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AN ABSTRACT OF THE THESIS OF Sandra Gee Kang for the Master of Science
in Chemistry presented 27 November 1974.

Title: The Development of an Arsenic(V) Selective Electrode

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

David K. Roe, Chairman

Dennis W. Barnum

Edward M. Perdue

The object of this research was to develop an arsenic(V) selective electrode. The electrode is based on a solid state membrane prepared by pressing a precipitate of silver arsenate-silver sulfide into a pellet. After the electrode was made, experiments were designed to check for three general characteristics of the electrodes: dependence of potential on pH for constant arsenic(V) concentration; dependence of potential on arsenic(V) concentrations at constant pH and extent of interference due to phosphate and arsenic(III) ions. From these measurements, it was found that Ag_2HAsO_4 was formed originally in the membranes containing a small fraction of arsenic(V) and that this compound was converted to Ag_3AsO_4 on the electrode surface in alkaline solutions.

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of Sandra Gee Kang
presented 27 November 1974.

David K. Roe, Chairman

Dennis W. Barnum

Edward M. Perdue

APPROVED:

Gary L. Gard, Chairman, Department of Chemistry

David T. Clark, Dean of Graduate Studies

THE DEVELOPMENT OF AN ARSENIC(V) SELECTIVE ELECTRODE

by

SANDRA GEE KANG

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in

CHEMISTRY

Portland State University
1974

To My Parents

For Their Understanding and Confidence

ACKNOWLEDGMENT

I wish to express my deep appreciation to Dr. David K. Roe for his painstaking guidance, recommendations, and criticisms.

Since I came to the United States, I have had the privilege of serving as a teaching assistant in the Department of Chemistry. I am especially grateful to the University for giving me the opportunity to work closely with the faculty.

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INTRODUCTION

Originally, I became interested in analyzing natural waters for arsenic because of a disease prevalent in a village in Taiwan. This disease is reportedly due to accumulation of arsenic in the drinking water. This incidence of arsenic in water is not one of human pollution but rather is due to the course which is followed by the water. It is known that the water flows through some underground tunnels which contain minerals that are high in arsenic before it reaches the community reservoirs. Arsenic is a cumulative poison which builds up slowly in the body. According to some medical sources, long term arsenosis may not be detectable for 2 to 6 years or longer(1). A side effect of arsenic poisoning is the possibility of skin rashes and other types of contact dermatitis in sensitive people. Pentavalent arsenic as arsenate is nontoxic in normal concentrations, is excreted rapidly largely through the kidneys, probably does not accumulate in human tissues, is a normal constituent of food, and may perform some unknown physiological function(2).

Arsenic is introduced into the environment through volcanic eruptions, and is thus found in sedimentary rocks. Due to human activity, increasing amounts of arsenic are being introduced into food and water sources through usage in pigments, herbicides, insecticides, and phosphate laundry detergents.

The U. S. Public Health Service gives tolerances of 10 parts per billion (ppb) (recommended) and 50 ppb (mandatory) of arsenic in drinking water(1). Arsenic values of 2 to 8 ppb have been measured in the Kansas River(1). This clearly is quite close to the critical

concentration recommended by the Health Department. It is therefore surmised that a rapid, inexpensive, accurate method for measuring arsenic concentration is needed.

It is stated by Myers and Osteryoung that "...the most common methods of arsenic analysis involve the generation of arsine gas followed by the determination of AsH_3 according to the Gutzeit method(3), by silver diethyldithiocarbamate(4), by atomic absorption(5-9), or by emission spectroscopy(10). However, it has been reported(11) that the recovery of small quantities of AsH_3 is difficult. Also, it is desirable for an analytical procedure to distinguish between the possible oxidation states of arsenic, and these methods are inherently incapable of such a distinction. While isotope dilution(12) and colorimetric(13, 14) methods can describe the distribution of arsenic between the arsenate and arsenite species, these procedures are slow and tend to be rather insensitive. Thus, electrochemical methods are a reasonable alternative to other analytical techniques"(15).

Voltammetric techniques are commonly used in trace metal work. One particular technique is called polarography. This method is signified by use of a dropping mercury electrode and theoretically deals with the measurement of small electrical currents as a function of applied potential. The determination of the presence of arsenic in its oxidation states and at low concentration has been extensively investigated(16, 17). The results of these investigations have been compiled by Arnold and Johnson(18).

In general, it is found that the most complicated and irreversible polarograms occur in noncomplexing acid media, e.g., HCl , H_2SO_4 , HNO_3 ,

where as in the presence of such complexing agents as tartaric acid, citric acid or pyrogallol, simpler waves are produced. Some polarography was employed in this work to determine arsenic(V) and arsenic(III) in a 2M HClO_4 -0.5 M pyrogallol medium. Three well defined waves were produced due to reduction of an arsenic(V)-pyrogallol complex to arsenic(III), arsenic(0) and AsH_3 . These determinations were also conducted using different supporting electrolytes such as 1 M HCl , 12 M HCl , or 4 M HClO_4 to determine both arsenic(V) and arsenic(III). With these electrolytes, SnCl_4 was added in order to generate at the electrode surface a reducing agent, Sn^{+2} , which might reduce arsenic(V) to (III). This would be a catalytic current and could be used to measure the arsenic(V) concentration. The rate of the catalytic reaction was too slow to be useful. Other catalyts were tried without success.

