

METHODS OF CHEMICAL ANALYSIS

DETERMINATION OF 10^{-5} - 10^{-7} % IMPURITIES IN ARSENIC AND IN GALLIUM ARSENIDE BY THE INVERSION VOLT-AMPEROMETRIC METHOD

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A chemico-spectral method [1] has been proposed for determining up to 10^{-6} % of Zn, Cd, Pb, and Cu impurities in gallium arsenide. An "APN" method has also been proposed, but its sensitivity is no greater than $1 \cdot 10^{-5}$ % [2, 3]. For determining nanogram quantities of silver in semiconductor materials by the polarographic method, there is an absence of data. For determining tellurium a method of sensitivity up to 10^{-6} % has been proposed [3, 4].

This investigation was aimed at increasing the sensitivity of the inversion volt-ampere method of determining Zn, Cd, Pb, and Cu in concentrations up to 10^{-6} %, and of Ag in concentrations up to 10^{-7} % in arsenic and gallium arsenide.

The polarization curves were recorded with the aid of a type LP-60 polarograph, and oscillographic polarographs type OP-1-61 and TsKB-GEOKhI, of the Academy of Sciences of the USSR, using a three-electrode system operating under anodic and cathodic polarization conditions. The measurements were carried out in a quartz cell with a standard mercury electrode in the form of a stationary drop [5] for determining Zn, Cd, Pb, and Cu, and with a carbon paste electrode for determining Ag. In both cases the reference electrode was a saturated calomel electrode, and all the potentials were referred to this electrode.

The carbon paste electrode was prepared in accordance with Adams' method [6]. Six grams of powdered carbon was mixed with 3.5 ml of α -bromonaphthalene until a homogeneous paste was obtained. The paste was stored in a jar made from dark glass fitted with a ground glass stopper. A glass tube of internal diameter 5-7 mm was filled with the paste, its end being rubbed with tracing paper.

The solution in the cell was stirred with a stream of nitrogen during the process of filling, the rate of nitrogen flow being controlled by means of a capillary type water rheometer.

For determining silver, additional stirring was provided by a magnetic stirrer. The nitrogen was purified from oxygen by passing it through a solution of vanadium (II).

The crucible and the equipment used for distillation were made from quartz. In determining Zn, Pb, and Cu the crucible was cleaned by steeping in chemically pure concentrated HNO_3 for 12-16 h, and was then carefully rinsed out with distilled water and steamed out.

The instrument for analyzing the sample after treatment with gallium arsenide was treated several times with hot nitric acid, and was then treated with boiling HCl containing bromine for 2-3 h. After chemical purification, the mercury was twice distilled in vacuo.

The following reagents were used: chemically pure HCl twice distilled on a Teflon bath [7]; HClO_4 , chemically pure, twice distilled in vacuo in a quartz vessel; HBr, AR grade; Br_2 , chemically pure, washed three times with the second distillate, and distilled three times in a quartz vessel (Br collected under the bidistillate); HNO_3 , chemically pure; water, demineralized with ion-exchange resins, but subjected to one additional distillation in KMnO_4 at pH 7.0, to remove traces of organic substances, and distilled a second time without KMnO_4 ; a solution of KOH, especially pure NaOH, or a solution of NH_4OH obtained by saturating the bidistillate with ammonia in a Teflon bath, using the isopycnic method; redistilled ethyl ether (the ether must be saturated with H_2SO_4 the same day as the extraction).

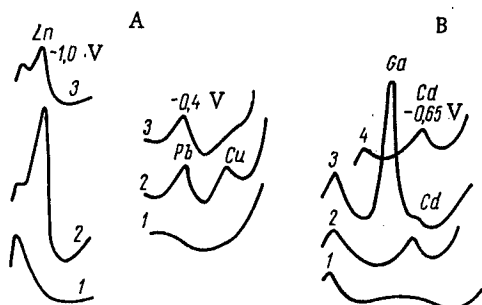


Fig. 1. Effect of As and Ga on the values of the anodic peaks for Zn, Cd, Pb, and Cu: A: 1) base electrolyte 0.5 M HCl; 2) anodic peaks for 0.03 µg/ml Zn; 0.01 µg/ml Pb; 0.02 µg/ml Cu; 3) the same, plus 3 µg/ml As; B: 1) Base electrolyte 0.5 M HCl; 2) anodic peak for 0.01 µg/ml Cd; 3) the same, plus 5 µg/ml Ga; 4) $\varphi_{bu} = -0.8$ V.

