

# Electrochemical Preparation of Arsenic and Its Compounds

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**Abstract**—Electrochemical processes are used to recover elemental arsenic from  $\text{NaH}_2\text{AsO}_3$  solutions, oxidize  $\text{As}_2\text{O}_3$  suspensions to arsenic acid, and reduce arsenic acid to arsine. The electrolysis conditions are optimized for obtaining elemental arsenic: 0.8–0.9 M  $\text{NaH}_2\text{AsO}_3$ , 0.03–0.05 A/cm<sup>2</sup>, 20–25°C. The introduction of tetraalkylammonium salts containing C<sub>9</sub>–C<sub>12</sub> substituents, e.g., trimethylcetylammmonium bromide, is shown to stabilize the current efficiency in terms of As at a level of 45–50%. The current efficiency of copper cathodes attains 89% in 1–2 M  $\text{H}_3\text{AsO}_4$  solutions at a current density of 0.2 A/cm<sup>2</sup>. In the electrosynthesis of arsenic acid, quantitative substance and current yields are achieved in 2–3 M HCl solutions. Low-waste processes are proposed for preparing arsenic,  $\text{H}_3\text{AsO}_4$ , and  $\text{As}_2\text{O}_5$  from  $\text{As}_2\text{O}_3$ . The resulting arsenic is suitable for producing high-purity (99.9999%) material. The physicochemical processes underlying arsine generation are examined, and a bench-scale electrochemical arsine generator is described which can be used in the manufacturing of semiconductor materials.

## INTRODUCTION

Arsenic compounds find various applications in priority areas of science and technology. Of particular promise is the use of high-purity arsenic compounds in microelectronics, optoelectronics, laser engineering, and solar energy conversion. The physicochemical properties of semiconducting and optical As-containing materials depend in large measure on the purity of the starting substances, which must contain the minimum possible amounts of contaminating impurities [1, 2].

Arsenic,  $\text{As}_2\text{O}_3$ ,  $\text{AsCl}_3$ , and  $\text{AsH}_3$  are of key importance in the preparation of high-purity arsenic compounds.

Earlier, the physicochemical principles of the recovery of arsenic from sulfide ores were described in detail by Pashinkin and Fedorov [2]. They analyzed the research in this field and the processes for obtaining high-purity arsenic from arsenic-containing raw materials. It was concluded that the chloride process is the most suitable for commercial-scale production of high-purity arsenic from conventional raw materials.

The hydride process offers the possibility of obtaining the purest arsenic-containing products but is difficult to implement on a commercial scale because of the rather costly equipment (synthesis of magnesium arsenite, its hydrolysis, and low-temperature rectification) and environmental problems [3].

An alternative source of raw materials for commercial-scale production of high-purity arsenic and its compounds is offered by processing (detoxication) of chemical warfare agents, in particular, lewisite (~7000-t stock

in Russia). An approach was proposed which includes a complete cycle of lewisite processing, from detoxication to commercial-scale production of high-purity As-containing substances and related articles. Comparison of the procedures for lewisite neutralization with allowance made for environmental security and suitability of the products for the production of high-purity arsenic compounds demonstrates that alkaline hydrolysis followed by electrolysis of the resulting sodium arsenite solutions is the most effective process for large-scale lewisite disposal [3].

Given that arsenic compounds are highly toxic, use should be made of low-waste technologies in order to minimize the amount of wastewater. One way of resolving this issue is by using electrochemical processes, since they can be run at room temperature and atmospheric pressure, which facilitates the development of environmentally sound technology.

Attempts to employ electrolysis for the synthesis of arsenic compounds were reported in [4, 5]. Figure 1 shows the general scheme of the possible electrochemical transformations of the most important arsenic compounds:

(I) electrolysis of arsenous acid or arsenite solutions, yielding a fine arsenic precipitate, which is then thoroughly purified;

(II) reduction of crude elemental arsenic to arsine, which is also suitable for the production of high-purity arsenic;

(III) reduction of arsenous acid to arsine;

(IV) reduction of arsenic acid to arsine;

(V) oxidation of arsenous acid to arsenic acid.

In this paper, we describe a systematic study of the processes underlying the electrochemical preparation of elemental arsenic and arsine from different raw materials.

### EXPERIMENTAL

In our experiments, we used crude arsenic(III) oxide (99%) and sodium arsenite,  $\text{NaH}_2\text{AsO}_3$ , prepared from unconventional raw materials (lewisite) via alkaline detoxication [3]. As background electrolytes, we used reagent-grade  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HCl}$ .

Current–voltage ( $I$ – $V$ ) measurements were made using stationary electrodes and a PI-50-1 potentiostat at a constant potential sweep rate of 0.2 V/s. The potential of the working electrode was measured relative to a silver–silver chloride reference electrode. Before each measurement cycle, the electrodes were ground and thoroughly rinsed with acetone and distilled water. The oxygen dissolved in the solution was removed by bubbling electrolytic hydrogen for 20 min.

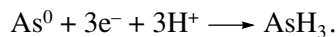
The process was run, for the most part, in a filter-press electrolyzer fitted with  $5 \times 6$  cm electrodes. The cathodic and anodic zones were separated by a Nafion-304 or MF4-SK cation-exchange membrane. The electrolyte was circulated by a centrifugal pump or gas-lift system, depending on the goal of the experiment. The set temperature was maintained by heat exchangers incorporated in the circulation lines of the two circuits.

### PREPARATION OF ELEMENTAL ARSENIC

It is well known that aqueous solutions of arsenous acid can be reduced to elemental arsenic and arsine [4]. The process is believed to involve several steps. In the first step, elemental arsenic is formed,

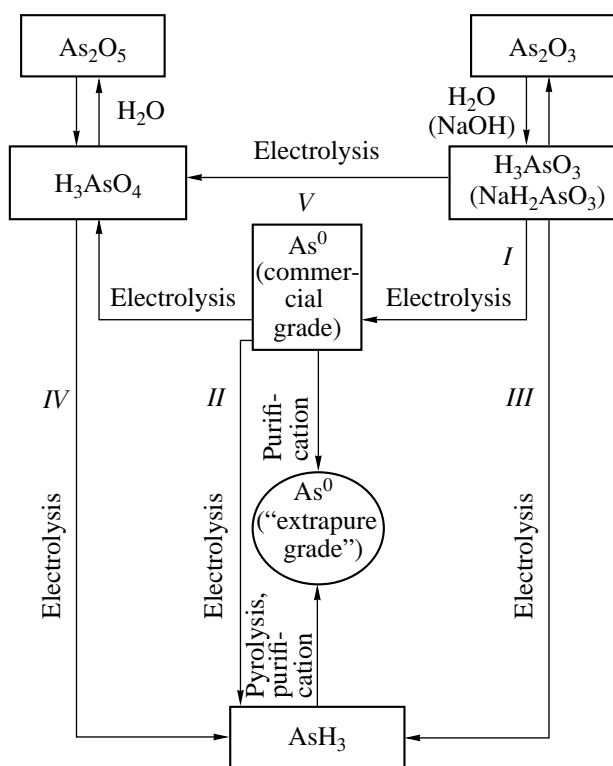


which can then be reduced to arsine;



Electrolysis of  $\text{As}^{3+}$  solutions in  $\text{H}_2\text{SO}_4$  on the surface of a mercury cathode yields fine-particle arsenic in high yields [6]. This method is, however, incapable of producing Hg-free arsenic and, hence, cannot be used on a production scale. To obtain coarser crystalline powders, use should be made of a pulsed flow [7].

We examined conditions under which elemental arsenic can be obtained on a solid electrode in quantitative yields. As shown earlier [8], it is reasonable to use alkaline solutions of  $\text{As}^{3+}$  in the production of arsenic. In alkaline media,  $\text{As}_2\text{O}_3$  converts to arsenites. Table 1 summarizes results obtained with a lead cathode under identical conditions. It can be seen that the main electrolysis product in the alkaline solution is arsenic,



**Fig. 1.** General scheme of the process for preparing arsenic and its compounds by electrochemical means (see text).

whereas in the acid solution, a significant amount of arsine is formed.

