THE POTENTIOMETRIC DETERMINATION OF PHOSPHATE

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THE POTENTIOMETRIC DETERMINATION
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PREFACE

This thesis reports the results of an investigation into possible methods for the determination of the phosphate ion using ion-specific electrodes. Several types of electrodes were constructed and evaluated. A bismuth billet electrode was developed for use as an end-point detector in the potentiometric titration of phosphate ion with bismuth nitrate solution. A bismuth amalgam electrode was constructed and utilized in the direct potentiometric determination of phosphate ion.

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CHAPTER I

INTRODUCTION

The thesis which this paper proposes to establish is that it is possible to determine inorganic orthophosphate in water solution under specified conditions by the use of an ion-selective electrode. The relevance of the work can best be evaluated against a background of the need to determine phosphate ion and the difficulties which are inherent in this determination.

The current and rising interest in air and water pollution, including its identification, the determination of its effect on the environment, and the evaluation of control methods and standards, has brought into sharp focus the need for a rapid and reliable method for phosphate determination.

Phosphate is a necessary plant food. It is available in soil to a limited degree, and is often added in relatively large amounts in commercial fertilizers. In recent years, the use of these commercial fertilizers has expanded in both scope and volume to the point where run-off from fields is carrying increasing amounts of the fertilizer, including phosphate, into the streams and lakes of the nation. In the water it continues to serve as a fertilizer, stimulating the growth of water plants, both large and small. This results in the excessive growth of algae, leading to the development of green scum on recreational waters and objectionable taste and odor in drinking water supplies. The ecological balance of the streams and lakes is also disturbed, with long range detrimental effects on all the wildlife in the area. In addition to the phosphate which enters streams and lakes from over-fertilized fields, an additional amount of phosphate enters these bodies of water from industrial wastes and from sewage waters. Most of the phosphate in waste water came originally from detergents.

An example of the need to determine phosphate in environmental water is found in a study now in progress at this university. Keystone Reservoir, near Tulsa, is being studied and, as a part of this study, it is desirable to monitor the concentration of various ions, including phosphate, by remote sensing. The output of the sensors could be recorded for evaluation in the computer center. Such sensors exist for several ions. If one were available for phosphate, it would find immediate use by research teams, ecologists, and industrial and governmental laboratories.

With such demand existing, the question arises why the problem has not already been studied. The answer, of course, is that it has been and is being studied but, thus far, without very much success. The literature review identifies some of these studies, and others often appear in the rumors and shop-talk at conventions of chemists. James

Ross, of Orion Research, has affirmed his company's active interest in a phosphate sensitive electrode, and the grapevine indicates that researchers at a southern university are working on an enzyme electrode that may be sensitive to phosphate. Published results of this work are not yet available.

The reasons why all this interest and activity have not brought more satisfactory results can be found in the nature of phosphate salts. In an orthophosphate system, the species containing the phosphorus is PO_4^{-3} , HPO_4^{-2} , $H_2PO_4^{-1}$, and the phosphoric acid molecule, H_3PO_4 . The distribution of these species in a solution is a function, primarily, of the hydrogen ion concentration. This means that the investigator is dealing with a material which is present in four different forms at the same time, and which readily shifts from one form to another in response to the varying acidity of the solution. Each of these species carries a different charge, or no charge at all, which makes it impossible for a single electrode to be reliably responsive to all of them. Any method which senses one of these species must necessarily also include careful pH control, since the concentration of the species being sensed is pH dependent. The size and charge of these species combine to cause low mobility relative to most other common ions. The continued activity and interest in this study, even in the face of these discouraging conditions, is evidence of the need for a better method for phosphate determination. This thesis is reporting progress toward that goal.

Chapter II surveys the literature in the areas related to the study. These areas include other methods of phosphate determination, and the theory and applications of ion-selective electrodes in general.

Chapter III describes the theoretical considerations which were dominant in setting the direction of, and the limitations upon, the experimental design.

Chapter IV describes the experimental activity in detail, including intermediate results which led to further changes in experimental design.

Chapter V reviews the more significant results, discusses their implications, and draws conclusions with regard to the originally stated thesis.

The Appendix consists of a paper, based on this dissertation, which is being submitted for publication.

CHAPTER II

SURVEY OF THE LITERATURE

Various Methods for Phosphate Analysis

The time and effort required for the determination of phosphorus as phosphate, together with an increasing demand for this type of determination, has led to the development of a great variety of methods.

The classical ammonium phosphomolybdate method is the one which is usually described in texts on quantitative analysis (17)(22)(26) and is one of the official methods of the Assocaition of Official Agricultural Chemists (18). This method has been modified from gravimetric to volumetric to reduce the time of analysis (48)(19)(49), but it is still very time consuming and has a definite tendency to yield high results (24)(27). A magnesia method has been described which improves accuracy, but it is very time consuming (15)(25). A closely related method is based on the precipitation of phosphate by quinolinium molybdate (35). This results in great accuracy and has been recommended as a referee method for international trade (4), but it is also very slow.

An increase in speed was attained with the development of the molybdovanate method (30)(21)(23), a colorimetric procedure which compares favorably with the ammonium phosphomolybdate method for accuracy (12)(44), and is applicable to very low concentrations of phosphorus (1). Another indirect colorimetric method using lanthanum chloranilate has been described (20).

The extremely low solubility of bismuth phosphate has led several workers to try to develop methods utilizing bismuth. One method (46)(9) determined the precipitated bismuth polarigraphically, and another (16) titrated the excess bismuth with EDTA. Both of these methods suffered from many interferences.

A potentiometric method was developed in which phosphate was precipitated by silver ion in a buffer at pH 9 and the end-point was determined with a silver electrode (13)(7)(31). This was used effectively in the standardization of biological solutions, but suffered many interferences. An indirect potentiometric method has been reported which uses ion-exchange techniques to convert phosphate salts to phosphoric acid which is then titrated at at constant ionic strength with standard base between two previously determined pH values (29). This method was successfully applied to the rapid determination of phosphate in commercial fertilizer, but it is less useful for small concentrations of phosphate.

Current Status of Ion-Selective Electrodes

The recent development and application of several types of specific-ion electrodes encourages the hope that it might be possible to use one of these types for phosphate determination. The theory, design, and current applications of specific-ion electrodes to 1969 is well reviewed and summarized in the report of a State-of-the-Art Symposium on the subject of Ion-Selective Electrodes conducted by the National Bureau of Standards (10). The Newsletter, published by Orion Research, also reports the current progress in this field, and G. A. Rechnitz and his co-workers at the State University of New York are actively involved in the evaluation and application of these electrodes (39)(41).

A thorough study of ion-selective electrodes in general is beyond the scope of this paper, but it will be useful to review the fundamental concepts upon which potentiometric determinations are based, and to summarize the parameters which control the application of these methods to the determination of phosphate.