TABLE 2. Results Obtained in Assessing the Possible Losses of Zn, Cd, Pb, and Cu Impurities under the Conditions Used for the Analysis of Gallium Arsenide

Content in blank	Total content	Value on subtracting blank
Zinc--amount taken 0.30 µg		
0,22	0,50	0,28
0,22	0,51	0,29
0,22	0,49	0,27
0,22	0,52	0,30
Average deviation < 10%		
Lead--amount taken 0.10 µg		
0,02	0,09	0,07
0,02	0,10	0,08
0,02	0,12	0,10
0,02	0,13	0,10
0,02	0,11	0,085
Mean deviation < 20%		
Copper--amount taken 0.20 µg		
0,016	0,20	0,18
0,016	0,18	0,16
0,016	0,19	0,17
0,02	0,15	0,13
0,02	0,17	0,15
Mean deviation < 20%		
cadmium--amount taken 0.10 µg		
Not determined	0,08	0,08
	0,08	0,08
	0,10	0,10
	0,09	0,09
	0,08	0,08
Mean deviation < 20%		

TABLE 1. Results of Determining Zn, Cd*, Pb, Cu, and Ag Impurities in Very Pure Arsenic

Number of determinations	Element determined	Found, %	Standard deviation
Blank			
3	Zn	$1,3 \cdot 10^{-5}$	$\pm 2,2 \cdot 10^{-6}$
3	Pb	$3,7 \cdot 10^{-6}$	$\pm 8,8 \cdot 10^{-7}$
3	Cu	$2,3 \cdot 10^{-6}$	$\pm 4,5 \cdot 10^{-7}$
Content in As (deducting blank)			
3	Zn	$3,4 \cdot 10^{-5}$	$\pm 1,25 \cdot 10^{-6}$
3	Pb	$1,8 \cdot 10^{-6}$	$\pm 6,0 \cdot 10^{-7}$
4	Cu	$1,0 \cdot 10^{-5}$	$\pm 2,6 \cdot 10^{-6}$
3	Ag	$1,9 \cdot 10^{-6}$	$\pm 1,58 \cdot 10^{-7}$

*Cadmium was not detected in this sample.

Standard solutions of zinc, cadmium, copper, and silver were prepared from the salts of these metals, these being the chemically pure grades of concentration 10^{-3} M. The solutions of metal concentration 10^{-8} - 10^{-9} M were obtained by appropriate dilution on the day of the experiment.

Arsenic Assay

In the case of artificial mixtures containing 10^{-8} M, Zn, Cd, Pb, and Cu, it has been established that it is necessary to remove arsenic completely. At a concentration of As in the solution of up to 30 µg As per 10 ml solution the presence of As affects the peaks for other metals besides the lead. Thus, the zinc peak is significantly reduced, and the copper peak disappears completely (Fig. 1A).

For determining the Zn, Cd, Pb, and Cu impurities a 0.5 g weighed quantity of arsenic was dissolved in the instrument with 2 ml of a 7 M solution of HCl, with the gradual addition of 2 ml of bromine. A further 1.5 ml of 7 M HCl was added, and the arsenic was evaporated off by heating on a hot plate, until a transparent colorless liquid formed in the flask (but not a syrup). The contents of the flask were then rinsed several times with water in a quartz crucible and the solution was evaporated to dryness on a water bath. The residue was dissolved in 10 ml of 0.1 M hot HCl, cooled and transferred to a cell, and the concentrations of impurities were determined after 5-15 min stirring with nitrogen at $E = -1.2$ V in the case of Zn, and at $E = -1.0$ V in the case of Cd, Pb, and Cu.

Such a difference in the build up potentials is necessary if the content of zinc is significantly higher than that of the other impurities. In using a type LP-60 polarograph for determining zinc, the HCl solution should be adjusted to pH 4-5 as measured with universal indicator paper, by adding KOH or NH_4OH . In view of the considerable resolving power of the oscillographic polarograph, zinc can also be determined in more acid solutions.