While these experiments were being conducted, a prototype commercial arsenic(V) ion selective electrode was obtained. This electrode, which failed after some experiments was subsequently withdrawn from the market. It was at this time that I decided to construct some electrodes.

During recent years, solid state ion selective membrane electrodes have been constructed which are sensitive to cations and anions as well as complexes. These electrodes have been designed and used for a wide range of analytical applications.

It is observed that electrodes can be made from lanthanum fluoride, silver sulfide, mixed silver sulfide - silve halide, mixed silver sulfide - metal sulfide, etc. Silver sulfide is an ionic conductor of low resistance in which the silver ions are the mobile species. The

exceedingly low solubility product of Ag_2S , its excellent resistance to oxidizing and reducing agents, and the ease with which it can be fabricated into dense polycrystalline membranes by conventional pellet pressing techniques, makes it an ideal material for electrode use (19). In this work, precipitates were prepared by adding AgNO_3 to aqueous solutions containing varying amounts of Na_2S and Na_2HAsO_4 . The resulting precipitate was washed, dried, and pressed into a solid pellet which was then made into a membrane electrode.

The response of an ideal solid-state membrane containing Ag_2S is determined by the activity of silver ions which in turn is determined by the solubility of silver arsenate in the presence of dissolved arsenate.

The potential for a silver sulfide electrode is given by:

$$E = \text{constant} + \frac{2.3 RT}{F} \log [\text{Ag}^+]$$

Since silver arsenate is much more soluble than Ag_2S , the sulfide can be considered as a chemically inert matrix material through which silver ions are free to move. At the membrane-solution interface, the silver arsenate equilibrates with the sample solution resulting in a silver ion level given by the solubility of silver arsenate in the presence of dissolved arsenic(V).

$$[\text{Ag}^+] = \left(\frac{\text{Solubility product of silver arsenate}}{[\text{As(V)}]} \right)^{1/m}$$

m = mole ratio of silver to arsenic(V) in solid

Substitution into the Nernst equation for a silver ion conducting membrane gives the result that a mixture of this type behaves as though the membrane were a pure arsenic(V) ion conductor.

$$E = \text{constant} - \frac{2.3 RT}{mF} \log [\text{As(V)}]$$

After the first set of electrodes was constructed, two types of measurements were made. The experiments initially were concerned with finding the optimum range of pH over which the electrodes operate. Secondly, it was necessary to determine over what range of arsenic concentration the electrodes respond. Interferences were expected and I checked initially for problems involving phosphate and arsenic(III) ions because these ions would be expected to be present in water samples.

Electrode measurements served my primary purpose; they are fast and a steady reading can be obtained within a few minutes. Also the samples used are in no need of pretreatment except possible pH adjustment and are not subsequently destroyed. One expects that with electrochemical techniques small sample size can be used at low concentration. Construction of the electrodes and related instruments is very simple and quite inexpensive. Future work is needed to develop electrodes of improved precision.

MATERIALS, APPARATUS, AND PREPARATION OF MEMBRANE ELECTRODES

All the chemicals, such as $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, Na_2HAsO_4 , AgNO_3 which were used to form the precipitates were of analytical reagent grade (Mallinckrodt Chemical Works, St. Louis, Missouri) and were used without purification. Distilled water was used throughout these experiments.

The arsenate-sensitive membrane materials were prepared by coprecipitation of silver sulfide and silver arsenate. Different mole ratios of Na_2S and Na_2HAsO_4 were precipitated by addition of dilute AgNO_3 solution, but slightly less than the stoichiometric amount of AgNO_3 was added. Many electrodes were constructed in the course of this investigation but the discussion here will be restricted to the three representative electrodes in Table 1. The tabulated moles of Na_2S and Na_2HAsO_4 which were in a volume of about 200 ml and the moles of AgNO_3 which were in a volume of about 800 ml. The pH during the precipitation was monitored and held at about 6-7 by addition of 1 M NaOH. The precipitations were carried out with rapid stirring.

The precipitate was filtered, very thoroughly washed with hot water then with carbon disulfide, acetone, hot water, and dried in an oven at 110°C overnight.

The precipitate was then set in a die with a 13 mm diameter plunger (Harco Industries, Phoenix, Arizona). Approximately 0.6-0.8 grams of the precipitate was heated on a hot plate to 110°C , and then was pressed for various lengths of time. The pressure was typically 6000 lbs/sq. in. as indicated by the gauge on the hydraulic jack. The thickness of the disc used in electrode construction was 0.3-0.8 mm. After the disc was removed from the die, a copper wire was attached to one face using a

TABLE I

IDENTIFICATION OF THREE ELECTRODES

Code	Membrane Material (moles)			pH While Precipitating
	Na_2S	Na_2HAsO_4	AgNO_3	
B ₁	0.06	0.01	0.12	6.2
B ₂	0.06	0.01	0.12	6.2
B ₃	0.02	0.03	0.11	6.8

Figure 1. Model of the Arsenic(V) Selective Electrode

silver-filled epoxy (Cerac, Menomonee Falls, Wisconsin) and cured at 110°C for 8 hours. Silicon rubber adhesive was used to secure the disc to the polished end of a 13 mm pyrex tube. Fig. 1 shows the model of the electrode.

