

	Single results, $\mu\text{g}$	Mean, $\mu\text{g}$
Set 1	$0.25 \pm 0.05$	$0.25 \pm 0.02$
Set 2	$0.49 \pm 0.14$	$0.49 \pm 0.05$
Set 3	$1.05 \pm 0.14$	$1.05 \pm 0.05$

Table 3

Results of analyses of arsenic in a germanium matrix

Sample No.	As, ppm
1	0.333
2	0.301
3	0.319
4	0.233
5	0.300
6	0.323
7	0.273
8	0.305
9	0.272
$\bar{x}$	0.295
$s_x$	0.031
$s_m$	0.010

Confidence limits at 0.05 level:

Single results  $\bar{x} \pm s_{x,t} = 0.30 \pm 0.07$ Mean  $\bar{x} \pm s_{m,t} = 0.30 \pm 0.02$ 

Table 4

Linearity of the proposed method

Sample No.	As, added, ppm	As, found, ppm
1	0	0.007
2	0.242	0.255
3	0.500	0.555
4	0.496	0.509
5	0.998	1.090
6	0.999	1.081

*Analysis of the reagents for arsenic*

The analysis of the reagents for an element can be carried out separately in every single reagent used in the analytical procedure, or alternatively, as a blank analysis for the whole procedure. In the latter case the chemical method applied to the actual samples is repeated in exactly the same way, but using only the reagents and no samples.

This procedure was applied to the reagents used in the determination of arsenic in germanium. Various analyses were performed; the results are listed in Table 5. Since the number of repeated experiments is reasonably large, a good estimate of the precision or reproducibility of the method can be obtained, considering the value of the standard deviation.

Table 5  
Analysis of the reagents or blank analysis for arsenic

Run No.	As, $\mu\text{g}$	Run No.	As, $\mu\text{g}$
1	0.0589	13	0.0574
2	0.0663	14	0.0670
3	0.0678	15	0.0674
4	0.0475	16	0.0682
5	0.0596	17	0.0663
6	0.0642	18	0.0661
7	0.0692	19	0.0614
8	0.0668	20	0.0640
9	0.0620	21	0.0662
10	0.0495	22	0.0568
11	0.0711	23	0.0555
12	0.0663	24	0.0622
		25	0.0639

$$\bar{x} = 0.063 \mu\text{g}$$

$$s_x = 0.006$$

$$s_m = 0.001$$

Confidence limits at 0.05 level:

$$\text{Single result } \bar{x} \pm s_x t = 0.063 \pm 0.012 \mu\text{g}$$

$$\text{Mean } \bar{x} \pm s_m t = 0.063 \pm 0.002 \mu\text{g}$$

**Discussion**

The results presented in Table 1 give the accuracy of the proposed method. It can be seen that there is a good agreement between the arsenic present and found.

The reproducibility or precision is evaluated in Table 3. The standard deviation obtained in nine repeated experiments shows that the scattering of data is not large.

The linearity of the method can be judged from Table 4 and Fig. 1, for a concentration range from zero to 1 ppm of arsenic in germanium. The results are

even better as far as accuracy, precision and linearity are concerned, for samples containing higher proportions of arsenic. As it has been shown,<sup>4</sup> the errors in isotopic dilution analysis increase in proportion to the value of  $a/x$ . When the amount of material to be analysed ( $x$ ) increases, the fraction  $a/x$  diminishes and so does the error.

The method can be applied to advantage for the analysis of reagents. The preparation and purification of high-purity analytical reagents have become a very important problem, owing to the high sensitivity of modern analytical methods, such as activation analysis and atomic absorption spectrometry.

The activation analysis of reagents faces some problems that other techniques may ignore. The importance of these problems is well pointed out by BECKER and SMITH,<sup>11</sup> and a short revision seems appropriate. Effects of nuclear bombardment, such as nuclear recoil and gamma heating, may enhance the introduction of contaminations from the container into the reagent sample, and may increase the kinetic rate of exchange of impurities between sample and container. Decomposition of the material during irradiation may also cause problems especially in the case of liquid reagents with the possibility of gas formation. These gases build up pressures which may rupture the containing vessel, although this is not very common. Nevertheless, the accumulated pressure may constitute a serious hazard during the opening of irradiation containers. This is an important problem in the case of acid and caustic substances, and particularly in the irradiation of hydrochloric acid, when decomposition gives rise to chlorine and hydrogen, which may undergo an explosive recombination reaction upon exposure to light.

In cases such as these, isotopic dilution followed by activation analysis of the recovered element may be a good substitute for straightforward activation analysis.

The method applied to the reagents used (nitric acid, hydrochloric acid, lead nitrate, ammonium hydroxide solution) showed an excellent reproducibility in 25 repeated experiments, with very small standard deviations of the single values and the mean.

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## SUMÁRIO

A determinação de arsênico em germânio, por meio de análise por ativação, pode ser afetada pela formação de isotópos de arsênico formados como consequência da reação nuclear dos nêutrons com a própria matriz. A técnica de diluição isotópica pode eliminar este tipo de interferência mas, por outro lado, exige a determinação de massas extremamente pequenas de arsênico. Portanto, a sensibilidade do método ficaria dependente da técnica adotada para a determinação daquela pequena massa (gravimetria, p. ex.). Tal determinação pode ser feita por análise por ativação. Para aplicar tal método, adiciona-se uma quantidade conhecida de  $As-76$ , de atividade também conhecida, à matriz de germânio que se quer analisar. A amostra é processada, o arsênico é separado e o rendimento químico é determinado. A massa de arsênico que é recuperada no processo de diluição isotópica é então determinada por ativação. Discutem-se, no trabalho, a exatidão, precisão e linearidade do método proposto.