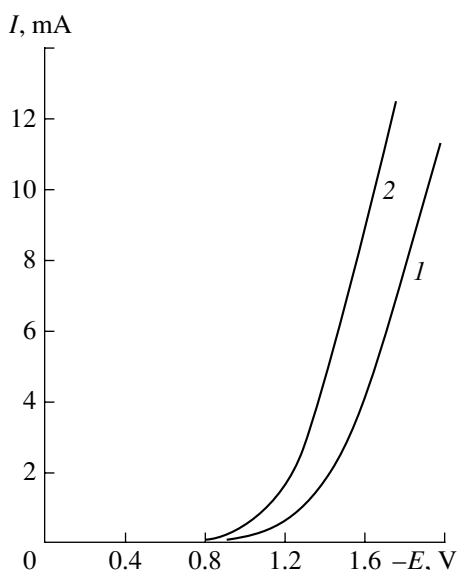
No data on the polarization of solid electrodes in alkaline solutions of arsenites are available in the literature. To address this issue, we tested copper, cadmium, nickel, stainless steel, and glassy carbon electrodes. After experiments, the glassy carbon electrode was covered with a nonconducting arsenic film. The  $I$ – $V$  curves of the copper and nickel electrodes are shown in Figs. 2 and 3. It can be seen that, at an  $\text{As}^{3+}$  concentration of  $\sim 10^{-3}$  mol/l, a slight depolarization occurs. The

**Table 1.** Reduction of As(III) compounds in acidic and alkaline solutions

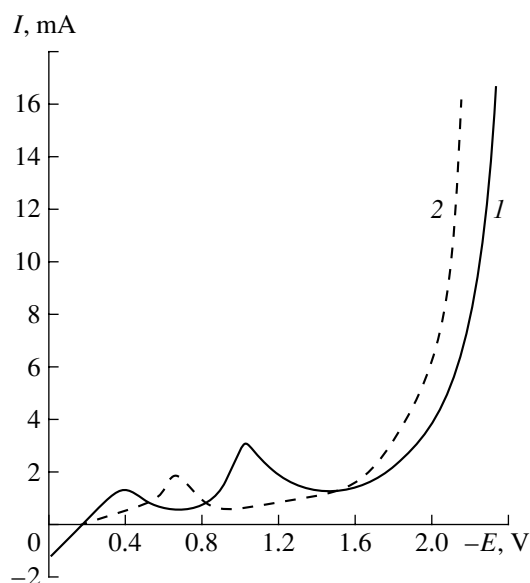
Catholyte composition	Current efficiency, %			Yield, %	
	$\text{As}^0$	$\text{AsH}_3$	$\text{H}_2$	$\text{As}^0$	$\text{AsH}_3$
0.3 M $\text{H}_2\text{SO}_4$	0.2	7.15	91	2.7	97.3
0.2 M $\text{As}^{3+*}$					
2.5 M $\text{NaOH}$	45.6	1.26	52.0	97.3	2.7
0.75 M $\text{As}^{3+}$					

Note: Pb cathode and anode; cation-exchange membrane; 10%  $\text{H}_2\text{SO}_4$  anolyte;  $j = 0.05$  A/cm<sup>2</sup>;  $t = 25 \pm 1$ °C;  $Q = 100\%$  in terms of  $\text{As}^{3+}$  to  $\text{As}^0$  reduction.

\* Saturated solution.



**Fig. 2.** Cyclic voltammograms of a nickel cathode in 1 M NaOH (background electrolyte): (1) 1 M NaOH, (2) 1 M NaOH + 0.001 M  $\text{As}^{3+}$ ; potential sweep rate of 0.2 V/s.



**Fig. 3.** Cyclic voltammograms of a copper cathode in 1 M NaOH (background electrolyte): (1) 1 M NaOH, (2) 1 M NaOH + 0.001 M  $\text{As}^{3+}$ ; potential sweep rate of 0.2 V/s.

potential at which the current through the electrode in the presence of  $\text{As}^{3+}$  began to exceed the current in the background electrolyte was regarded as the potential of the onset of arsenic precipitation (Table 2). Of particular interest is the copper cathode, which was covered with an oxide layer in the alkaline solution. The reverse  $I$ - $V$  curve shows two peaks corresponding to the reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$  and then to  $\text{Cu}$  metal. In the presence of  $\text{As}^{3+}$ , these peaks are missing, and a new peak emerges at  $E = -0.6$  V, which seems to be related to the formation of a copper arsenide film. The subsequent process occurs on this film. Only at  $E = -1.6$  V do we observe a steep rise in current.

Since arsenous acid is tribasic, we carried out electrolysis of solutions dominated by the  $\text{H}_2\text{AsO}_3^{2-}$ ,  $\text{HAsO}_3^{2-}$ , and  $\text{AsO}_3^{3-}$  anions.

**Table 2.** Potentials of the onset of arsenic formation (vs.  $\text{Ag/AgCl}$ ) at different metals in 1.0 M NaOH background electrolyte

Cathode material	$-E$ , V
Copper (M-1)	0.30
Stainless steel (Kh18N9T)	0.83
Nickel (N 0)	0.85
Iron (St-3)	1.08
Titanium (VT 1-0)	1.10

Note: 0.2 M  $\text{As}^{3+}$ , 20°C.

In the  $\text{Na}_2\text{HAsO}_3$  solution, we tested lead, zinc, copper, iron, stainless steel, and titanium cathodes (Table 3). The highest arsenic yield was attained with the lead cathode, which, however, partially disintegrated in the course of operation. For this reason, in subsequent experiments we used stainless steel, which was found to be corrosion resistant under the conditions of our study. With this cathode, we found that, in going from  $\text{Na}_2\text{HAsO}_3$  to  $\text{Na}_3\text{AsO}_3$  and to higher excess alkalinities, the yield of elemental arsenic decreases (Table 4). Increasing the temperature and current density has an adverse effect on the electrolysis process. In both cases, the arsenic yield changes little, but the yield of arsine, an undesirable product, increases. The data in Table 5 illustrate the effect of current density on the reduction process. The arsenic yield is notably higher in more concentrated  $\text{As}^{3+}$  solutions (Table 6). However, above 1 mol/l, the current efficiency decreases.

The results thus obtained were used to choose the main electrolysis parameters for producing elemental arsenic: 0.8–0.9 M  $\text{NaH}_2\text{AsO}_3$ ,  $j = 0.03$ – $0.05$  A/cm<sup>2</sup>, and  $t = 20$ – $25^\circ\text{C}$ .

Note that, during the first 4–5 h of reduction, a black spongy deposit consisting of arsenic flakes was formed on the cathode. The surface morphology of the cathode is illustrated in Fig. 4 at different magnifications. Clearly, the observed changes must influence the activity of the cathode during long-term electrolysis. Indeed, in a prolonged series of consecutive experiments with a stainless steel cathode, whose surface was not cleaned throughout the series, we observed a gradual reduction in arsenic yield (Fig. 5, curve 1). The reason is that the

**Table 3.** Effect of cathode material on the arsenic and arsine yields in the reduction of Na<sub>2</sub>HAsO<sub>3</sub>

Cathode material		Pb	Cu	Fe	Ni	As*	Stainless steel Kh18N9T	Cd	Ti
Current efficiency, %	As <sup>0</sup>	54.2	47.8	47.2	46.9	45.3	45.6	34.1	21.3
	AsH <sub>3</sub>	1.4	1.6	1.5	1.6	1.4	1.3	2.0	1.6

Note: Pb anode; cation-exchange membrane; initial Na<sub>2</sub>HAsO<sub>3</sub> concentration in the catholyte, 0.75 M; 10% H<sub>2</sub>SO<sub>4</sub> anolyte;  $j = 0.05 \text{ A/cm}^2$ ;  $t = 20\text{--}25^\circ\text{C}$ ;  $Q = 100\%$  in terms of As<sup>3+</sup> to As<sup>0</sup> reduction.

\* Steel St-3 electroplated with arsenic [9].

arsenic layer on the electrode surface becomes denser with time, impeding arsenite-ion diffusion to the electrode surface.

One way to prevent arsenic deposition on the electrode is to introduce a surfactant, which will adsorb on the electrode surface, reducing the adhesion between the deposit and electrode. We tested a large number of surfactants (Ftoron, tetraalkylammonium salts, sulfonic acids, polyglycols, and others). The results demonstrate that the most effective surfactants are salts of long-chain quaternary ammonium bases, e.g., trimethylcetyl ammonium bromide, or quaternary salts containing C<sub>9</sub>–C<sub>12</sub> alkyl substituents. When introduced into the solution at intervals, surfactant additions stabilize the arsenic yield at a level of 45–50% at a current density of 0.05 A/cm<sup>2</sup> (Fig. 5, curve 2).

The present results are insufficient for elucidating the mechanism underlying the effect of surfactants. Visual observation revealed that, in the presence of tetraalkylammonium salts containing long-chain substituents, only a thin arsenic layer was deposited on the cathode, and its thickness remained constant during electrolysis. Moreover, numerous uncoated areas were left. Clearly, as arsenic microcrystals grow, they break away from the electrode and pass into the solution, leaving a clean electrode surface.

Note that the introduction of excess surfactant prevents further reduction of arsenites and leads to a sharp increase in hydrogen release.