Electrode B₁ was anodized at applied currents from 0.2 to 1.2 mA for 2 to 10 minutes in a solution of 0.2 M Na₂HAsO₄ and 0.1 M KNO₃. The counter electrode was a carbon rod. Electrode B₂, however, was not anodized.

The electrodes were stored at room temperature in distilled water and were thoroughly washed and wiped clean before use.

Potentiometric measurements were made in the conventional manner by using the arsenic-sensitive membrane electrode as the indicator electrode and a saturated calomel electrode (Beckman) as the reference electrode which was separated from the tested solution by a 0.1 M potassium nitrate liquid junction. A Data Precision digital voltmeter (Model 245) was used. A Corning Model 7 pH meter was used to measure the pH. Adjustment of the meter was made with two buffers, pH 6.85 and pH 4.0.

EXPERIMENTAL PROCEDURE

Potentials were measured as a function of arsenic(V) concentration, pH, buffer concentration and arsenic(III) concentration. In all of these measurements, the ionic strength was maintained at 0.1 M by the addition of KNO_3 . The calomel reference electrode was isolated from the test solution by 0.1 M KNO_3 and the liquid junction was made through a porous Vycor plug. All measurements were made at room temperature, 23°-25°C.

It was crucial to determine over what pH range there was no significant change in the potential reading. To achieve this, an experiment was conducted under the conditions of constant arsenic(V) concentration and the pH was changed over the range of 3 to 12 pH units. The change in pH was made by additions of either sodium hydroxide to increase the pH or perchloric acid to decrease the pH; the value was monitored with a pH meter during the measurements. The change of pH was no more than 0.5 pH units for each addition of either acid or base. Results are shown in Figure 2.

To study the electrode response to arsenic(V) ion, various concentrations of test solutions were prepared. A stock solution of 0.1 M arsenic(V) was prepared from Na_2HAsO_4 and then successively diluted down to 10^{-6} M. In all solutions the ionic strength was 0.1 M and a dilute buffer established the pH 9.5. Figure 3 gives the results.

The influence of the phosphate concentration on the electrode response at constant pH was tested by the following procedure; additions of 0.5 ml, 1 ml, 2 ml, 5 ml, 10 ml, 15 ml, 20 ml of 0.05 N potassium dihydrogen phosphate was made to a selected concentration of arsenic(V).

Figure 2. B_1 electrode response as a function of pH for the various concentrations of arsenic(V) solution.

Figure 3. Response of B₁, B₂ arsenic(V) sensitive electrodes vs. arsenic(V) concentration

The pH was kept at 9.0 in this case. The results are given in Figure 4.

An experiment was designed to determine the effect caused by the presence of arsenic(III) on the potentiometric measurements done in arsenic(V) solutions. The experiments were carried out under constant ionic strength and constant pH which was held at 9.00 by using a 10^{-4} M phosphate buffer. Each step of the experiment was carried out with a constant concentration of arsenic(V) ions, the decade ranges covered 10^{-5} M to 10^{-2} M. In each of the solutions additions of arsenic(III) were made over the range from 10^{-6} M to 10^{-3} M. The added volumes were quite small and no significant change in volume resulted. Stock solutions of arsenic(III) were prepared from arsenic trioxide (As_2O_3) analytical reagent (Mallinckrodt Chem. Works) which first was dissolved in sodium hydroxide, and the pH adjusted to 9.0. Figure 5 gives the results.

Generally, all the electrodes reached a stable potential within 2 minutes. For some cases, solutions were stirred by a Teflon covered magnetic bar in the beaker and a magnetic stirrer. The difference between potential reading with stirring and nonstirring was generally observed to be linearly displaced to a lower potential value.

Between measurements, the electrodes were polished by rubbing on fine emery paper, then rinsed thoroughly with distilled water. Anodization of electrode B_1 was done before each series of measurements.

The solubilities of silver arsenate and silver arsenite at controlled pH values were determined from precipitation titrations using a silver ion electrode (Chemtrix, Inc., Type C800Ag) to follow the concentration changes. For these titrations, 50.0 ml of 0.0100 M AgNO_3 was

Figure 4. The Interference of various concentrations of phosphate ion relative to arsenic(V) concentrations of 10^{-6} , 10^{-4} , $10^{-2} M$, at $pH = 9.0$.

Figure 5. The Interference of various concentrations of arsenic(III) ion to arsenic(V) concentrations of 10⁻⁵, 10⁻⁴, 10⁻³, 10⁻² M at pH 9.0.

titrated with a 0.0102 M solution prepared from $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ or with a 0.0199 M solution of H_3AsO_3 prepared from As_2O_3 . During the titrations, the pH was held at 4.5 or 8.0, using 0.1 M NaOH and 0.1 M HClO_4 to adjust the pH. At these pH values, the dominant arsenic(V) species are H_2AsO_4^- and HAsO_4^{2-} , respectively; at pH = 8.0, the arsenic(III) species is H_3AsO_3 . The titration curves are shown in Figures 6 and 7.

Figure 6. Potentiometric titration of 50.0 ml 0.0100 M AgNO₃ with 0.0102 M Na₂HAsO₄ at pH = 8.0 and pH = 4.5, using a silver ion selective electrode.