Electrodes of the First Class.

Three general categories of ion-selective electrodes are recognized. Electrodes of the first class consist of half-cells formed when a metal is placed in contact with a solution of its ions. The difference in chemical potential between the metal and the ions in the solution causes an electrical potential difference which is a function of the concentration of the ions in the solution, $[M^{n+}]$.

This relationship is expressed by the Nernst Equation:

$$E = E^{\circ} - (0.059/n) \log \left[M^{n+}\right] \qquad (1)$$

In actual practice, of course, measuring the potential of a half-cell requires the addition of another half-cell to serve as the reference electrode. The only requirement for this reference electrode is that its potential be stable, and that it not affect or be affected by the solution being measured. When the cell has been completed by the addition of a reference electrode, the measured cell potential is a function of the potential of the metal electrode, the potential of the reference electrode, the sum of the junction potentials formed when the cell is assembled, and the internal resistance of the cell. Also, since the metal electrode is sensitive to the activity of the metal ion rather than to its concentration, the total cell potential is a function of the ionic strength of the solution. It would be very difficult to calculate accurately the value of each of these parameters each time the indicator electrode is used. Fortunately, such calculations are not necessary; it is sufficient that all of these variables except one be held constant, causing variations in the cell potential to depend only on the parameter that is being permitted to vary. If this parameter is the concentration of the metal ion, then equation (1) assumes the form:

$$E_c = E_r - (0.059/n) \log \left[M^{n+}\right] \qquad (2)$$

In this equation, E_c is the measured cell potential, and E_r is the effective potential of the reference electrode in the cell, including effects of junction potentials, internal resistance, and the ionic strength. Under these conditions, the cell potential is a logarithmic function of the metal ion concentration and a plot of the measured cell potential versus the logarithm of the metal ion concentration is a straight line. Usually the term labeled E_r is substantially different from the theoretical half-cell potential of the reference electrode, since it includes several other effects, so it is better simply to call it a constant, K, which is characteristic of the experimental conditions in which the cell is used. If the response of the indicator electrode is truly Nernstian, and if the experimental temperature is 25° C, the slope of the line will be 59/n millivolts per decade concentration of metal ion. This shows that the sensitivity of an electrode for monovalent ions is twice as great as for divalent ions and is three times as great as for trivalent ions. Sometimes the electrode response is more complex than the ideal case described here, causing the slope of the plotted line to differ from that predicted. However, the response usually is still useful as a standardization curve (40). It is not uncommon to find that the value of "K" is also something less than perfectly constant, particularly near the limit of sensitivity, causing the plot to vary from a straight line. If the plot is used as a calibration or standardization curve, however, even parts of this non-linear portion can be used (43).

Electrodes of the Second Class.

The second category of electrodes is very similar to the one just described, except that it consists of a metal coated with a slightly soluble salt of that metal. The potential of a cell containing such an electrode is a function of the activity of the anion of the salt. The range of the electrode is limited by the solubility of the salt. The necessity for maintaining a uniform coating of salt on the metal causes many problems if the electrode is used in solutions of widely varying composition. Electrodes of this type, such as silver-silver chloride and calomel electrodes, are more commonly used as reference electrodes than as indicator electrodes.

Membrane Electrodes.

The third category of electrodes includes all of the membrane electrodes. These can vary all the way from simple non-selective membranes which indicate only total differences in ion concentration or mobility to highly selective membranes of glass or crystal whose potential is far more sensitive to certain ions than to others.

For a membrane to be useful as an electrode, it must have sufficient resistance to the passage of electricity to allow the development of a measurable potential between the solutions, but it must not offer so much resistance that it effectively opens the electrical circuit of the cell. It must, furthermore, allow this very limited current to flow by selectively permitting the passage of certain ions and blocking others. Ideally, one would like a membrane which allows passage of only one kind of ion and completely blocks all others, but such a condition is, st best, only approximated.

Membrane electrodes may be divided into four categories, depending upon the nature of the membrane. These are the solid ion-exchangers, liquid ion-exchangers, solid state, or "crystal", membranes, and the heterogeneous membranes.

Solid ion-exchange membranes. These membranes are characterized by having sites which are relatively fixed. The ion being determined moves from site to site through the membrane. Eisenman (11) has described the basic principle by which this type of electrode functions, using the glass electrode as an example. He has also developed in some detail the two principal parameters which affect the electrode's sensitivity. The parameters are the ion-exchange equilibrium constant and the mobility of the ion in the membrane. Bates (2) has also described in great detail the theory and use of the glass electrode for pH determination.

Liquid ion-exchange membranes. These membranes differ from the solid variety in that the sites themselves are mobile. The selectivity of the membrane rests in its ability to accept or reject ions at the interface between the solution and the ion-exchanger. These ion-exchangers are typically high-molecular-weight organic compounds with low dielectric constants. As such, they have low volatility and very low solubility in the aqueous solutions with which they will be used. Ross (43) has described the construction and mechanism of this type of electrode, and lists eight different examples of liquid membrane systems together with many of their selectivity constants. The Orion Calcium Ion Electrode is the best known example of this category.

Solid state membrane electrodes. Also known as crystal membrane electrodes, the members of this category are characterized by a membrane which consists of a thin sheet of a crystalline material having the property of conducting an electric current at room temperature. Usually only one of the ions in the crystal lattice is mobile enough to be involved in the conduction, and this is normally the one that is smaller in radius and charge. If the crystalline material is mechanically stable, inert in the sample solution, and relatively insoluble, it can be ef fective and selective as an electrode. Conduction through a crystal is by a lattice defect mechanism, causing this type of electrode to be very selective in the ions which can be mobile within the crystal. Ross(43) describes typical electrodes of this type and lists ten of them, together with their principal interferences. At the present time, the only suitable crystals for this type of electrode are the lanthanum halides and various silver salts; nearly all other crystals exhibit too little ion conductivity. Ross (43) predicts that only small univalent ions can have sufficient mobility in a solid crystal to be utilized in this type of electrode. The fluoride-ion selective electrode containing a lanthanum fluoride crystal membrane is an outstanding example of this category.

Heterogeneous membrane electrodes. The membrane in this type of electrode actually consists of two phases; it is composed of small particles of inert material embedded in an inert matrix. Many different types of particles have been used for these electrodes, but the ones most commonly used are ion-exchange resins and slightly soluble salts. Covington (8) has reviewed the history of the development of this type of electrode and summarized the construction, applications, and limitations of typical useful examples. Membranes of this type were evaluated for their possible value as phosphate indicators, as a part of this present work, and the details and results are described in Chapter IV.