Based on the above results, we devised an apparatus for recovering arsenic from aqueous sodium arsenite solutions (Fig. 6). The process is run in a filter-press membrane electrolyzer (1) equipped with a lead anode and stainless steel cathode. An aqueous 20% H<sub>2</sub>SO<sub>4</sub> solution is used as an anolyte, which is circulated by a gas-lift system employing the oxygen released at the anode, which is vented to the atmosphere through a gas separator (5). The water loss in the anodic circuit is replenished from a gage tank (7). The cathodic circuit is equipped with a pump circulation system (centrifugal pump 2). The temperature is maintained at 20–25°C by heat exchangers (3, 4) incorporated in the two circuits. A 0.75–0.9 M NaH<sub>2</sub>AsO<sub>3</sub> solution circulates through the cathodic chamber. The forming arsenic suspension is fed by gravity to two settling tanks (10, 10') alter-

nately. After settling, a portion of the solution is decanted, and the rest is fed to a pressure filter (11, 11'), where arsenic is collected and washed with water. Next, the arsenic is fed to a drier (12) to remove water in flow-

**Table 4.** Effect of catholyte composition (excess alkalinity) on the arsenic and arsine yields in the reduction of As<sup>3+</sup> solutions at different alkali concentrations

Na : As molar ratio		1.03	2.37	3.72	4.50	5.09
Current efficiency, %	As <sup>0</sup>	54.6	54.2	49.5	35.5	30.7
	AsH <sub>3</sub>	1.0	1.6	1.8	3.7	8.1

Note: Stainless steel (Kh18N9T) cathode; Pb anode; cation-exchange membrane; initial As<sup>3+</sup> concentration in the catholyte, 1.0 M; 10% H<sub>2</sub>SO<sub>4</sub> anolyte;  $j = 0.05 \text{ A/cm}^2$ ;  $t = 20\text{--}25^\circ\text{C}$ ;  $Q = 100\%$  in terms of As<sup>3+</sup> to As<sup>0</sup> reduction.

**Table 5.** Effect of current density on the arsenic and arsine yields in the reduction of aqueous Na<sub>2</sub>HAsO<sub>3</sub> solutions

$j, \text{ A/cm}^2$		0.025	0.050	0.075	0.100	0.150
Current efficiency, %	As <sup>0</sup>	50.6	50.7	50.9	45.2	50.2
	AsH <sub>3</sub>	0.4	0.9	1.7	2.1	4.0

Note: Stainless steel (Kh18N9T) cathode; Pb anode; cation-exchange membrane; initial Na<sub>2</sub>HAsO<sub>3</sub> concentration in the catholyte, 0.75 M; 10% H<sub>2</sub>SO<sub>4</sub> anolyte;  $t = 20 \pm 3^\circ\text{C}$ ;  $Q = 100\%$  in terms of As<sup>3+</sup> to As<sup>0</sup> reduction.

**Table 6.** Effect of the initial Na<sub>2</sub>HAsO<sub>3</sub> concentration on the arsenic and arsine yields in the reduction of As<sup>3+</sup>

Na <sub>2</sub> HAsO <sub>3</sub> in the catholyte, mol/l		0.14	0.27	0.67	0.93	1.02
Current efficiency, %	As <sup>0</sup>	15.8	18.3	45.6	54.5	49.5
	AsH <sub>3</sub>	1.3	1.4	1.5	1.6	1.8

Note: Stainless steel (Kh18N9T) cathode; Pb anode; cation-exchange membrane; 10% H<sub>2</sub>SO<sub>4</sub> anolyte;  $j = 0.05 \text{ A/cm}^2$ ;  $t = 20 \pm 3^\circ\text{C}$ ;  $Q = 100\%$  in terms of As<sup>3+</sup> to As<sup>0</sup> reduction.



**Fig. 4.** Micrograph of arsenic deposited on a stainless steel cathode: (a)  $\times 1000$ , (b)  $\times 300$ , (c)  $\times 100$ ; 0.75 M  $\text{NaH}_2\text{AsO}_3$ ,  $j = 0.05 \text{ A/cm}^2$ , electrolysis duration of 0.5 h.

ing nitrogen at 150–200°C. The filtrate, clarified catholyte solution, and boiled-down wash water are introduced into a stirred reactor (13). After adding  $\text{As}_2\text{O}_3$  to the reactor in order to compensate for the loss of sodium arsenite, the regenerated catholyte is directed to a measuring tank (8). Next, a steady flow of the catholyte enters the electrolyzer. To maintain the activity of the cathode, a tetraalkylammonium salt (0.02 wt %) is added daily to the catholyte in circulation. After leaving the gas separator (6), the hydrogen containing arsine enters a furnace (9), where  $\text{AsH}_3$  decomposes at 600–700°C to form crystalline arsenic.

The arsenic obtained via electrolysis is 97+% pure. The main impurities are water and  $\text{As}_2\text{O}_3$ .

Using a bipolar ion-exchange membrane for separating the cathodic and anodic zones, one can devise a practically waste-free process, in which the water transfer from the anodic to the cathodic zone does not exceed the water loss through decomposition in the course of electrolysis. Wastewater then results only from washing the apparatus during routine maintenance.

The material balance over the apparatus operating in a continuous mode with a bipolar membrane is presented in Table 7. The process requires only electric power ( $\approx 12800 \text{ kW h}$  per ton of arsenic), water,  $\text{As}_2\text{O}_3$ , and a tetraalkylammonium salt. If the catholyte is regenerated, the consumption of the salt is very low.

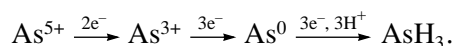
The crude arsenic obtained via electrolysis has the form of ultrafine powder. According to differential thermal analysis (DTA) data, its degassing takes a rather long time (DTA curves show no peaks). X-ray diffraction analysis indicates the presence of two phases: arsenic and  $\text{As}_2\text{O}_3$ . Thermogravimetric scans demonstrate that the material contains up to 20 wt % moisture and gas impurities.

Arsenic obtained electrochemically is a convenient starting material for producing high-purity (99.9999%) arsenic. As an example, Table 8 lists typical impurity concentrations in arsenic produced via alkaline hydrolysis of lewisite, followed by electrochemical recovery from the reaction mixture and vacuum sublimation, and in arsenic produced by the chloride process (elemental synthesis of  $\text{AsCl}_3$  at reduced temperatures, followed by multistep purification and hydrogen reduction [10]).

As follows from the data in Table 8, electrolysis of lewisite detoxication products and subsequent vacuum sublimation yield a rather pure arsenic, which can be used as a starting reagent for producing various As-containing materials. Indeed (Table 8), the multistep process in question yields high-purity arsenic containing less than 1 ppm of contaminating impurities, which compares well with the products of leading foreign manufacturers.

## ELECTROCHEMICAL SYNTHESIS OF ARSINE

Arsine can be synthesized via electrochemical reduction of elemental arsenic, arsenous acid, or arsenic acid according to the scheme



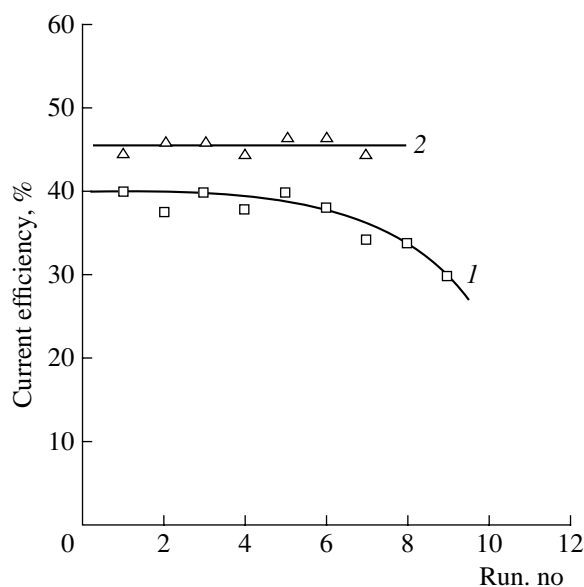
The reduction of elemental arsenic is energetically more favorable. The feasibility of this approach was confirmed in [11, 12], but the reported data were contradictory. An arsine generator based on the reduction of elemental arsenic was reported in [13], where the advantages of electrochemical reduction were mentioned, but details of the process were not given. According to Vorotyntsev *et al.* [14], the reduction of an As electrode in a sodium sulfate solution at 20°C and current densities of 0.07–0.08 A/cm<sup>2</sup> may ensure a quantitative yield of arsine. However, their experiments were carried out in a small electrolyzer, and the procedure used to analyze results was not quite correct. They also described experiments in a larger electrolyzer but did not specify the arsine yield.