Figure 7. Potentiometric titration of 50.0 ml 0.0100 M AgNO₃ with 0.0199 M H₃AsO₃ at pH 8.0 using a silver ion selective electrode

DISCUSSION OF RESULTS

Measurements of Solubility Products

Solubility products and the molecular formulas of silver arsenate and silver arsenite were determined from the titration curves shown in Figures 6 and 7. The millimole of 0.0102 M arsenic(V) is one-third the millimole of 0.0100 M silver(I) at pH = 8 and nearly the same fraction at pH = 4.5. Therefore the mole ratios clearly indicate that the precipitate is Ag_3AsO_4 , even though the dominant arsenic species is HAsO_4^- at pH = 8 and H_2AsO_4^- at pH = 4.5. The same considerations reveal that the formula of the silver arsenite precipitate is Ag_3AsO_3 at pH = 8.0, since the millimole of 0.0199 M arsenic(III) was one-third of the millimole of 0.0100 M silver(I). The dominant species is H_3AsO_3 at pH = 8.0.

Calculations of the solubility products were based on the silver(I) concentration at the calculated equivalence point. The silver(I) concentration was determined by comparing the initial potential of the titration with the equivalence point potential using the Nernst equation:

$$E = k + 2.3 \frac{RT}{nF} \log [\text{Ag}^+] \quad 1$$

at the temperature of the titration 23°C, the coefficient of the log term is 0.059 v. The term k is a constant for a given silver electrode and reference electrode.

At the beginning of the titration the potential E_i is given by

$$E_i = k + 0.059 \log [\text{Ag}^+]_i \quad 2$$

At the equivalence point of the titration the potential E_{eq} is given by

$$E_{eq} = k + 0.059 \log [\text{Ag}^+]_{eq} \quad 3$$

Subtracting the equation 2 from equation 3 gives

$$E_{eq} - E_i = 0.059 \log \frac{[Ag^+]_{eq}}{[Ag^+]_i} \quad 4$$

Using the data from Figures 6 and 7, $[Ag^+]_{eq}$ was calculated from equation 4 and the results are given in Table II.

The titration reaction of arsenic(V) and silver(I) at pH = 8.0 is

and at the equivalence point, the concentration of arsenic(V) is $1/3 [Ag^+]_{eq}$, or $[HAsO_4^{-2}] = 1.47 \times 10^{-5} M$, since $HAsO_4^{-2}$ is the dominant species at pH = 8.0. The equilibrium constant for this reaction, written as an apparent solubility product, K_{sp}' , is

$$K_{sp}' = \frac{[Ag^+]^3 [HAsO_4^{-2}]}{[H^+]}$$

but the dissociation constant for $HAsO_4^{-2}$ is

$$K_3 = \frac{[AsO_4^{-3}] [H^+]}{[HAsO_4^{-2}]} = 3.95 \times 10^{-12}$$

The three dissociation constants for the arsenic acid are given in Table III. So the solubility product for Ag_3AsO_4 , K_{sp} is given by

$$K_{sp} = K_{sp}' K_3$$

The calculated value is given in Table II and may be compared with the literature value of 1.08×10^{-22} at 20°C(20).

At pH = 4.5, the titration reaction is

In a similar manner, the apparent solubility product for this reaction is given by

$$K_{sp}'' = \frac{[Ag^+]^3 [H_2AsO_4^{-}]}{[H^+]^2}$$

TABLE II

SOLUBILITY PRODUCTS OF SILVER ARSENATE AND SILVER ARSENITE
FROM POTENTIOMETRIC TITRATIONS

Titrant	pH	E _i mv	E _{eq} mv	[Ag ⁺] _i	[Ag ⁺] _{eq}	[As(V)] _{eq}	K _{sp} [*]	Solid Phase
HAsO ₄ ⁼	8.0	463	324	0.0100 M	4.41 x 10 ⁻⁵	1.47 x 10 ⁻⁵ M	5.0 x 10 ⁻²²	Ag ₃ AsO ₄
H ₂ AsO ₄ ⁻	4.5	460	396	0.0100 M	8.23 x 10 ⁻⁴	2.74 x 10 ⁻⁴ M	1.0 x 10 ⁻²²	Ag ₃ AsO ₄
H ₃ AsO ₃	8.0	466	310	0.0100 M	2.27 x 10 ⁻⁵	7.6 x 10 ⁻⁶ M	5.3 x 10 ⁻¹³	Ag ₃ AsO ₃

* Solubility product at an ionic strength about 0.1 M for the reactions:

TABLE III

DISSOCIATION CONSTANTS OF INORGANIC ACIDS
IN AQUEOUS SOLUTIONS

Acid	T°C	Step	K	pK	Reference
Arsenic acid	25°C	1	5.62×10^{-3}	2.25	(21)
Arsenic acid	25°C	2	1.70×10^{-7}	6.77	(21)
Arsenic acid	25°C	3	3.95×10^{-12}	11.60	(21)
Arsenious acid	25°C	1	6×10^{-10}	9.23	(21)
Arsenious acid	25°C	2	3×10^{-14}	13.5	
Phosphoric acid	25°C	1	7.52×10^{-3}	2.12	(22)
Phosphoric acid	25°C	2	6.23×10^{-8}	7.20	(22)
Phosphoric acid	25°C	3	2.2×10^{-13}	12.4	(22)

Since the dominant arsenic species is H_2AsO_4^- , its concentration at the equivalence point is $1/3 [\text{Ag}^+]_{\text{eq}}$ or 2.74×10^{-4} M. Including the second dissociation step of arsenic acid, $K_2 = 1.70 \times 10^{-7}$ (Table III) gives

$$K_{\text{sp}} = K_{\text{sp}}'' K_2 K_3$$

This value of K_{sp} 1.0×10^{-22} , listed in Table II agrees better with the literature value, but the titration curve is not very good.