CHAPTER III

THEORETICAL CONSIDERATIONS AND LIMITATIONS

In planning this investigation, consideration was given to several theoretical factore related directly to phosphate determinations. These factors suggest certain lines of approach which might be profitably investigated and they also describe certain limitations which might be expected. All of these factors were taken into account in the design of the experiments and in the interpretation of the results.

pH Dependence of Phosphate Activity

Any aqueous solution containing orthophosphate salts must satisfy all of the following equilibria:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_1 = 7.5 \times 10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2} \qquad K_2 = 6.2 \times 10^{-8}$$

$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3} \qquad K_3 = 4.7 \times 10^{-13}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

Considering the relative magnitude of the ionization constants, it is apparent that the total phosphorus will be distributed among all four possible species in solution, and that this distribution will vary with the hydrogen ion concentration. It is also apparent that if excess hydrogen ions be added to such a solution, the equilibria will be shifted to the left and a buffer system will exist which will tend to resist small changes in pH. Since the concentration of any one of the phosphate species in the solution is a function only of the pH and the total phosphorus, the concentration of all the species can be calculated if the concentration of one of them, together with the pH, can be determined. For purposes of this investigation, two factors stand out as important: first, the response of the proposed electrode will be pH dependent, and, second, since potentiometric measurements do not significantly modify the activity of the ion being sensed, it is not of critical importance which of the three possible ions the proposed electrode senses.

Solubility Characteristics of Phosphate Salts

The factor of the solubility of phosphate salts can assume importance in the experimental design at any of three points. The first point is in consideration of Pungor-type heterogeneous membrane electrodes, which require a salt of very low solubility to be suspended in an inert matrix. The second point is in consideration of an electrode of the second class, which requires a metal electrode coated with a slightly soluble salt of that metal. The third point where the solubility of phosphate salts must be considered is in the designing of precipitation titrations to utilize a potentiometric method for end-point determination. Although many phosphate salts are only slightly soluble in neutral or basic solutions, only the phosphate salt of bismuth is still only very slightly soluble in 0.01 M nitric acid. This suggests bismuth phosphate as being worthy of consideration for any of the three applications listed above. The solubility product constant for bismuth phosphate is 1.3×10^{-23}.(33)

Low Mobility of the Phosphate Ion

Phosphate ions are relatively large and their charge is large and diffuse. These factors combine to give the ions very low mobility. This is an important consideration in experimental designs which require movement of these ions through crystals or through ion-exchange membranes.

Bismuth Electrode Reactions

The low solubility of bismuth phosphate suggests the possibility of using bismuth metal as an indicator electrode in a precipitation titration. The electrode reduction reaction to be expected is:

$$BiO^{+} + 2H^{+} + 3e^{-} \rightleftharpoons Bi^{\circ} + H_2O \qquad E^{\circ} = 0.32\ v$$

This reaction would predict a half-cell whose potential would change about 19.7 mv per decade of activity. This means that if such an electrode can be used for direct potentiometry, the sensitivity will not be great. Ross (43) points out that the sensitivity of an electrode like this, having a three-electron transfer, can easily contain an uncertainty of as much as 20 percent, even with careful potential measurements. Precisely the same limitation exists, for the same reason, if the bismuth electrode were to be coated with bismuth phosphate and used as an electrode of the second class. This degree of uncertainty is inherent in this type of measurement, however, and is not prohibitive, in itself. If, however, the electrode is used as an end-point detector, instead of in direct potentiometry, then the three electron change in the half-reaction causes fewer problems; the rate of change becomes more important than the magnitude of the change.

The absolute value of a metallic electrode potential is dependent, to some degree, upon the physical condition of the surface of the electrode in contact with the solution. Physically, bismuth is soft, brittle, and tends to solidify in large irregular crystals. Chemically, it is moderately active. All of these features combine to suggest that a uniform and reproducible surface might be difficult to obtain and to maintain on a bismuth electrode. This is an important consideration in using such an electrode either directly or as an end-point detector in a titration.

Characteristics of Bismuth Solutions

If a bismuth salt, such as bismuth nitrate, is placed in pure water, the bismuth ion hydrolyzes to precipitate bismuth oxide. This precipitate persists until the pH is lowered to approximately one. When the hydrogen ion concentration approaches tenth molar, the oxide precipitate dissolves and the bismuth species present in the solution is apparently BiO^+ (33). This solution is stable so long as the high acidity is maintained. In acid solution containing phosphate, the following reaction seems to occur:

$$BiO^+ + H_2PO_4^- \rightleftharpoons \underline{BiPO_4} + H_2O$$

The precipitate is very fine and tends to deposit initally as a thin white film on the container, stirring rod, etc. Arsenate and iodate ions also precipitate bismuth from this acid solution. The appearance of bismuth arsenate is very similar to that of bismuth phosphate, but K_{sp} for the arsenate is on the order of 10^{-13} compared to 10^{-23} for the phosphate. Bismuth iodate is also white, but it is not so fine and it tends to settle faster than either the phosphate or the arsenate.

With regard to experimental design, these properties of bismuth solutions suggest that if bismuth is to be used as a titrant, the reaction solution must be maintained at a high acidity. These properties also suggest that arsenate or iodate ions would interfere in the titration to some degree but that, at this pH, little else would be expected to interfere; all other common phosphate and bismuth compounds are soluble. In the presence of the thiocyanate ion, however, bismuth forms a very stable orange-colored complex ion which might be expected to interfere. In practice, these three interfering ions must either not be present in the sample, or steps must be taken to remove them before bismuth is used as a titrant.