Our experiments show that, in Na<sub>2</sub>SO<sub>4</sub> solutions, the current efficiency for the arsenic-to-arsine conversion is no higher than 31% [15]. Moreover, the process in question has two serious drawbacks. First, the consumable electrode is to be replaced at intervals. Second, the cathode partially disintegrates even at low current den-

**Table 7.** Material balance for NaH<sub>2</sub>AsO<sub>3</sub> electrolysis (based on 6 faradays for 2 mol of As<sup>0</sup>)

Substance	mol	g	Substance	mol	g
loaded			obtained		
Anolyte					
H <sub>2</sub> O	20	360	H <sub>2</sub> O	11.0	306
H <sub>2</sub> SO <sub>4</sub>	1.0		H <sub>2</sub> SO <sub>4</sub>	1.0	
			O <sub>2</sub>	3.0	48
Catholyte					
NaH <sub>2</sub> AsO <sub>3</sub>	2	296	Na <sub>2</sub> H <sub>2</sub> AsO <sub>3</sub>	0.94	139.12
H <sub>2</sub> O	20.0	360	H <sub>2</sub> O	28.12	398.16
			NaOH	1.06	42.4
			As <sup>0</sup>	1.0	75
			AsH <sub>3</sub>	0.06	4.68
			H <sub>2</sub>	1.32	2.64
Total					
H <sub>2</sub> O		720	H <sub>2</sub> O		704.16
		1016			1016

Note: Current efficiency of 50% in terms of As<sup>0</sup> and 6% in terms of AsH<sub>3</sub>.

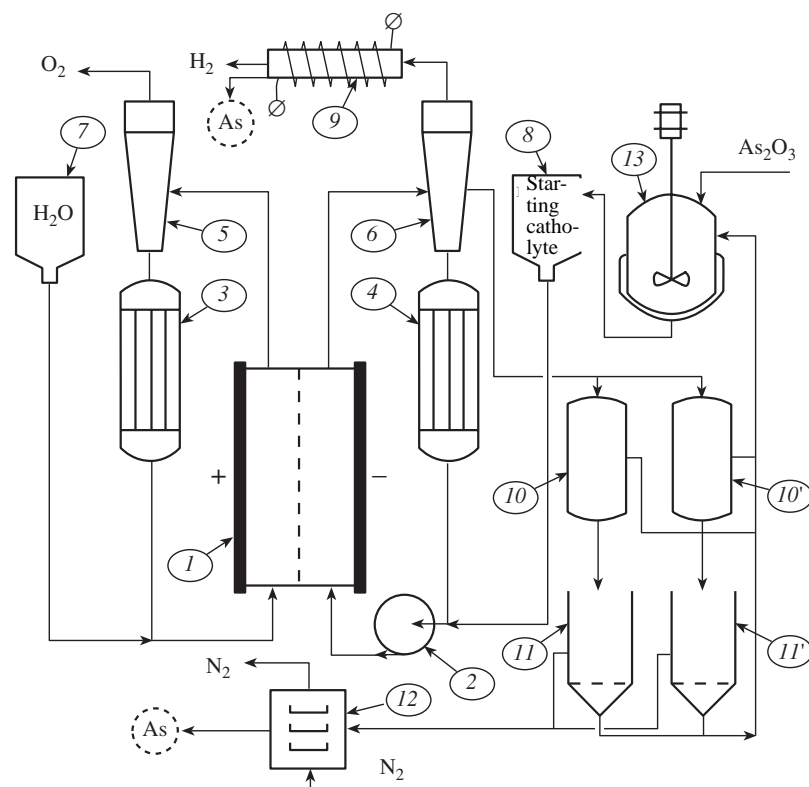


**Fig. 5.** Variation in the current efficiency in terms of elemental arsenic in a series of consecutive experiments; stainless steel cathode, As<sup>3+</sup> concentration of 5%,  $j = 0.05$  A/cm<sup>2</sup>,  $Q = 100\%$ ; (1) no additions, (2) with trimethylcetyl ammonium bromide additions.

sities, leading to the formation of an arsenic suspension. As a result, the catholyte needs to be replaced frequently.

**Table 8.** Impurity concentrations in crude arsenic (I) before and (II) after purification by vacuum sublimation and (III) in arsenic prepared via hydrogen reduction of high-purity AsCl<sub>3</sub>

Impurity	Weight percent		
	I	II	III
Fe	$4 \times 10^{-3}$	$5 \times 10^{-5}$	$5 \times 10^{-7}$
Al	$2 \times 10^{-4}$	$1 \times 10^{-5}$	$<1 \times 10^{-6}$
Mn	$5 \times 10^{-5}$	$<1 \times 10^{-6}$	$5 \times 10^{-7}$
Cr	$6 \times 10^{-4}$	$<2 \times 10^{-6}$	$1 \times 10^{-6}$
Mg	$2 \times 10^{-4}$	$6 \times 10^{-5}$	$<5 \times 10^{-7}$
Na	$2 \times 10^{-3}$	$2 \times 10^{-4}$	$<5 \times 10^{-6}$
K	$5 \times 10^{-1}$	$1 \times 10^{-5}$	$<5 \times 10^{-6}$
Si	$2 \times 10^{-4}$	$1 \times 10^{-4}$	$5 \times 10^{-6}$
Zn	$5 \times 10^{-3}$	$6 \times 10^{-5}$	$1 \times 10^{-6}$
Cu	$8 \times 10^{-5}$	$2 \times 10^{-6}$	$<5 \times 10^{-7}$
Ni	$4 \times 10^{-4}$	$5 \times 10^{-5}$	$<3 \times 10^{-6}$
Ti	$1 \times 10^{-3}$	$1 \times 10^{-6}$	$<1 \times 10^{-6}$
Pb	$6 \times 10^{-3}$	$2 \times 10^{-5}$	$<2 \times 10^{-6}$
Cd	$8 \times 10^{-3}$	$1 \times 10^{-4}$	$1 \times 10^{-6}$
S + Se + Te	$>1 \times 10^{-2}$	$3 \times 10^{-4}$	$<5 \times 10^{-6}$
C	2.9	$5 \times 10^{-3}$	$<5 \times 10^{-5}$



**Fig. 6.** Schematic of the apparatus for producing fine-particle arsenic via electrolysis of an aqueous  $\text{NaH}_2\text{AsO}_3$  solution: (1) electrolyzer, (2) centrifugal pump, (3, 4) heat exchangers, (5, 6) gas separators, (7) measuring tank for water, (8) measuring tank for the catholyte, (9) furnace for decomposing arsenic, (10, 10') settling tanks for the arsenic suspension, (11, 11') pressure filters, (12) drier, (13) catholyte regenerator.

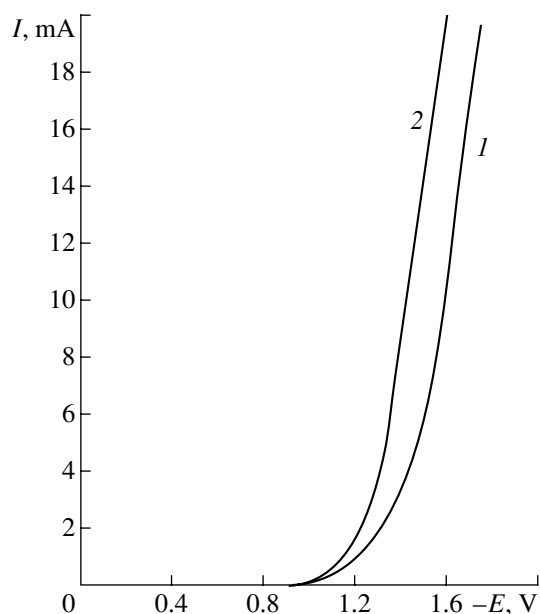
Presumably, it is for this reason that a great deal of attention has been paid to the electrolysis of aqueous acidified solutions of arsenous acid [16–18]. Vorotyntsev *et al.* [18] hold that cadmium is the best cathode material: in an  $\text{As}_2\text{O}_3$  (15 g/l) + 0.1 M  $\text{H}_2\text{SO}_4$  electrolyte at  $j = 0.3 \text{ A/cm}^2$  and  $t = 40^\circ\text{C}$ , it ensures an arsine yield of up to 78%. According to our earlier results [19], the best cathode material is lead, which ensures current efficiencies in terms of  $\text{AsH}_3$  from 65 to 70%. Gladyshev *et al.* [20] prepared arsine via  $\text{As}^{3+}$  reduction in a prototype apparatus and devised an electrolyzer for the synthesis of volatile hydrides. Our attempts to use this process showed that the Pb electrode disintegrates considerably during long-term electrolysis. The most serious drawback of this method is the formation of arsenic as a reaction by-product, which accumulates in the solution in the form of suspended particles. As a result, the electrolyzer has to be cleaned at intervals.