Silver arsenite at $\text{pH} = 8.0$ dissolves according to the reverse of the titration reaction

However, arsenious acid is very weak and the third dissociation constant has not been measured. For the first dissociation, $K_1 = 6.0 \times 10^{-10}$ and for the second, $K_2 = 3 \times 10^{-14}$. Since it is not possible to obtain a solubility product which is independent of pH , the constant has been calculated for

Using the same equation as before, the calculation of the solubility product follows from the data of the titration curve and $K_{\text{sp}} = K_{\text{sp}}' K_1$. The result is given in Table II. Although this solubility product is considerably larger than the constant for Ag_3AsO_4 , the concentration of silver(I) is smaller at a given pH due to the protons in the reaction involving arsenite.

Optimum pH for Arsenic(V) Response

The measurements of potential over the pH range of 2.5 to 12 reveals not only the optimum pH range but also several important characteristics of the electrode. In Figure 2, electrode B₁ has a plateau in potential from pH values of 6 to 9; the plateau is very distinct at low

arsenic(V) concentrations but with time at 10^{-2} M arsenic(V) the curve became rather steep. Since electrode B₁ was not anodized just before these measurements, the behavior is the same as that of B₂. The plateau suggests that the electrode responds to the ion HAsO_4^{--} since this is the dominant species over this pH range. Theoretical plots are given in Figure 2 for this case and for the case where the response is due to AsO_4^{-3} , the derivation of the equations for these curves is in the Appendix. It is evident that the experimental curves agree well with the slope of the theoretical curve for HAsO_4^{-2} up to pH 9, but then beyond this pH the agreement is with the theoretical curve for AsO_4^{-3} . Since these measurements were made from low to high pH values it appears that the electrode contained initially Ag_2HAsO_4 which was converted to Ag_3AsO_4 in alkaline solutions. It would be expected that the conversion would be time and concentration dependent and this is why the curve in Figure 2 for 10^{-2} M arsenic(V) does not have a distinct plateau. Also, if the pH was decreased during these measurements, the potentials were not reproducible but were lower. Such hysteresis clearly is due to a change in the electrode.

When electrode B₁ was anodized in an arsenic(V) solution, and then used to determine the effect of pH, the curve, as shown in Figure 2, agreed in shape with the theoretical plot for response to the AsO_4^{-3} ion. It is expected that Ag_3AsO_4 forms on the electrode surface during anodization since this is the only compound that was found in the potentiometric titration curves regardless of pH (see Figure 6). It remains then, to explain why electrodes of the composition used for B₁ and B₂ responded initially to the ion HAsO_4^{-2} . The most direct reason

Figure 8. Response of B₂, B₃ electrodes vs. arsenic concentration.

— = experiments done before exposure to solutions of pH 12.
 --- = similar experiments done later.
 Two electrodes were used, B₂ and B₃

is that this ion is preferentially incorporated into the Ag_2S lattice during the coprecipitation because the ionic charge is the same as that of sulfide ion. With time and exposure to alkaline solutions, the Ag_2HASO_4 is converted to Ag_3AsO_4 because the latter is much more insoluble.

Composition of the Membrane

Figure 8 indicates a marked change in the potential response to the arsenic(V) concentration of B_2 and B_3 electrodes after exposure to solutions of pH 12 and arsenic(V) concentration of 10^{-2} M. It is observed that there were almost no potential response for both electrodes whereas before, the potential changes were normal. This is an extreme case and can be explained by the formation on the electrode surface of a heavy Ag_3AsO_4 layer which is a non-ionic conductor. Similar results also were obtained when electrode B_1 was anodized for a long time. These observations agree with the preceeding conclusions that the electrodes undergo changes with time under certain conditions.

Notice that in Figure 8, the slopes of the measurements before contact with high pH solutions indicate that Ag_2HASO_4 and Ag_3AsO_4 were initially present on the surface of electrodes B_2 and B_3 , respectively, since the slopes are approximately 30 and 20 mv./decade. These conclusions are arrived at by use of the Nersnt equation:

$$E = k - 0.059/m \log [\text{As(V)}]$$

The slopes stated above are equal to $0.059/m$, where m is the mole ratio of silver to arsenate(V) in the solid. So for electrode B_2 , the value of m must be 2 and for B_3 the value of m must be 3. The composition of these two electrodes is given in Table 1; B_2 contains no more than 16 mole percent of arsenate and B_3 contains about 60 mole percent of

arsenate. In the precipitation process, HAsO_4^{-2} was apparently incorporated into the crystal lattices of Ag_2S when the latter was in excess. However, when the arsenate was in excess, it is quite reasonable to assume that Ag_3AsO_4 formed as a separate phase mixed with Ag_2S .