CHAPTER IV

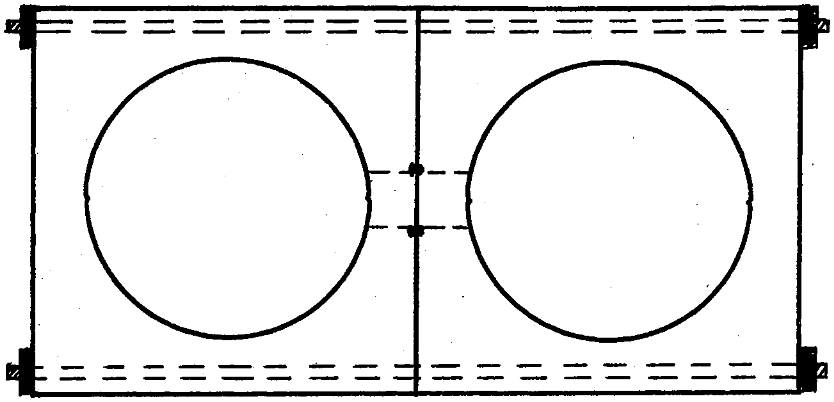
EXPERIMENTAL ACTIVITY

Membranes Containing Phosphate Salts

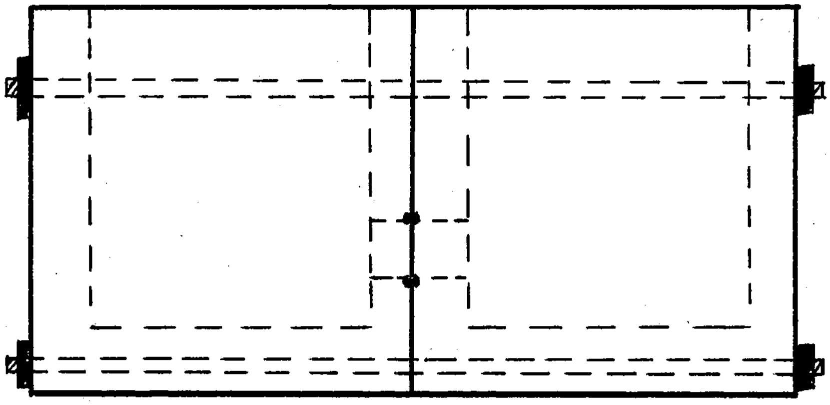
The cell used for evaluation of membrane potentials was machined from block teflon and consisted of two cylindrical cavities, one and one-half inch in diameter and one and one-half inch deep, joined by a passage one quarter inch in diameter. The cell was made in two parts so that the experimental membrane could be inserted across the passage between the two cavities and sealed firmly into position by neoprene o-rings on each side of the membrane. The halves of the cell were held together by threaded brass rods and knurled nuts. In operation, reference electrodes were placed in each cavity. A standard solution was then placed in one cavity and the sample solution was placed in the other cavity. The potential across the membrane was read on the millivolt meter. Figure 1 shows the appearance and construction details of this cell.

The meter used for E. M. F. measurements with this cell was a Leeds and Northrup Model 7401 high impedence voltmeter. Reference electrodes were Fisher Saturated Calomel Electrodes having porous plug liquid junctions.

Stirring was accomplished by a magnetic stirrer placed



Top View



Side View

Figure 1. Cell for Evaluation of Membrane Potentials

to rotate stir-bars in both cavities at the same time. Air bubbles were sometimes trapped in the horizontal passage adjoining the membrane when the cavity was filled, so a medicine dropper with a 90° bend in the tip was used routinely to remove them.

Standard and sample phosphate solutions were made by dissolving reagent grade potassium dihydrogen phosphate in distilled water. Less concentrated solutions were made by dilution of the standard. The potassium chloride and the calcium phosphate that were used in some solutions were also reagent grade. The chemicals were sometimes Fisher Certified Reagents and sometimes Baker Analyzed Reagents.

The first phosphate membranes used in this cell were heterogeneous membranes of the Pungor type (36). They were made by dispersing calcium phosphate in melted paraffin and forming the resulting mix into discs. These discs were placed in a cell with a standard potassium phosphate solution on one side and solutions of varying phosphate concentration on the other side.

When the potential across these membranes was measured, it was found that if the proportion of salt to wax was less than approximately fifty percent by weight, the resistance was so high that the meter would not give a reliable reading. If the salt proportion was raised to more than about fifty percent by weight, the potential dropped completely and no significant difference could be observed, regardless of the concentration of phosphate in the solutions. The meter acted as if the cell were short-circuited. The high salt concentration in the paraffin caused the disc to be fragile, and great care had to be taken to avoid cracking the membrane while clamping it into the test cell. Microscopic examination of these discs, made even before they were inserted into the test cell, gave evidences of tiny passages caused, perhaps, by tiny cracks in the matrix or by separation of the matrix from the crystals. No usable positive results were obtained from these paraffin discs, although more than a dozen of them were built and tested.

In an attempt to make a heterogeneous membrane which would have greater mechanical strength than the paraffin membranes had, but which would, at the same time, be very thin, a series of membranes were made by dispersing calcium phosphate in epoxy resin. The matrix was ordinary epoxy resin glue, made by the Borden Company, consisting of the resin and the hardener which are mixed at the time of use. The first membranes were made by rubbing the dry calcium phosphate into the mixed resin with a spatula, on a glass plate. After hardening, the cast discs were polished on both sides with emery paper. These first discs appeared to be of doubtful value because the abrasive action of the salt had caused the stainless steel spatula to discolor the paste during mixing. In addition, the paste was so thick that the mixing action with the dry salt caused tiny air bubbles to be trapped; not all of these bubbles had worked their way out of the resin before it had hardened. The value of these discs was so doubtful that they were not even tested. Instead, new discs were made by a different technique. This time, the mixed resin was thinned slightly with toluene and the calcium phosphate was wet with toluene before mixing. The paste was made by rubbing on a glass plate with a polyethylene-covered stirring rod. Drops of the paste were placed on a polyethylene plate and allowed to spread into discs. These discs did not adhere to the polyethylene plate. After thorough hardening, which required at least twenty-four hours, the discs were polished on both sides by rubbing on fine emery paper. This gave plane surfaces, very nearly parallel, and removed the glaze of pure resin from the surfaces. The proportion of salt to resin was more than one-to-one in every case. Thickness of the discs varied from about two millimeters in the thickest ones to as thin as could be ground without breaking. The thin ones were very translucent. After polishing on both sides to expose the surfaces of the crystals, it seems reasonable to assume that continuous crystal-to-crystal contact might exist from one side of the membrane to the other. No holes or cracks were visible in the membranes under the microscope until the thickness was reduced to approximately the thickness of the individual crystals.

In spite of the facts that these membranes were smooth strong, thin, and had a high salt content, they proved not to be useful for electrodes. The resistance was too high for all but the thinnest membranes; the voltmeter acted as if the circuit were open, which it effectively was. In the case of the thinnest membranes used, no potential at all would develop, indicating holes or cracks in the membrane. No usable data was obtained with these membrane electrodes either.

In an effort to gain greater ionic mobility in the membrane, another type of membrane was constructed. Potassium phosphate was fused and then cooled quickly to form a glass instead of a crystal, and the membranes were formed from this glass. Glasses were made from both the hydrated and the dehydrated form of the salt, but in both cases the glass was too soluble to be useful. It would begin to dissolve before the entire cell could be assembled and any measurements made. This line of investigation was abandoned.

Ion-Exchange Membranes

The ion-exchange resin membranes used in this study were made of Nalfilm-2 [*]. This is a film of polyvinylbenzyltrimethylammonium hydroxide, an anion exchanger. Its wet thickness is 3.5 mils and its resistance in 0.15M KCl is 20-25 ohms/cm^2. The membrane was prepared for use by soaking it in methanol to remove the polyvinly alcohol backing and then by soaking it in 0.10 M potassium phos-

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[*] The Nalfilm Resin was supplied through the courtesy of the National Aluminate Company, 6218 West 66th Place, Chicago, Illinois.

phate to convert it to the phosphate form. The soaked membranes, cut into squares of approximately three-quarters inch, were stored in the phosphate soaking solution until they were used. At that time, the membrane was rinsed briefly in distilled water to remove excess phosphate solution before being clamped into the test cell, and was returned to the soaking solution after each use. These membranes are tough and flexible and are well suited mechanically for this type of test.