The reduction of  $\text{As}^{5+}$  is essentially unexplored because this process requires much power (8 faradays per mole of arsine). We could find only one report on the reduction of arsenic acid (at a platinum cathode) [21]. The electrolysis products in that work were arsine and trace levels of metallic arsenic; arsenous acid was

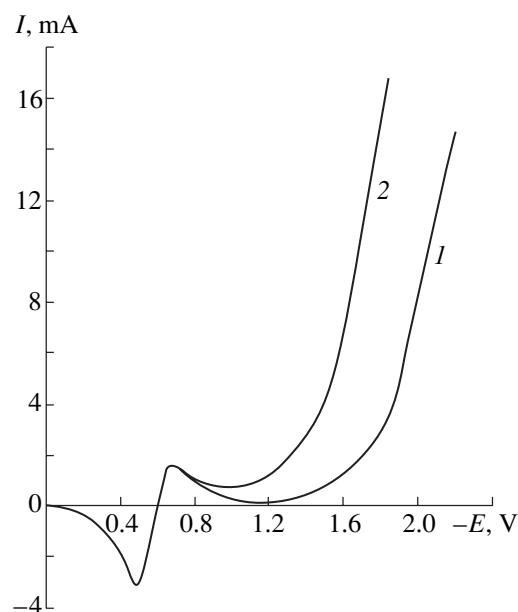
not detected. The highest current efficiency in terms of arsine was 12–15%. In view of the high selectivity of the cathodic process, we carried out a more in-depth study of the electrochemical reduction of arsenic acid and its salts.

Preliminary experiments showed that the electrochemical activity of  $\text{As}^{5+}$  compounds depended primarily on the state of  $\text{As}^{5+}$  in solution:  $\text{AsO}_4^{3-}$  ions in strongly alkaline ( $\text{pH} > 12$ ) media,  $\text{HAsO}_4^{3-}$  and  $\text{H}_2\text{AsO}_4^-$  in the range  $\text{pH} 4$ – $10$ , and arsenic acid in strongly acidic media. In alkaline and neutral solutions,  $\text{As}^{5+}$  compounds could be reduced at none of the electrodes studied, and only in strongly acidic solutions ( $\text{pH} < 2$ ) did we obtain arsine. In this  $\text{pH}$  range, effective reduction of  $\text{H}_3\text{AsO}_4$  to  $\text{AsH}_3$  was observed for a number of metals [22]. It is, therefore, reasonable to believe that the cathodic process involves undissociated arsenic acid.

A key feature of this process is that arsine is the main product of  $\text{H}_3\text{AsO}_4$  reduction. Under certain conditions, there were little or no by-products containing arsenic in other oxidation states. The reason is that the reduction of arsenic acid requires a more negative

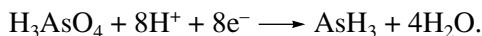


**Fig. 7.** Voltammogram of  $\text{As}^{5+}$  on a titanium cathode in 1.0 N  $\text{H}_2\text{SO}_4$  background electrolyte at  $23 \pm 1^\circ\text{C}$ : (1) 1.0 N  $\text{H}_2\text{SO}_4$ , (2) 1.0 N  $\text{H}_2\text{SO}_4 + 0.1 \text{ M As}^{5+}$ .



**Fig. 8.** Voltammogram of  $\text{As}^{5+}$  on a lead cathode in 1.0 N  $\text{H}_2\text{SO}_4$  background electrolyte at  $23 \pm 1^\circ\text{C}$ : (1) 1.0 N  $\text{H}_2\text{SO}_4$ , (2) 1.0 N  $\text{H}_2\text{SO}_4 + 0.1 \text{ M As}^{5+}$ .

potential in comparison with elemental arsenic and, particularly,  $\text{As}^{3+}$ . As a result, the transition of the eight electrons occurs in a single step:



Owing to this feature, the solution contains little or no dispersed arsenic throughout electrolysis.

$I$ - $V$  measurements in a 1 N  $\text{H}_2\text{SO}_4$  solution (Figs. 7–9) show that, in the case of copper, lead, and titanium cathodes, arsenic acid acts as a depolarizer. However, the potential corresponding to the current upturn depends on the electrode material. The steep rise in current begins at  $-1.22 \text{ V}$  for lead,  $-1.20 \text{ V}$  for titanium, and  $-0.7 \text{ V}$  for copper. It is reasonable to assume that, much as in the reduction of arsenous acid, an intermediate step of the process is the formation of copper arsenides on the cathode.

In preparative electrolyses, we used aqueous solutions of arsenic acid, with no background electrolyte, to assess the effects of major process parameters on the yields of arsine and by-products.

The data in Table 9, obtained with a ceramic membrane in 1 M arsenic acid at a current density of  $0.1 \text{ A/cm}^2$ , illustrate the effect of cathode material on the arsine yield. The current efficiency exceeds 32% with the cadmium cathode and is somewhat lower with the copper cathode. Surprisingly enough, the arsine yield is very low on the lead cathode. Thus, the overpotential for hydrogen release plays an insignificant role in the formation of arsine. Increasing the cathode potential by raising the current density to  $0.2 \text{ A/cm}^2$  has a positive effect on arsine formation.

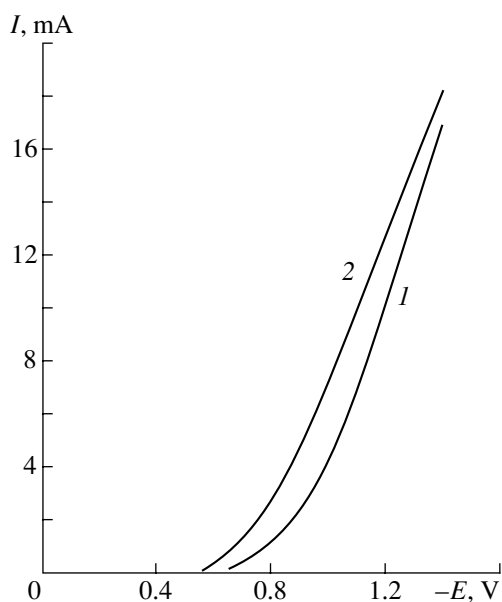
In subsequent studies, we used a cation-exchange membrane which precluded intermixing of the catholyte and anolyte, in contrast to the porous membrane. This allowed us to reach higher yields. Our purpose was to assess the stability of electrode materials. The materials tested were cadmium, copper, and lead (Table 10). Each electrode was used in a series of experiments without surface treatment. As a result, a black, fine-particle deposit was formed on the cathode surface. In the first run, the arsine yield was lower than that in subsequent runs, independent of the cathode material.

**Table 9.** Effect of cathode material on the arsine yield in the reduction of arsenic acid

Cathode material	Cd	Cu	Stainless steel	Sn	Ti	Ni	Pb
Current efficiency in terms of $\text{AsH}_3$ , %	32.9	20.7	16.6	14.1	13.9	12.6	7.8

Note: Platinum anode; ceramic membrane; cylindrical electrolyzer; initial  $\text{H}_3\text{AsO}_4$  concentration in the catholyte, 1.0 M; 40%  $\text{H}_3\text{PO}_4$  anolyte;  $j = 0.1 \text{ A/cm}^2$ ;  $t = 25 \pm 1^\circ\text{C}$ ;  $Q = 50\%$  in terms of  $\text{H}_3\text{AsO}_4$  to  $\text{AsH}_3$  reduction.





**Fig. 9.** Voltammogram of  $\text{As}^{5+}$  on a copper cathode in 1.0 N  $\text{H}_2\text{SO}_4$  background electrolyte at  $23 \pm 1^\circ\text{C}$ : (1) 1.0 N  $\text{H}_2\text{SO}_4$ , (2) 1.0 N  $\text{H}_2\text{SO}_4 + 0.1 \text{ M As}^{5+}$ .

With the aim of developing an arsine generator, we studied the effect of process parameters on the formation of by-products—elemental arsenic and arsenides—which may accumulate in the electrolyte, impeding its circulation. In all runs with high arsine yields, we observed active arsenic precipitation and

**Table 10.** Activity of cathode materials for arsine electrosynthesis in a series of consecutive experiments without surface treatment

Cathode	Run. no.	Current efficiency, %	
		$\text{AsH}_3$	$\text{As}^*$
Cd	1	48.0	0.5
	2	56.0	2.7
	3	74.0	4.9
	4	71.0	2.7
	5	72.0	2.7
Cu	1	39.6	1.3
	2	71.6	3.2
	3	71.6	3.0
Pb	1	26.3	<0.1
	2	38.2	6.0

Note: Platinum anode; cation-exchange membrane; initial  $\text{H}_3\text{AsO}_4$  concentration in the catholyte and anolyte, 1.0 M;  $j = 0.2 \text{ A/cm}^2$ ;  $t = 20^\circ\text{C}$ ;  $Q = 20\%$  in terms of  $\text{H}_3\text{AsO}_4$  to  $\text{AsH}_3$  reduction.  
\* Arsenic and arsenides in terms of elemental arsenic.

minor gas evolution during the first 3–4 min of the reaction. As a result, the solution turned opaque. During the next 10–15 min, the particles coalesced, and a dark brown precipitate was formed. Subsequently, the hydrogen and arsine yields stabilized. Thus, the yield of by-products decreases with increasing electrolysis time (amount of charge passed) (Table 11).