In the formation of the membrane materials, it is preferable to lower the pH below 10 to avoid Ag_2O formation. Ag_2O is an electronic conductor and the electrodes should be only ionic conductors. The presence of Ag_2O gives poor selectivity and sluggish electrode potential response to arsenic(V) solutions.

Effect of Anodizing Currents and Anodizing Times

Since silver arsenate can be dissolved out of the membrane surface with time, especially at low pH values, attempts were made to reform silver arsenate on the electrode surface by anodizing in a solution of 0.2 M Na_2HAsO_4 . To improve solution conductivity, KNO_3 was added.

Different anodizing times and currents were tried in the anodization of the electrodes. There was no large change in potential as long as the time and current were kept within several minutes and between 0.2 to 1.2 mA. Anodizing the electrode served to build a thin silver arsenate layer on Ag_3AsO_4 on the surface of the electrode membrane. Silver ions are mobile and move through the silver sulfide. At the membrane surface silver arsenate formed by reaction of silver ions with arsenate from the solution. If the matrix was anodized too long, the Ag_3AsO_4 layer became too thick and acted as an insulator resulting in non-nernstian behavior. When a large current was used to anodize the electrode, the Ag_3AsO_4 layer adsorbed irregularly, resulting in a poorly

amorphous appearing layer which also gave non-nerstian behavior.

It was found experimentally that a new electrode surface could be obtained by dipping the electrode in perchloric acid. Good results were obtained when the electrode was allowed to stand in dilute perchloric acid for approximately 15 minutes. While perchloric acid is necessary whenever adsorbed ions are to be removed, distilled water is sufficient for routine washing.

Concentration Range of Arsenic(V) for Useful Response

An experiment was designed to determine over what range of arsenic(V) concentrations the electrodes would be useful. Two calibration curves of arsenic(V) sensitive electrodes are shown in Figure 3. Both of the electrodes have been pressed from the same precipitate. The electrode identified as B₁ was anodized with a current 400 μ A for 5 minutes while the electrode B₂ was not. Nernstian response for both electrodes was obtained over a range extending from 10^{-5} M to 10^{-2} M. The average slopes of the curves were calculated to be 27.5 and 16.3 per decade change in arsenic(V) concentration for the electrodes B₂ and B₁, respectively. Concentrations below 10^{-5} M arsenic(V) are below the detection limits of the electrodes and the constant potential response is indicated by a plateau seen in both calibration curves.

Interference due to Various Ions

Nernstian response in an arsenic(V) membrane device requires that the membrane be in equilibrium with only the arsenate ion in the sample solution. This will not be the case if there are interfering species present in the sample solution which can react with the components of

the membrane. The most common type of reaction involves an ion in the sample solution which also forms an insoluble silver salt. Phosphate ion, for example, can interfere with arsenic(V) measurements if the reaction

takes place.

This reaction will not proceed to the right unless the ratio of the phosphate ion activity to the arsenate ion activity exceeds a value given by the ratio of the solubility products of silver phosphate to silver arsenate, assuming that the activity ratio of the two solids is constant.

Pungor has given a generalized equation(23), which for a bromide electrode in the presence of several anions (including bromide) takes the form:

$$E = \text{constant} - \left(\frac{RT}{F}\right) \ln \left[A_{\text{Br}} + \sum_i K_{\text{Br-i}} \left(\frac{A_i}{A_{\text{Br}}} \right) \right]$$

where A_{Br} , A_i are the bromide and anion activity and $K_{\text{Br-i}}$ is the selectivity constant.

For the arsenic(V) sensitive electrodes in the presence of interfering ions X^{-m} , we can rewrite this equation as follows:

$$E = \text{constant} - \left(\frac{RT}{mF}\right) \ln (A_{\text{As}} + K_{\text{As-X}} A_X)$$

and the selectivity constant is interpreted in terms of the equilibrium constant for the exchange process

Usually, the activity ratio of the solid phase is assumed to be unity. Multiplying the numerator and denominator by $(\text{Ag}^+)^3$, the selectivity constant becomes

$$K_{\text{As-X}} = \frac{(\text{Ag}^+)^3 (\text{AsO}_4^{-3})}{(\text{Ag}^+)^3 (\text{X}^{-m})^{3/m}} = \frac{(K_{\text{sp}})_{\text{As}}}{(K_{\text{sp}})_{\text{X}}^{3/m}}$$

where $(K_{\text{sp}})_{\text{X}} = (\text{Ag}^+)^m (\text{X}^{-m})$ and m may be 1, 2, 3,

From this general equation, approximate values of the selectivity constant can be calculated; values for some common ions are listed in Table IV. If the ion X^{-m} is protonated at the pH of the measurement, the apparent solubility product must be used in the above equation. Also, if the arsenic(V) species is not as written, a similar correction is necessary.