For these experiments, the standard reference solution was 0.10 M potassium dihydrogen phosphate in distilled water. The test solutions were made by dilution of this solution. A platinum wire electrode was used in the reference side of the test cell, and a saturated calomel electrode was used in the test side. Measurements were made using the solutions in various order, and using a fresh membrane each time. The potential was allowed to stabilize each time before reading; this usually required less than thirty and often less than ten seconds. At concentrations greater than or equal to 10^{-3} molar, the results were very reproducible, but near 10^{-4} molar they became erratic and deviated widely from what would be predicted. Representative data from these measurements are listed in Table I and plotted in Figure 2. The linear part of the plot has a slope of approximately 30 mv/decade.

A variation of this technique was made by using an Orion Calcium-Ion Electrode body instead of the teflon test cell. The liquid ion-exchange resin was removed and the internal calcium reference solution was replaced with saturated calcium phosphate solution. A cork borer was used to cut small discs of the anion exchange resin film to replace the filter membrane disc that normally fits into the calcium-ion electrode. Some care was required to prevent leakage of the internal solution around the membrane, but when this was avoided, the results obtained were similar to those obtained with the teflon cell. The overall potential was different because of the different reference electrodes being used. Table II lists representative data obtained with this electrode and Figure 3 shows that these data plot into a line whose linear portion has a slope of approximately 35 mv per decade.

TABLE I

RESPONSE OF AN ANION EXCHANGE MEMBRANE ELECTRODE TO CHANGES IN PHOSPHATE ION CONCENTRATION IN A CELL

Phosphate Ion Concentration	Observed Cell Potential
1×10^{-1} M	50 mv; 51 mv
1×10^{-2} M	20 mv; 19 mv
1×10^{-3} M	-10 mv; -11 mv
1×10^{-4} M	-20 mv; -15 mv

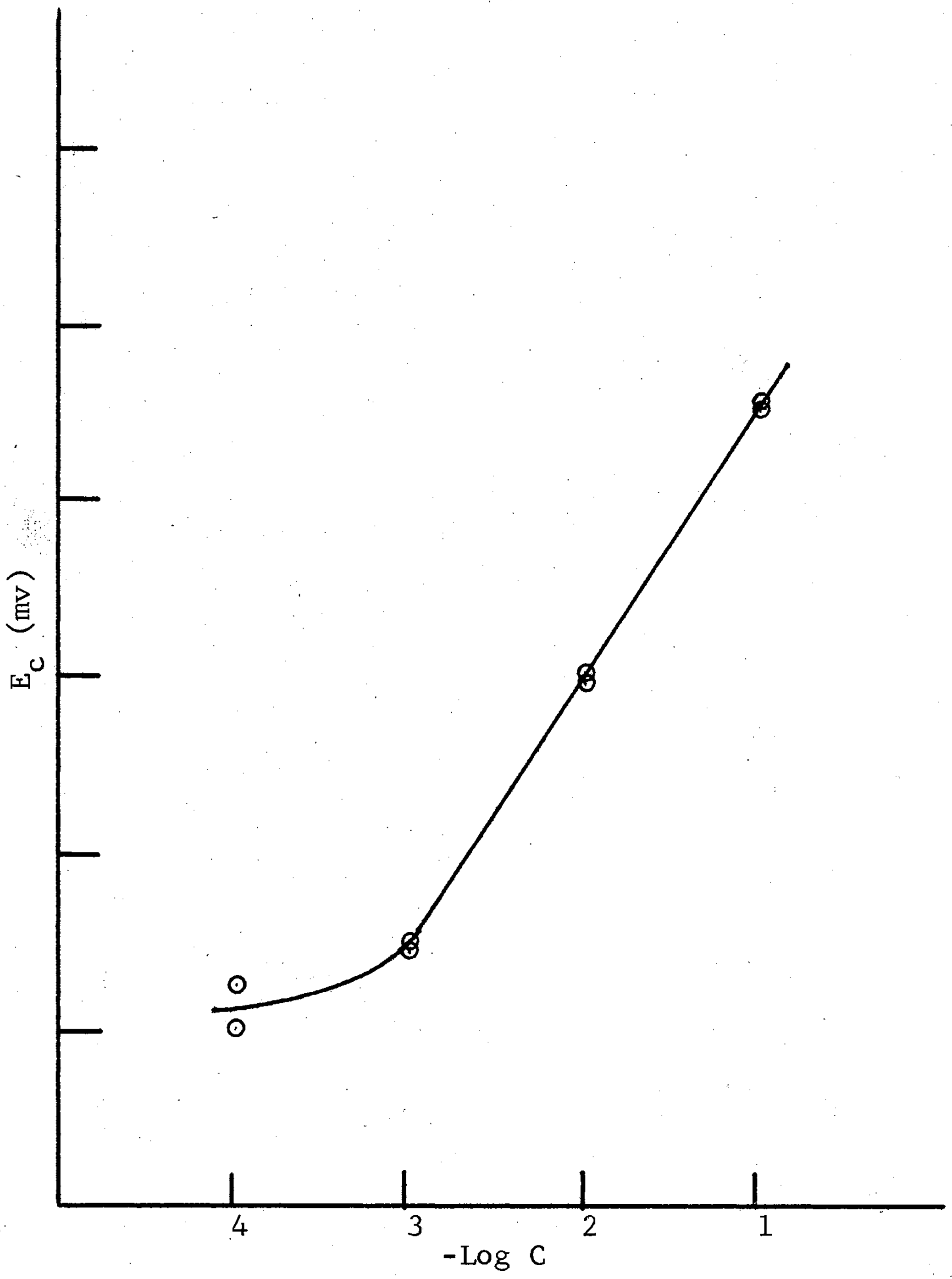

Figure 2. Response of an Anion-Exchange Membrane Electrode to Changes in Phosphate Ion Concentration in a Cell

TABLE II

RESPONSE OF AN ANION EXCHANGE MEMBRANE ELECTRODE TO CHANGES IN PHOSPHATE ION CONCENTRATION, MEASURED IN A MODIFIED CALCIUM-ION ELECTRODE BODY

Phosphate Ion Concentration	Observed Potential
1×10^{-1} M	350 mv; 348 mv
1×10^{-2} M	314 mv; 317 mv
1×10^{-3} M	280 mv; 282 mv
1×10^{-4} M	290 mv; 280 mv

After the response of these cells containing Nalfilm had been established with pure potassium phosphate solutions, a 0.10 M solution of potassium chloride was added dropwise to the indicator side of the cell. The potential proved to be extremely sensitive to these additions, varying sharply to indicate a higher concentration. Measurements were repeated as described above, except that the solutions were all 0.10 M in potassium chloride. Under these conditions, with nearly constant ionic strength on both sides of the membrane, the potential across the membrane was very small and its variation as a function of phosphate concentration practically disappeared, being lost in the random fluctuations of two or three millivolts from solution to solution.