If, between experiments, the cathode and catholyte were isolated from air, each application of a current also led to precipitation of some amount of arsenic. In an experiment with a cadmium cathode and two 23-h arrests ( $Q = 18 \text{ A h}$ ,  $j = 0.2 \text{ A/cm}^2$ ), the total current efficiency in terms of arsenic was 5.7%, and the arsine yield was 65.3%.

With increasing temperature, the arsenic yield rises (Table 12). Increasing the concentration of arsenic acid leads to a slight increase in the amount of elemental arsenic (Table 13). In concentrated (above 3 M) arsenic acid solutions, arsenic precipitates most rapidly, and the catholyte contains arsenous acid.

The cadmium cathode turned out to be unsuitable for long-term operation since a brown spongy deposit was formed on its surface. The composition of the deposit was not determined. Its thickness was 3–4 mm ( $Q = 100 \text{ A h}$ ,  $j = 0.2 \text{ A/cm}^2$ ). After electrolysis under identical conditions, the copper cathode was covered with a thin black deposit consisting, most likely, of copper arsenide (Fig. 10). In view of this, further studies were performed with a copper cathode.

It should be emphasized that, before reaching a high, stable level, the arsine yield on the copper cathode rises only gradually, as illustrated by the data in Table 14. Before that series of experiments, the cathode surface was cleaned with nitric acid. The yield increased in the first four runs and then saturated around 88%. The observed increase in arsine yield is associated with changes in surface condition. Thus, one way of activating copper is by performing three or four “idle” runs. The activity of copper cathodes remains unchanged over a very long time if they are isolated from air.

To devise an arsine generator, it is necessary to assess the total material balance in a system equipped with a Nafion cation-exchange membrane. In addition to the electrode processes, one should take into account the migration of arsenic acid out of the anolyte and the migration of water through the cation-exchange membrane. A schematic illustrating the processes in the generator is displayed in Fig. 11. Theoretically, at 100% current efficiency, the passage of 8 faradays of charge leads to the decomposition of 1 mol of arsenic acid and the formation of 1 mol of arsine and 4 mol of water. Concurrently, 2 mol of oxygen is released at the anode. At least 8 mol of water passes from the anodic to the cathodic zone via electrotransport. An amount of arsenic acid diffuses together with water into the cathodic zone. This amount depends mainly on the porosity of the membrane and can be determined only in experiment.

**Table 11.** Effect of electrolysis time on the arsenic yield in arsine electrosynthesis

Cathode		Cd			Cu		
Electrolysis time, h		0.5	1.0	3.0	1.0	1.5	3.0
$Q$ , A h		3.0	6.0	18.0	6.0	9.0	18.0
Current efficiency, %	As	10.0	2.7	0.6	3.0	1.8	0.5
	AsH <sub>3</sub>	68.0	72.0	69.0	71.6	67.2	70.7

Note: Platinum anode; cation-exchange membrane; H<sub>3</sub>AsO<sub>4</sub> concentration in the catholyte, 1.0 M throughout the run; 2.0 M H<sub>3</sub>AsO<sub>4</sub> anolyte;  $j = 0.2$  A/cm<sup>2</sup>;  $t = 20$ –30°C.

**Table 12.** Temperature effect on the arsenic yield in arsine electrosynthesis

Cathode		Cd		Cu	
$Q$ , A h		6.0		18.0	
$t$ , °C		30–33	63–67	15–19	45–50
Current efficiency, %	As	2.7	9.5	0.6	2.3
	AsH <sub>3</sub>	66.0	57.0	76.1	65.1

Note: Platinum anode; cation-exchange membrane; H<sub>3</sub>AsO<sub>4</sub> concentration in the catholyte, 1.0 M throughout the run; 2.0 M H<sub>3</sub>AsO<sub>4</sub> anolyte;  $j = 0.2$  A/cm<sup>2</sup>.

To this end, we studied H<sub>3</sub>AsO<sub>4</sub> and water transport through a cation-exchange membrane (Table 15). According to our results, the H<sub>3</sub>AsO<sub>4</sub> transport through the membrane depends little on the relationship between the H<sub>3</sub>AsO<sub>4</sub> concentrations in the catholyte and anolyte and does not vary with temperature (Table 15, run 5). The decrease in the amount of H<sub>3</sub>AsO<sub>4</sub> in the catholyte owing to the formation of arsine is 10–20 times larger than the amount arriving from the anolyte. Consequently, in determining the optimal H<sub>3</sub>AsO<sub>4</sub> concentration, one should primarily take into

account water transport. Theoretically, at  $Q = 1$  A h,  $\approx 0.7$  ml of water must be transferred together with H<sub>3</sub>O<sup>+</sup> ions. As can be seen from Table 15, the optimal H<sub>3</sub>AsO<sub>4</sub> concentration in the anolyte from the viewpoint of maintaining a constant catholyte volume lies in the range 4–10 mol/l.

Our results indicate that, at a current density of 0.2 A/cm<sup>2</sup>, membrane area of 30 cm<sup>2</sup>, and H<sub>3</sub>AsO<sub>4</sub> concentration in the anolyte between 5.5 and 6.5 mol/l, maintaining the H<sub>3</sub>AsO<sub>4</sub> concentration in the catholyte at a level of  $\approx 1.5$  mol/l by adding 0.0010–0.0013 mol/(A h) (0.2–0.3 ml 13–14 M H<sub>3</sub>AsO<sub>4</sub> per A h) makes it possible to reduce the changes in the volumes of the catholyte and anolyte to  $\sim 0.5$  ml at  $Q = 1$  A h. Consequently, this allows one to achieve continuous electrochemical arsine generation with the use of arsenic acid as a raw material.

To maintain continuous operation of the generator, an excess catholyte must pass to the anodic zone, which is easy to achieve with the use of an overflow line. The arsenic precipitate accumulating in the settling tank of the cathodic circuit (a very small amount in a continuous mode of operation) can be transferred as needed to the anodic zone, where it will oxidize to arsenic acid. Concurrently, concentration H<sub>3</sub>AsO<sub>4</sub> must be fed to the cathodic zone in order to compensate for its consumption in the course of arsine electrosynthesis.

Such a generator is schematized in Fig. 12. The main unit of the generator is a filter-press electrolyzer (1) equipped with a platinum anode and copper cathode. The cathode circuit includes an ascending gas-lift line (2), gas separator (3), descending gas-lift line (4), heat exchanger (5), and buffer tank (6). The anodic circuit incorporates similar units (2'–6'). The buffer tanks are equipped with densimeters (7, 7') for monitoring the content of arsenic acid in the anodic and cathodic circuits. To maintain the desired acid concentration, 13–14 M H<sub>3</sub>AsO<sub>4</sub> is fed from a measuring tank (8). The catholyte level is controlled automatically with the use of an equalizing line (9). The elemental arsenic collecting at the bottom of tank 6' is withdrawn at regular intervals together with an amount of the catholyte and

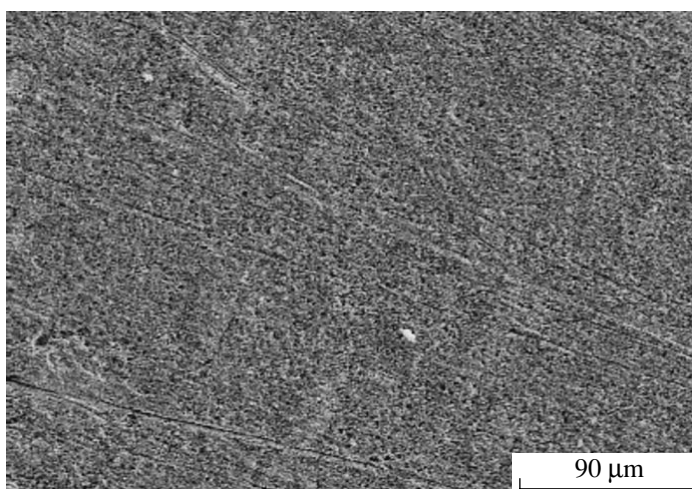
**Table 13.** Effect of H<sub>3</sub>AsO<sub>4</sub> concentration on the arsenic yield in arsine electrosynthesis

Cathode		Cd				Cu	
H <sub>3</sub> AsO <sub>4</sub> , mol/l*		0.4–0.5	0.9–1.0	2.2–2.3	3.14	1.0	1.8
Current efficiency, %	As	0.6	0.8	0.81**	$\sim 4.0$ **	0.7	1.7
	AsH <sub>3</sub>	69.0	72.6	43.70**	50.30**	73.7	68.3

Note: Platinum anode, cation-exchange membrane, 2.0 M H<sub>3</sub>AsO<sub>4</sub> anolyte,  $j = 0.2$  A/cm<sup>2</sup>,  $t = 14$ –17°C,  $Q = 18.0$  A h.