For determining the silver content of arsenic samples a weighed quantity of the arsenic sample containing 0.10 to 0.15 g was dissolved in a mixture of 2 ml HNO_3 and 4 ml HBr in a 20-25 ml quartz crucible. The solution was then evaporated to dryness on a water bath, 5 ml HBr was added and the solution was again evaporated to dryness, this operation being repeated three to four times until the arsenic was completely removed.

TABLE 3. Results Obtained in Determining Zn, Cd, Pb, Cu, Te, and Ag in Gallium Arsenide

Number of determination, n	Element determined	Found, %*	Standard deviation
4	Zn	$4,46 \cdot 10^{-5}$	$\pm 7,49 \cdot 10^{-6}$
4	Pb	$2,10 \cdot 10^{-6}$	$\pm 3,21 \cdot 10^{-7}$
4	Cu	$4,90 \cdot 10^{-6}$	$\pm 2,30 \cdot 10^{-6}$
3	Zn	$5,54 \cdot 10^{-5}$	$\pm 8,30 \cdot 10^{-6}$
3	Pb	$1,01 \cdot 10^{-6}$	$\pm 4,2 \cdot 10^{-7}$
3	Cu	$2,24 \cdot 10^{-6}$	$\pm 3,9 \cdot 10^{-7}$
3	Te	$2,40 \cdot 10^{-6}$	$\pm 8,2 \cdot 10^{-7}$
3	Ag	$1,8 \cdot 10^{-7}$	$\pm 1,1 \cdot 10^{-8}$
3	Zn	$3,97 \cdot 10^{-5}$	$\pm 1,48 \cdot 10^{-5}$
3	Pb	$1,39 \cdot 10^{-5}$	$\pm 6,20 \cdot 10^{-6}$
3	Cu	$9,20 \cdot 10^{-6}$	$\pm 1,50 \cdot 10^{-7}$
2	Zn	$1,82 \cdot 10^{-4}$	$\pm 2,18 \cdot 10^{-6}$
2	Pb	$1,57 \cdot 10^{-5}$	$\pm 3,55 \cdot 10^{-6}$
2	Cu	$2,16 \cdot 10^{-5}$	$\pm 1,91 \cdot 10^{-6}$
2	Zn	$1,25 \cdot 10^{-4}$	$\pm 3,6 \cdot 10^{-6}$
2	Cu	$5,20 \cdot 10^{-6}$	$\pm 3,85 \cdot 10^{-6}$
2	Pb	$5,40 \cdot 10^{-5}$	$\pm 8,5 \cdot 10^{-6}$
2	Cd	$1,41 \cdot 10^{-5}$	$\pm 1,70 \cdot 10^{-6}$
Blank			
5	Zn	$8,8 \cdot 10^{-6}$	$\pm 1,5 \cdot 10^{-6}$
5	Pb	$1,5 \cdot 10^{-6}$	$\pm 2,0 \cdot 10^{-7}$
5	Cu	$1,5 \cdot 10^{-6}$	$\pm 2,5 \cdot 10^{-7}$

*The results presented are arithmetic means with due allowance for the blank.

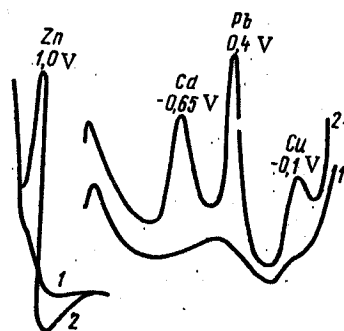


Fig. 2. Curves for the anodic solution of Zn, Cd, Pb, and Cu in a sample of GaAs: 1) base electrolyte 0.5 M HCl; 2) GaAs sample.

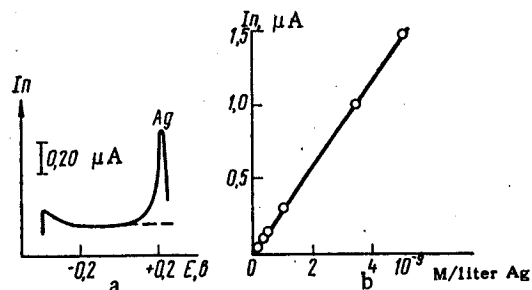


Fig. 3. Curve for the electrolytic solution of Ag, obtained in a sample of GaAs (a), and I_p for electrolytic solution as a function of the silver concentration (b).