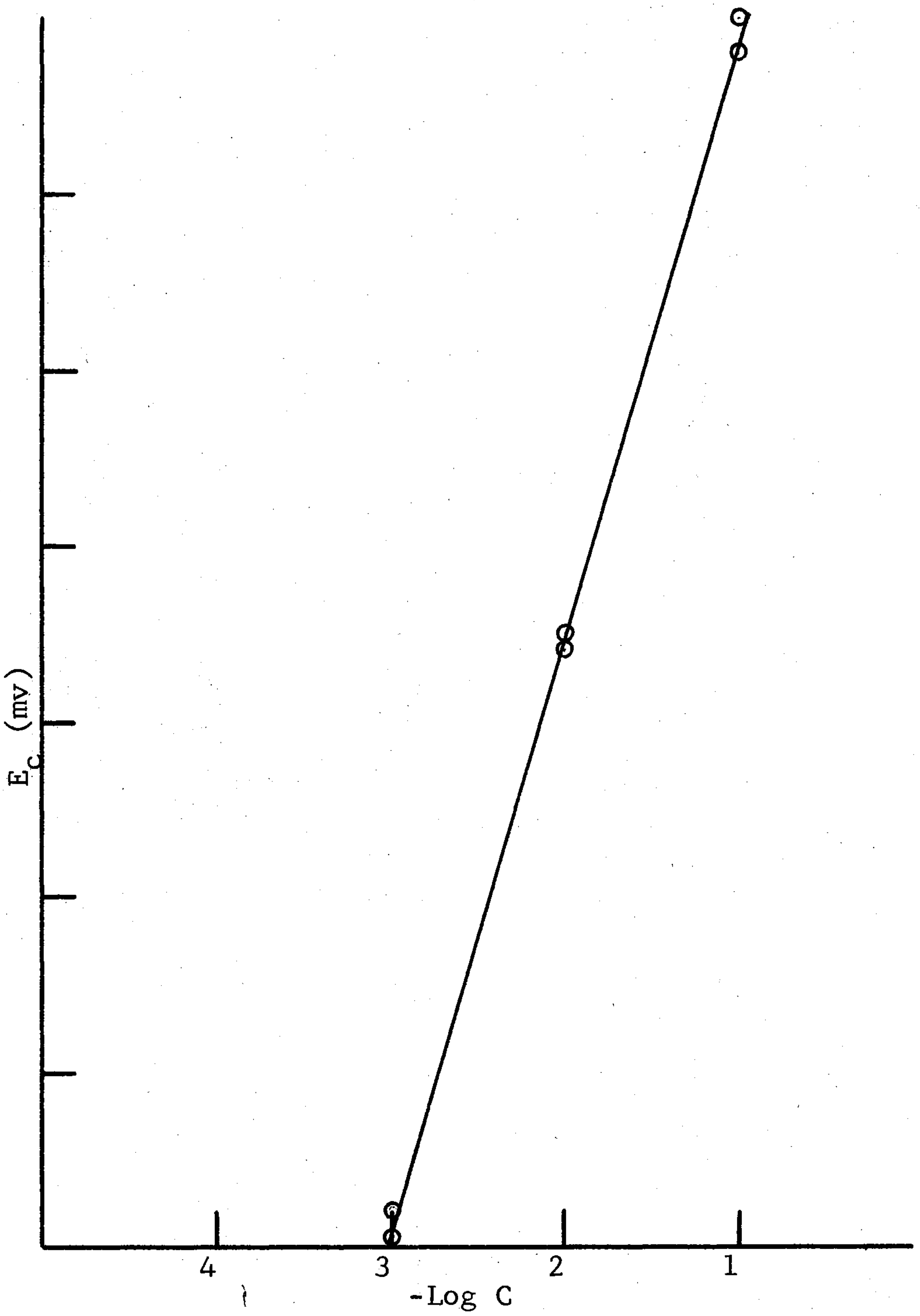

Figure 3. Response of an Anion-Exchange Membrane Electrode to Changes in Phosphate Ion Concentration, Measured in a Modified Calcium Ion Electrode Body

Bismuth Metal Electrodes

The bismuth used in these electrodes was Bismuth Metal Lumps, Fisher Scientific Company catalog number B-316, marked 99.98 percent pure.

Potential measurements were made on a Fisher Accumet Model 320 Expanded Scale Research pH Meter, used in the expanded mode. Graduations are at 1 mv intervals and estimates to the nearest 0.10 mv are entirely feasible. The temperature compensation was manual.

The output from the millivolt meter was usually also recorded on a Heath EU-20B Servo Recorder, equipped with a variable speed chart drive.

Chemicals used in the solutions were Baker Analyzed Reagents.

The reference electrode was a Fisher Saturated Calomel Electrode with a porous plug liquid junction. For certain experiments, an auxillary salt bridge was used.

To repress the hydrolysis of the bismuth ion and to provide reasonably constant ionic strength, both the standard bismuth solutions and the standard phosphate solutions were made in 0.10 M nitric acid. During the first few titrations, a second pH meter equipped with a combination glass electrode was used continuously to monitor the pH of the reaction solution. The pH was found to vary less than one tenth of a unit around pH = 0.9, so the monitoring was discontinued as being unnecessary.