\* Maintained throughout the run.

\*\* The results were obtained in a cylindrical electrolyzer with a ceramic membrane (40% H<sub>3</sub>PO<sub>4</sub> anolyte,  $j = 0.05$  A/cm<sup>2</sup>,  $t = 25 \pm 1$ °C,  $Q = 15\%$ ).



**Fig. 10.** Micrograph of an arsenic deposit on a copper cathode; 0.5 M  $\text{H}_3\text{AsO}_4$ ,  $j = 0.2 \text{ A/cm}^2$ , electrolysis time of 1 h.

added to the anolyte. Condenser *10* serves to remove moisture from the hydrogen + arsine mixture (about 50 vol %  $\text{AsH}_3$ ) leaving the cathodic circuit. Next the mixture is dried in a zeolite-packed column (*11*). The condensate is introduced into the anolyte. The amount of resulting arsine is easy to control by varying the electric current through the electrolyzer.

According to preliminary gas-chromatographic data,<sup>1</sup> the arsine synthesized by the electrochemical method is characterized by a high purity. The contents of major hydrocarbon impurities are  $(1.9 \pm 0.3) \times 10^{-3}$  vol %  $\text{CH}_4$ ,  $(7.3 \pm 1.1) \times 10^{-5}$  vol %  $\text{C}_2\text{H}_4$ , and  $\leq 3 \times 10^{-5}$  vol %  $\text{C}_2\text{H}_6$ . The concentrations of  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ , *i*- $\text{C}_4\text{H}_{10}$ , *n*- $\text{C}_4\text{H}_{10}$ , *i*- $\text{C}_4\text{H}_8$ , *cis*-2- $\text{C}_4\text{H}_8$ , *i*- $\text{C}_5\text{H}_{12}$ , and *n*- $\text{C}_5\text{H}_{12}$  are below the detection limit of gas-chromatographic analysis, estimated at  $(3\text{--}10) \times 10^{-6}\%$ . The contents of hydrides are  $< 5 \times 10^{-4}$  vol %  $\text{SiH}_4$ ,  $< 10^{-5}$  vol %  $\text{PH}_3$ ,  $< 7 \times 10^{-4}$  vol %  $\text{GeH}_4$ , and  $< 10^{-4}$  vol %  $\text{H}_2\text{S}$ . The Cl content is below  $5 \times 10^{-5}$  wt %.

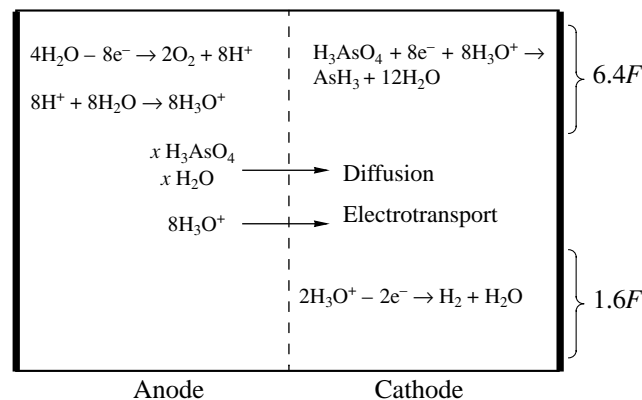
Thus, the present results provide a basis for the development of an electrochemical arsine generator. Equipped with a unit for removing microimpurities, such a generator can be used directly in the manufacturing of semiconductor materials. Another potential application area of high-purity arsine is the preparation of metallic arsenic with a higher purity compared to the chloride and alkoxide processes.

#### ELECTROCHEMICAL SYNTHESIS OF ARSENIC ACID

Arsenic acid is commonly prepared via oxidation of  $\text{As}_2\text{O}_3$  with concentrated nitric acid or hydrogen perox-

ide. The chemicals react violently, which poses a number of technical problems. As an alternative, attempts were made to oxidize alkaline solutions of As(III) [23–25], but this process yields a salt of arsenic acid, and the preparation of  $\text{H}_3\text{AsO}_4$  requires an additional step.

According to Niva Kitizo [26], arsenic acid can be prepared in the anodic chamber of an electrolyzer by electrochemical oxidation of an  $\text{As}_2\text{O}_3$  suspension on a  $\text{PbO}_2$  anode in an electrolyte containing 1 wt %  $\text{Na}_2\text{SO}_4$  and 1 wt %  $\text{H}_2\text{SO}_4$  at a current density of  $0.03 \text{ A/cm}^2$ , using a 20% alkali solution as a catholyte. This process was reported to yield 40%, or even more concentrated, arsenic acid solutions. The current efficiency of the process was not specified. A drawback to this approach is that the electrolyte contains foreign ions ( $\text{Na}^+$  and  $\text{SO}_4^{2-}$ ), which are difficult to remove. A serious impediment to the use of this process on a production scale is its slow rate (low current density). In this context, it is



**Fig. 11.** Schematic illustrating processes in an arsine generator.

<sup>1</sup> Analyses were carried out at the Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences (Nizhni Novgorod).

**Table 14.** Arsine electrosynthesis on a cleaned (nonactivated) copper cathode

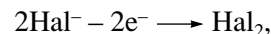
Run no.		1	2	3	4	5	6
Current efficiency, %	As	–	1.8	2.8	3.1	2.9	2.2
	AsH <sub>3</sub>	21.3	35.3	47.8	43.6	88.2	88.8

Note: Copper cathode; platinum anode; cation-exchange membrane; H<sub>3</sub>AsO<sub>4</sub> concentration in the catholyte, 1.1–1.5 M throughout the run; 2.0 M H<sub>3</sub>AsO<sub>4</sub> anolyte;  $j = 0.2 \text{ A/cm}^2$ ;  $t = 17\text{--}20^\circ\text{C}$ ;  $Q = 9.0 \text{ A h}$ .

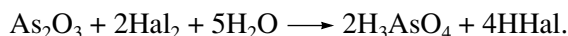
of interest to devise an electrochemical process for synthesizing high-purity arsenic acid from As<sub>2</sub>O<sub>3</sub>.

Preliminary experiments showed that aqueous solutions of arsenous acid have a low electrical conductivity. This led us to attempt oxidation of an As<sub>2</sub>O<sub>3</sub> suspension in arsenic acid solutions, which have good conductivity. It was found in a series of experiments with anolytes containing 1.0 to 10.0 M H<sub>3</sub>AsO<sub>4</sub> that, at current densities in the range 0.05–0.2 A/cm<sup>2</sup> and temperatures of 14–17°C, the current efficiency in terms of H<sub>3</sub>AsO<sub>4</sub> for lead and platinum anodes does not exceed 7%. On graphite, arsenic acid could be obtained with a current efficiency of up to 40%, but the graphite anode disintegrated in the course of the reaction.

Additions of hydrochloric or hydrobromic acid drastically change the situation. Halide ions in the system under consideration act as both catalysts and carriers. The halogen produced at the anode,



oxidizes the As<sub>2</sub>O<sub>3</sub> suspension by the reaction



We studied the effect of HCl concentration on the oxidation rate of As<sub>2</sub>O<sub>3</sub>. The data in Table 16 demonstrate that the presence of even 0.5 M Cl<sup>–</sup> ensures quantitative oxidation at a current density of 0.2 A/cm<sup>2</sup>.

By gradually adding As<sub>2</sub>O<sub>3</sub> to the anolyte, it is possible to obtain arsenic acid with a concentration of up to 5.0 mol/l. Both platinum and ruthenium–titanium oxide anodes can be used. Increasing the temperature from 10 to 50°C does not change the character of the process. Above 50°C, ruthenium–titanium oxide anodes disintegrate.

The electrochemical oxidation of As<sub>2</sub>O<sub>3</sub> in the presence of halogen acids offers the possibility of preparing high-purity H<sub>3</sub>AsO<sub>4</sub> or As<sub>2</sub>O<sub>6</sub>. The HCl present in the anolyte is fully removed by boiling down the solution. The distillate, containing HCl, is utilized to prepare the next portion of anolyte.