For the same arsenic(V) concentration, but different concentrations of the interfering ions X^{-m} , one equation may be obtained as follows:

$$E_1 - E_2 = \frac{0.059}{3} \log \frac{[\text{As(V)}] + K_{\text{As-X}}[\text{X}^{-m}]_1}{[\text{As(V)}] + K_{\text{As-X}}[\text{X}^{-m}]_2}$$

where E_1 and $[\text{X}^{-m}]_1$ are the potential and ion concentration at condition 1 and

E_2 and $[\text{X}^{-m}]_2$ are the potential and ion concentration at condition 2.

Since the ionic strength of the solution was kept constant, the ion concentration was used instead of ion activity. Then the selectivity constant can be calculated by means of the following expression:

$$\frac{[\text{As(V)}] + K_{\text{As-X}}[\text{X}^{-m}]_1}{[\text{As(V)}] + K_{\text{As-X}}[\text{X}^{-m}]_2} = 10^{\frac{-(E_1 - E_2)}{0.02}}$$

The experimental data and selectivity constants are listed in Table V.

TABLE IV

SELECTIVITY CONSTANT FOR VARIOUS IONS AT pH = 9.0

$$K_{As-X} = \frac{(K_{sp})_{As}}{(K_{sp})_X^{3/m}}$$

Ion X^{-m}	Solubility Product of Ag_mX	Selectivity Constant K_{As-X}
PO_4^{-3}	Ag_3PO_4 1.3×10^{-20}	4.3×10^{-4}
$As(III)$	Ag_3AsO_3 5.3×10^{-13}	1.8×10^1
Br^-	$AgBr$ 7.7×10^{-13}	5.5×10^{25}
Cl^-	$AgCl$ 1.56×10^{-10}	6.7×10^{18}
I^-	AgI 1.5×10^{-16}	7.5×10^{34}

TABLE V

DATA AND SELECTIVITY CONSTANTS FROM THE EXPERIMENTS OF
PHOSPHATE AND ARSENIC(III) INTERFERENCE

Arsenic(V) Concentration	Phosphate $[PO_4^{-3}]_1$ Concentration	Phosphate $[PO_4^{-3}]_2$ Concentration	E_1 mv	E_2 mv	K _{sc}
10^{-6}	2.0×10^{-4}	8.3×10^{-3}	274.5	255.5	1.22×10^{-3}
10^{-4}	2.0×10^{-4}	8.3×10^{-3}	261.8	252.2	2.63×10^{-2}
10^{-2}	2.0×10^{-4}	8.3×10^{-3}	232.0	233.5	0
Arsenic(V) Concentration	Arsenic(III) $[As(III)]_1$ Concentration	Arsenic(III) $[As(III)]_2$ Concentration	E_1 mv	E_2 mv	K _{sc}
10^{-5}	10^{-6}	10^{-3}	258	201	2.42×10^1
10^{-4}	10^{-6}	10^{-3}	242.5	201	1.34×10^1
10^{-3}	10^{-6}	10^{-3}	229	199	3.16×10^1
10^{-2}	10^{-6}	10^{-3}	216.5	192.5	1.50×10^{-2}

The selectivity constant is an approximate number which can be used only to estimate orders of magnitude of interference to be expected in a given case. It cannot be used to make corrections to electrode readings obtained in solutions which are contaminated with the interfering ions(24).

It is found both by experiments and theory that the arsenic(III) ion has an appreciable effect on the potential measurements. So, it is necessary to oxidize all the arsenic(III) to arsenic(V) before doing the measurements in order to get a meaningful result.

SUMMARY

An arsenic(V) selective electrode was developed by preparing the coprecipitate of silver sulfide and silver arsenate and pressing it into a thin membrane. From measurements of the response electrode as a function of membrane composition, arsenic(V) concentration and pH it was found that the electrode potential is dependent upon either HAsO_4^{-2} or AsO_4^{-3} . The electrodes prepared with an excess of silver sulfide responded initially to HAsO_4^{-2} but after being in contact with the solution of pH about 8 or higher became responsive to AsO_4^{-3} . This is explained by the Ag_2HAsO_4 in the membrane being converted to the more insoluble Ag_3AsO_4 on the electrode surface. The same effect could be accomplished by anodizing the electrode in a solution of arsenic(V) at pH 8. Electrodes prepared with an excess of silver arsenate showed initially response to AsO_4^{-3} since the form of the silver arsenate in the membrane was Ag_3AsO_4 .

Calibration curves of potential as a function of arsenic(V) concentration under optimum conditions reveal that the electrodes can be used to measure concentrations as low as 10^{-5} M (750 ppb).

Interferences due to arsenic(III) and phosphate were measured since these ions are often found with arsenic(V). The selectivity constants of the electrode for arsenic(V) in the presence of these two ions were 2.3×10^1 and 1.4×10^{-2} , respectively. So the concentration of arsenite must be kept less than 1/20 th the arsenate concentration in order to avoid interference by arsenic(III). Phosphate interferences are less of a problem and concentrations even ten times greater than the arsenic(V) concentration produce little error.

From the low solubility of silver arsenite at high pH values, it is apparent that an ion selective electrode could be made for arsenic(III) and that interferences due to arsenic(V) would be less than the converse situation above.

It may be concluded that optimum performance and stability of an arsenate-sensitive electrode would require having a high mole ratio of silver arsenate to silver sulfide. However, such a ratio also causes a decrease in the ionic conductivity of the membrane. Exactly where the compromise ratio is could be established by future experiments of the type used in this work.