The bismuth billet electrode was made by melting the metal in a porcelain crucible and casting a cylinder, using a form made by rolling a light aluminum sheet into a tube. During casting, the bottom end of the tube rested on a porcelain plate, forming a very smooth shiny surface on the end of the cylinder. This smooth end of the cylinder was the active surface of the electrode. The bismuth did not adhere to the aluminum sheet which formed the mold; after cooling, the form was simply untied and unrolled. A piece of copper wire was soldered to the top end of the cylinder for electrical contact. To prevent contact between the solution and any part of the bismuth billet except the active end, and to form an insulating body for the electrode, the sides of the billet were greased with silicone lubricant (Dow Corning High Vacuum Grease), a piece of quarter-inch polypropylene tubing was slipped over the wire down to where it joined the billet, and the entire assembly was enclosed in a piece of heat-shrink tubing (Chemical Rubber Company) which was shrunk firmly into place. This tubing is originally flexible, but upon heating it reduces its diameter by nearly 100 percent and the wall of the tubing becomes much thicker and stiffer. It forms, for the electrode, not only an insulating cover but a case that is mechanically strong and durable. To further insure against the possibility of capillary seepage of the solution between the side of the billet and the inside of the electrode cover, the polypropylene tube, which forms the upper part of the electrode assembly and contains the connecting copper wire, was poured full of beeswax. The completed electrode was eight millimeters in diameter and about twenty centimeters long with an exposed bismuth surface of approximately 1.25 cm^2. Figure 4 shows a diagram of this electrode. This design was the result of building and testing many previous electrodes, varying all the way from a piece of bismuth metal glued into the end of a plastic tube to small cast wires and plates. For many of these, the first problem was mechanical strength, since bismuth is both soft and brittle. For others, the difficulty came in keeping the exposed surface of the electrode constant during the test, since varying parts of it were being exposed to the solution. The electrode described above, designated in the notebooks as the red electrode because of the color of the heat-shrink tubing which encloses it, successfully avoided both of these difficulties, and all the titration results reported here were obtained with it.

This electrode was used as the indicator electrode versus the saturated calomel electrode in the precipitation titration of phosphate solution with bismuth solution. The reference electrode was joined to the solution by a potassium nitrate salt bridge. When the electrode response is plotted against the volume of titrant, the result is a typical S-shaped curve with the inflection point at the equivalence point for the precipitation of bismuth phosphate. The precipitate is fine and white and tends to deposit initially on the inside of the reaction vessel and

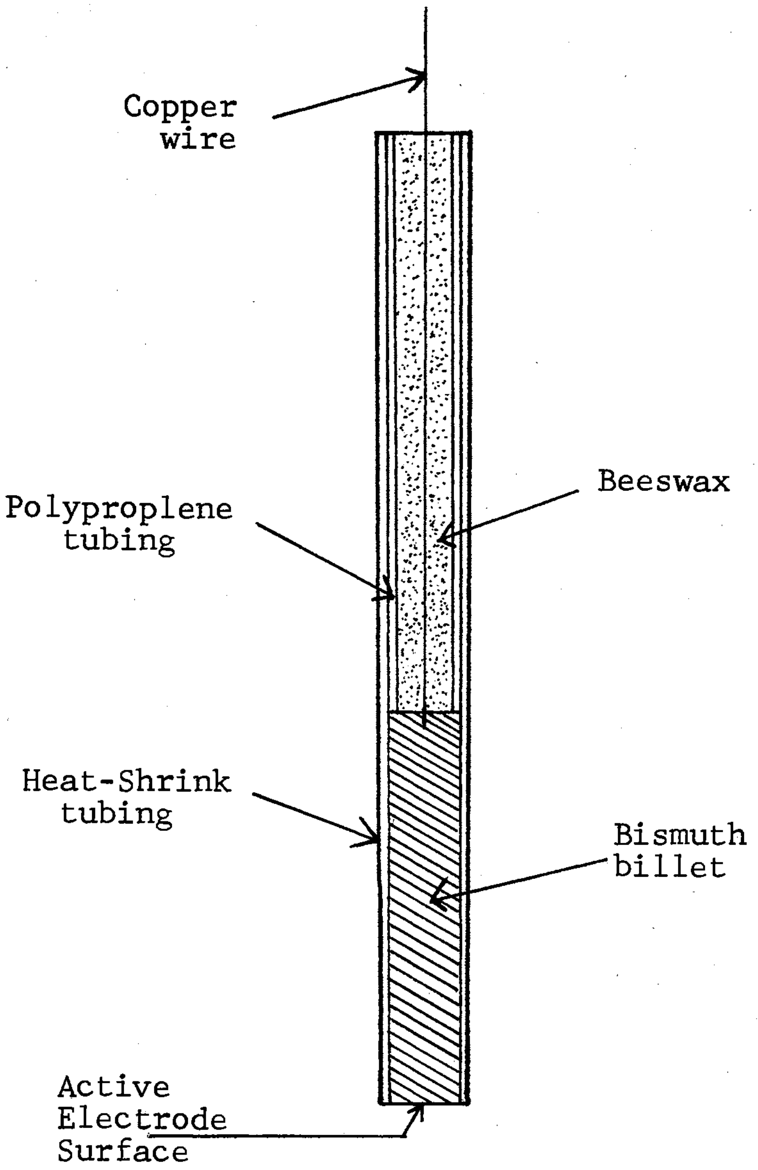

Figure 4. Structural Details of the Bismuth Billet Electrode

on the electrodes and stir-bar.

Figure 5 shows the plot of two successive titrations which are quite typical of the results obtained by this method. The inflection points are at the equivalence volume, but the actual end-point potential varies somewhat from sample to sample. The shape of the first curve very early in the titration is typical of the response of an electrode which has been recently cleaned or dried out. This deviation does not appear if the electrode is used immediately for a second titration.

Figure 6 shows the plot of another pair of successive titrations, made at another time and at different concentrations. Note that the inflection points are not at the same potential, but that they are at the correct volume. The initial drop in potential is again observed in the first titration, but not in the second.

The need for the auxillary potassium nitrate salt bridge is illustrated in curves such as those of Figures 7 and 8. These results were obtained when the saturated calomel electrode, with its porous plug bridge, was used directly in the reaction vessel. The results of these titrations of bismuth with phosphate invariably indicated that more phosphate had been added than, in fact, had been added. At first it was thought that the electrode might not be completely stabilized after each reading, but when the titration was carried out more slowly, using the recorder to determine that the electrode had certainly