**Table 15.** Effect of H<sub>3</sub>AsO<sub>4</sub> concentration on H<sub>3</sub>AsO<sub>4</sub> and water transport through the Nafion cation-exchange membrane in arsine electrosynthesis

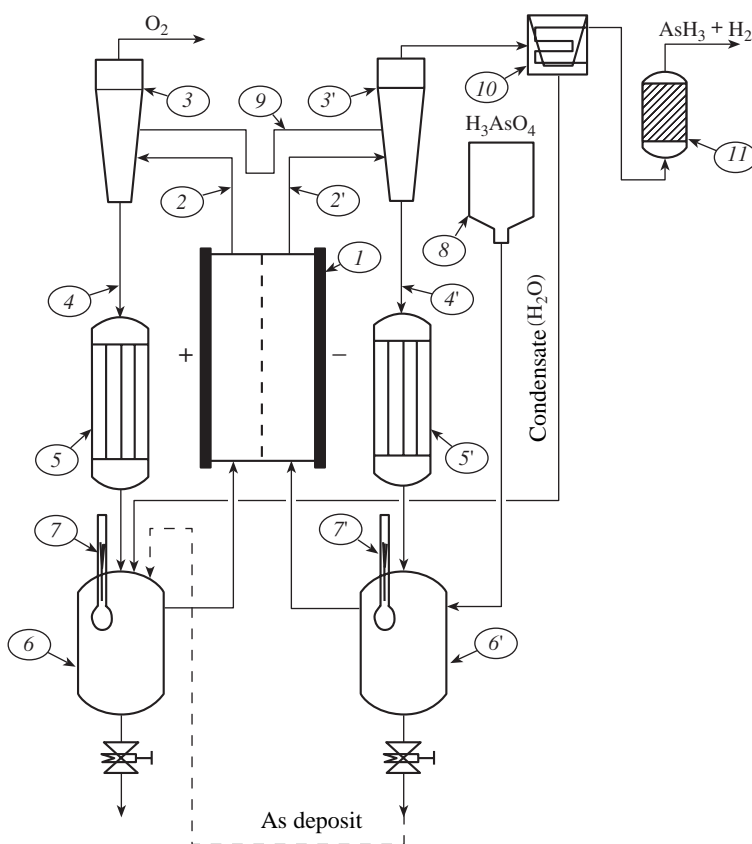
Run no.	H <sub>3</sub> AsO <sub>4</sub> in the catholyte, mol/l*	H <sub>3</sub> AsO <sub>4</sub> in the anolyte, mol/l	H <sub>3</sub> AsO <sub>4</sub> transport from the anolyte to catholyte, mol/(A h)	Change in catholyte volume, ml/(A h)	Change in anolyte volume, ml/(A h)
1	1.1	3.0–3.8	0.0011	+0.94	–1.36
2	1.1–1.0	3.2–3.9	0.0012	+1.05	–1.33
3	1.0	3.3–3.9	0.0016	+1.16	–1.5
4	1.0	3.1–4.2	0.0015	+1.19	–1.5
5**	1.1–1.0	3.3–4.2	0.0014	+0.83	–1.39
6	1.0–1.1	10.0	0.0009	–0.36	–0.17
7	1.3–1.0	10.1	0.0005	–0.47	–0.03
8	2.0–1.8	10.0	0.0010	+0.03	–0.31
9***	1.4–1.2	2.9–2.8	0.0040	+0.83	–1.17
10***	1.2–1.1	2.8–3.0	0.0033	+0.83	–1.17

Note: Copper cathode; platinum anode;  $j = 0.2 \text{ A/cm}^2$ ;  $t = 14\text{--}17^\circ\text{C}$ ;  $Q = 18.0 \text{ A h}$ ; initial catholyte volume, 135 ml; initial anolyte volume, 90–100 ml.

\* Maintained throughout the run.

\*\*  $t = 45\text{--}50^\circ\text{C}$ ,

\*\*\*  $Q = 6.0 \text{ A h}$ .



**Fig. 12.** Schematic of the arsine generator: (1) electrolyzer, (2, 2') ascending gas-lift tubes, (3, 3') gas separators, (4, 4') descending gas-lift tubes, (5, 5') heat exchangers and anodic chamber, (6, 6') buffer tanks for the anolyte and catholyte, (7, 7') densimeters, (8) measuring tank for concentrated  $\text{H}_3\text{AsO}_4$ , (9) equalizing line, (10) condenser, (11) drying column.

The flow chart of the batch process is shown in Fig. 13. To prepare the anolyte, use is made of the catholyte remaining from the previous cycle. Its concentration is adjusted to the required value by adding the hydrochloric acid obtained at the anolyte evaporation stage. The catholyte is prepared by diluting hydrochloric acid with distilled water. The catholyte volume is such that it equals the anolyte volume after electrolysis (an increase in volume owing to the electrotransport from the anolyte) and the addition of hydrochloric acid.  $\text{As}_2\text{O}_3$  is loaded directly into the anodic circuit, while stirring the solution, and forms a suspension.

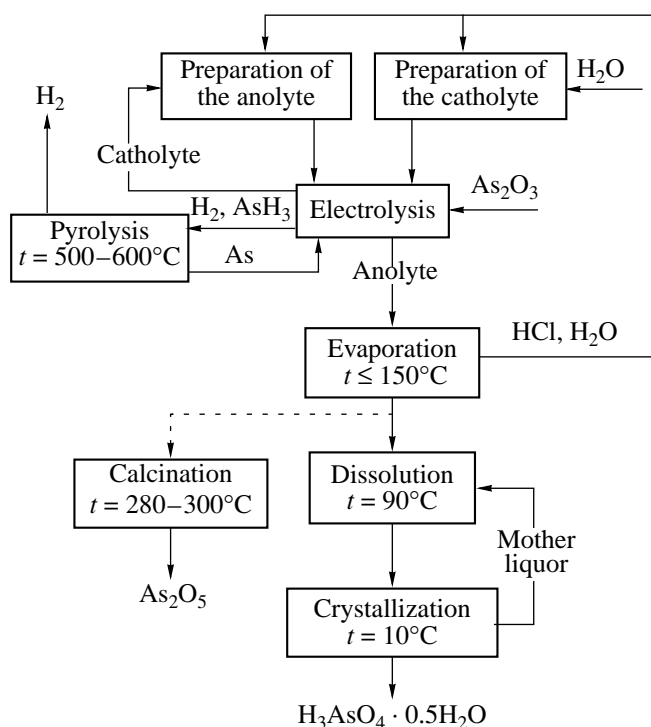
During electrolysis, the cathode gas is subjected to pyrolysis in order to prevent arsine from passing to the atmosphere. After electrolysis, the catholyte is used to prepare the anolyte for the next cycle, and the anolyte is evaporated to dryness. If  $\text{As}_2\text{O}_3$  is to be prepared, the solid residue is calcined at 280–300°C to a constant weight. To obtain arsenic acid, the evaporation residue is dissolved during heating and then crystallized during cooling to give  $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$ .

Thus, our results offer the possibility of developing a commercial-scale, almost waste-free process. An

**Table 16.** Effect of the HCl concentration in the anolyte on the arsenic acid and oxygen yields in the anodic oxidation of  $\text{As}_2\text{O}_3$

HCl, mol/l		0	0.25	0.5	1.0	2.0	3.0	4.0
$\text{H}_3\text{AsO}_4$ yield, %	current	7	62	85	86	96	98	97
	substance	40	93	94	98	98	99	99
Current efficiency in terms of $\text{O}_2$ , %		Not determined		9.6	3.4	1.5	0.7	0.8

Note: Platinum anode; tungsten cathode; cation-exchange membrane; anolyte,  $\text{As}_2\text{O}_3$  suspension in HCl solution; 1 M HCl catholyte;  $j = 0.2 \text{ A/cm}^2$ ;  $Q = 100\%$  in terms of  $\text{As}_2\text{O}_3$  to  $\text{H}_3\text{AsO}_4$  oxidation.



**Fig. 13.** Flow chart of the batch electrosynthesis of arsenic acid or  $\text{As}_2\text{O}_3$  in the presence of hydrogen chloride.

important point is that the purity of the product is determined in large measure by that of the  $\text{As}_2\text{O}_3$  used.

### CONCLUSIONS

Our results clearly demonstrate that electrolysis can be used for processing  $\text{As}_2\text{O}_3$ , the most abundant arsenic containing raw material, into elemental arsenic.

A process was tested for recovering elemental arsenic from the products of alkaline hydrolysis of lewisite. Subsequent multistep purification of the arsenic yielded a 99.9999%-pure material.

We also devised a low-waste process for preparing arsenic acid and  $\text{As}_2\text{O}_5$  from  $\text{As}_2\text{O}_3$ .

It was shown that arsenic acid can be used for the electrochemical synthesis of arsine.

We developed a stably operating, almost waste-free arsine generator. After the removal of microimpurities, the resulting arsine can be used in the manufacturing of semiconductor materials.

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