The residue was dissolved in a small volume of NH_4OH , and the solution was transferred to a 50 ml volumetric flask. The pH was adjusted to about 9.0 by adding NH_4OH and the solution was made up to the graduation

mark with a base electrolyte which was 0.01 M with respect to NH_4OH and 0.01 M with respect to NH_4NO_3 . No loss of silver was detected.

A 10-ml quantity of solution was placed in the electrolytic cell which was fitted with a carbon electrode. Using a magnetic stirrer and a stream of nitrogen, a potential of 0.5 V was established and the electrode was held at this potential for 5 min. This operation must be carried out before each determination. A potential of -0.4 V was then established, and the electrolytic deposition of silver was carried out over a period of 10 min. The magnetic stirrer was then switched off and the curve for the electrolytic solution of silver was plotted by taking readings at 30-sec intervals. The current was measured by drawing a perpendicular from the peak of the curve onto the curve for the base electrolyte [8]. All the impurities were determined by the addition method [9]. Table 1 shows the results obtained in determining Zn, Pb, Cu, Cd, and Ag in a very pure arsenic sample.

Gallium Arsenide Assay

After a three-fold extraction of gallium with ethyl ether from 6-7 M HCl, 40-60 μg remains in the aqueous phase (for a weighed sample of 1 g). This quantity of gallium affects only the cadmium peak (Fig. 1B). If there is an accumulation of Cd at a voltage $\varphi = -0.8$ V, then the effect of Ga is removed.

In the case of a weighed sample of gallium of about 0.1 g, silver does not interfere with the determination, and therefore in the analysis of GaAs only the As is removed together with the silver.

The method used for determining Zn, Cd, Pb, and Cu impurities in gallium arsenide involves several stages: decomposition of the weighed sample of gallium arsenide, evaporation of the arsenic, extraction of the gallium with

ethyl ether, evaporation of the HCl fractions, dissolving of the residue, and finally plotting the polarograms. The magnitude of the possible losses of Zn, Cd, Pb, and Cu in these operations were determined using artificial mixtures. The results are shown in Table 2. The accuracy of the method, with due allowance for the possible losses of impurities, amounted to ± 10 -20%, depending on the nature of the impurities.

For establishing the accuracy of determining silver in GaAs, known quantities of silver were added to three weighed quantities of the latter before dissolving, the remainder of the operation being exactly the same as in the analysis of arsenic. The following results were obtained on treating the results statistically: quantity of Ag used $1.08 \cdot 10^{-6}\%$ Ag; $n = 3$; $S^2 = 1 \cdot 10^{-16}$; quadratic error $1 \cdot 10^{-8}$; $S_{\bar{x}} = S/\sqrt{n} = 5.77 \cdot 10^{-9}$; Ag found at $\alpha = 0.95$, $1.08 \cdot 10^{-6} \pm 0.03 \cdot 10^{-6}\%$.

For the analysis of gallium arsenide a 1 g sample was ground up and placed in a quartz vessel for dissolving. After dissolving the sample the arsenic was evaporated off under the conditions given above. The solution containing the gallium and the impurities was then evaporated on a water bath until it turned to a syrup. The concentrate was transferred into 5 ml of 7 M HCl in a 25 ml separating funnel and the gallium was extracted three times with ethyl ether (15 ml portions), and saturated with hydrochloric acid.

The HCl fraction was evaporated to dryness on a water bath, the dry residue was treated with two to three drops of concentrated HClO_4 to decompose traces of organic substances, and the solution was evaporated to dryness on an electric hotplate. The dry residue was dissolved in 5 ml of 0.5 M HCl, which was used as the base electrolyte for Zn, Cd, Pb, and Cu, and determinations were then carried out on the oscillographic polarograph. On this instrument the peaks for Zn, Cd, Pb, and Cu are more clearly resolved (Fig. 2).

The silver was determined using a weighted quantity of about 0.10-0.15 g of GaAs and the assay was carried out under conditions similar to those used for arsenic. Figure 3a shows the oscillogram for silver obtained with one of the GaAs samples.

In the case of one sample of GaAs, tellurium was determined together with the Pb, Zn, Cu, and Ag impurities using 1 N HCl with precious accumulation in accordance with the method presented in [3].

The method described was used for the analysis of numerous samples of gallium arsenide. The results are presented in Table 3.

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