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APPENDIX

For the arsenic(V) sensitive electrode, assuming that the precipitate form in the membrane is Ag_2HAsO_4 , the mass balance of arsenic(V) is

$$\begin{aligned} [\text{As(V)}] &= [\text{H}_3\text{AsO}_4] + [\text{H}_2\text{AsO}_4^-] + [\text{HAsO}_4^{-2}] + [\text{AsO}_4^{-3}] \\ &= \frac{[\text{HAsO}_4^{-2}][\text{H}^+]^2}{K_1K_2} + \frac{[\text{HAsO}_4^{-2}][\text{H}^+]}{K_2} + [\text{HAsO}_4^{-2}] + \frac{[\text{HAsO}_4^{-2}]K_3}{[\text{H}^+]} \\ &= [\text{HAsO}_4^{-2}] \left[\frac{[\text{H}^+]^2}{K_1K_2} + \frac{[\text{H}^+]}{K_2} + 1 + \frac{K_3}{[\text{H}^+]} \right] \end{aligned}$$

$$\text{If } \alpha = \frac{[\text{H}^+]^2}{K_1K_2} + \frac{[\text{H}^+]}{K_2} + 1 + \frac{K_3}{[\text{H}^+]}$$

$$\text{By rearranging } \frac{[\text{HAsO}_4^{-2}]}{[\text{As(V)}]} = \frac{1}{\alpha} \quad 5$$

The silver electrode potential is given as

$$E = \text{constant} + 0.059 \log [\text{Ag}^+] \quad 6$$

$$\text{Since } [\text{Ag}^+] = \frac{K_{sp}}{[\text{HAsO}_4^{-2}]}^{\frac{1}{2}} \quad 7$$

where K_{sp} = solubility product of Ag_2HAsO_4 .

By substitution of 7 into the potential expression 6 we get the potential for the arsenic(V) sensitive electrode as follows:

$$E = \text{constant} - \frac{0.059}{2} \log \frac{[\text{HAsO}_4^{-2}]}{K_{sp}} \quad 8$$

$$\text{Since } [\text{HAsO}_4^{-2}] = \frac{[\text{As(V)}]}{\alpha}$$

$$E = \text{constant} - \frac{0.059}{2} \log \frac{[\text{As(V)}]}{K_{sp} \cdot \alpha}$$

$$= \text{constant} - 0.0295 \log [\text{As(V)}] + 0.0295 \log K_{sp}$$

$$+ 0.0295 \log \alpha$$

Since $[\text{As(V)}]$ and K_{sp} are constants, all the constant terms may be expressed as k'

$$E = k' + 0.0295 \log \alpha$$

The values of E were calculated from equation 9 over the full pH range and are plotted in Figure 2. The constant value was adjusted in order to coincide with the experimental curve over pH = 7-9.

Based on the precipitate Ag_3AsO_4 , the mass balance of arsenic(V) is $[\text{As(V)}] = [\text{H}_3\text{AsO}_4] + [\text{H}_2\text{AsO}_4^-] + [\text{HASO}_4^{-2}] + [\text{AsO}_4^{-3}]$

$$\begin{aligned} &= \frac{[\text{H}^+]^3 [\text{AsO}_4^{-3}]}{K_1 K_2 K_3} + \frac{[\text{H}^+]^2 [\text{AsO}_4^{-3}]}{K_2 K_3} + \frac{[\text{H}^+] [\text{AsO}_4^{-3}]}{K_3} + [\text{AsO}_4^{-3}] \\ &= [\text{AsO}_4^{-3}] \left(\frac{[\text{H}^+]^3}{K_1 K_2 K_3} + \frac{[\text{H}^+]^2}{K_2 K_3} + \frac{[\text{H}^+]}{K_3} + 1 \right) \end{aligned}$$

$$\text{if } \frac{[\text{H}^+]^3}{K_1 K_2 K_3} + \frac{[\text{H}^+]^2}{K_2 K_3} + \frac{[\text{H}^+]}{K_3} + 1 = \beta \frac{[\text{AsO}_4^{-3}]}{[\text{As(V)}]} \quad \frac{1}{\beta}$$

$$\text{Since } [\text{Ag}^+] = \left(\frac{K_{sp}}{[\text{AsO}_4^{-3}]} \right)^{1/3} \quad 10$$

where K_{sp} = solubility product of Ag_3AsO_4

By substitution of 10 into the equation 6 we get the potential for the arsenic(V) sensitive electrode based on Ag_3AsO_4 as follows:

$$E = \text{constant} - \frac{0.059}{3} \log \frac{[\text{AsO}_4^{-3}]}{K_{sp}}$$

$$\text{since } [\text{AsO}_4^{-3}] = \frac{[\text{As(V)}]}{\beta}$$

$$E = \text{constant} - \frac{0.059}{3} \log \frac{[\text{As(V)}]}{K_{sp} \cdot \beta}$$

since $[\text{As(V)}]$, K_{sp} Ag_3AsO_4 are constants,

$$\text{we get } E = k'' + 0.02 \log \beta \quad 11$$

The values of E were calculated from equation 11 over the pH range 3 to 12 and plotted in Figure 2. The constant value was adjusted in order

to coincide with the experimental curve over $\text{pH} = 9$ to 12.