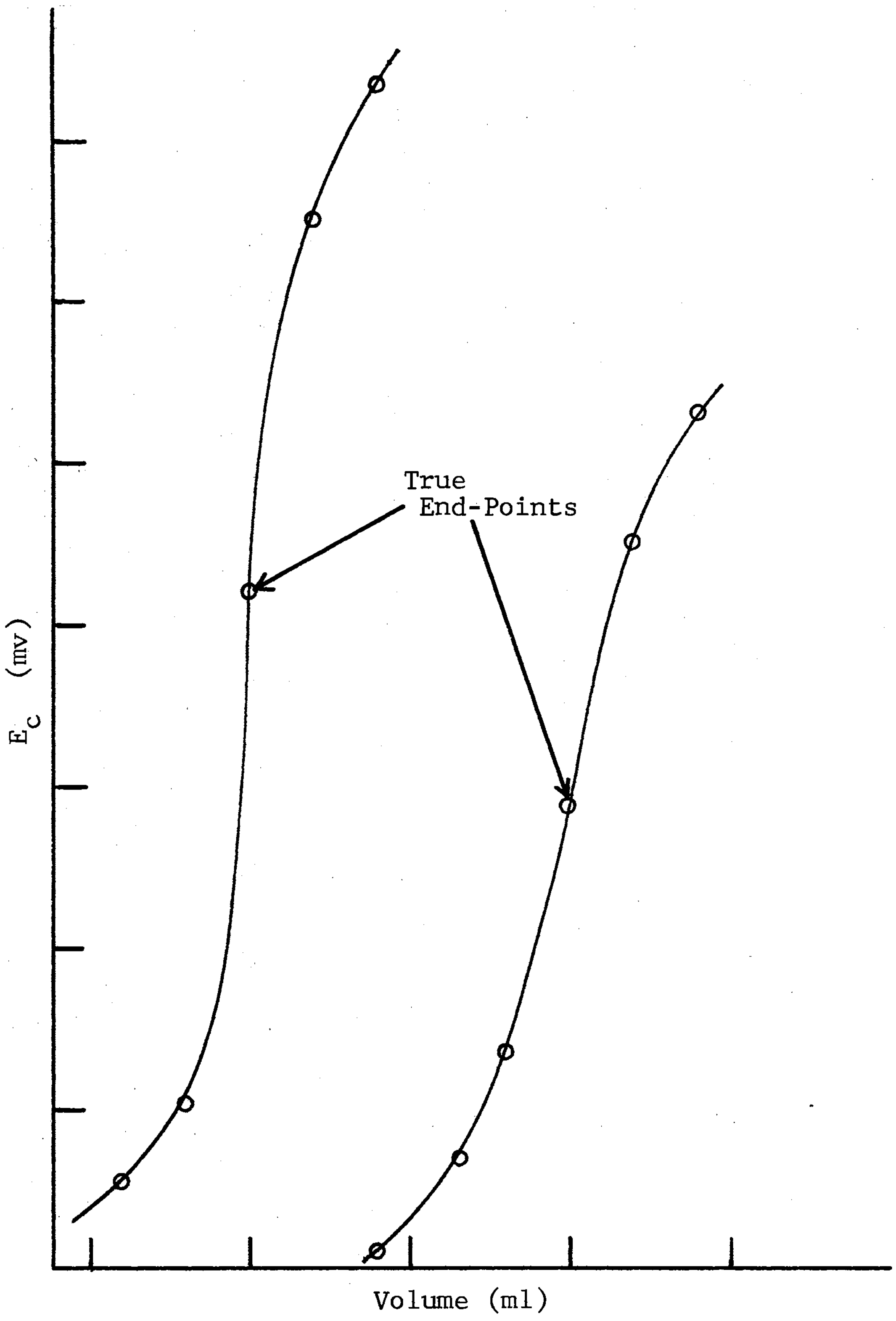

Figure 5. Titration Curves, using a Bismuth Billet Electrode with a Potassium Nitrate Salt Bridge

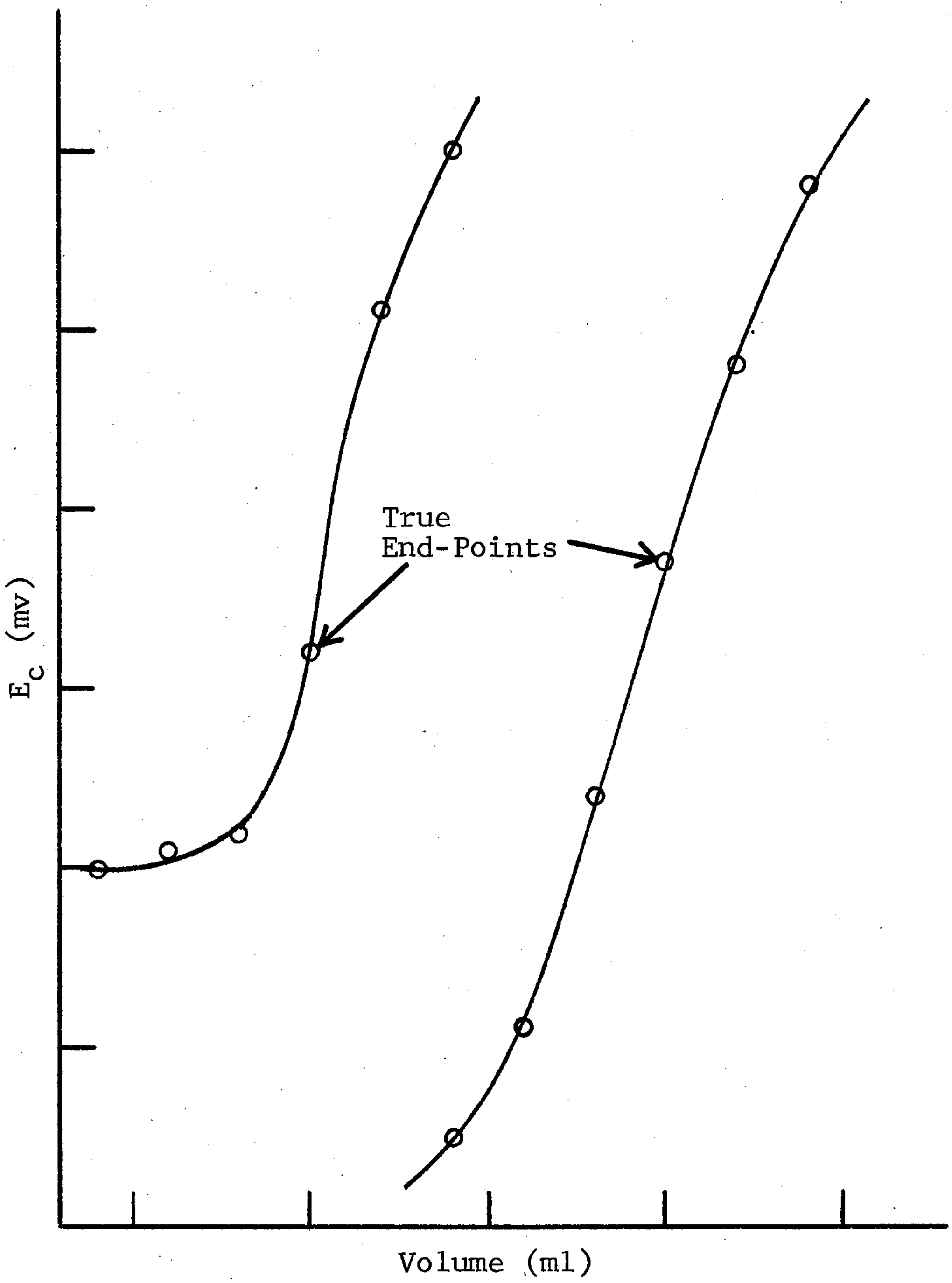

Figure 6. Comparative Titration Curves, using a Bismuth Billet Electrode and the Auxillary Salt Bridge

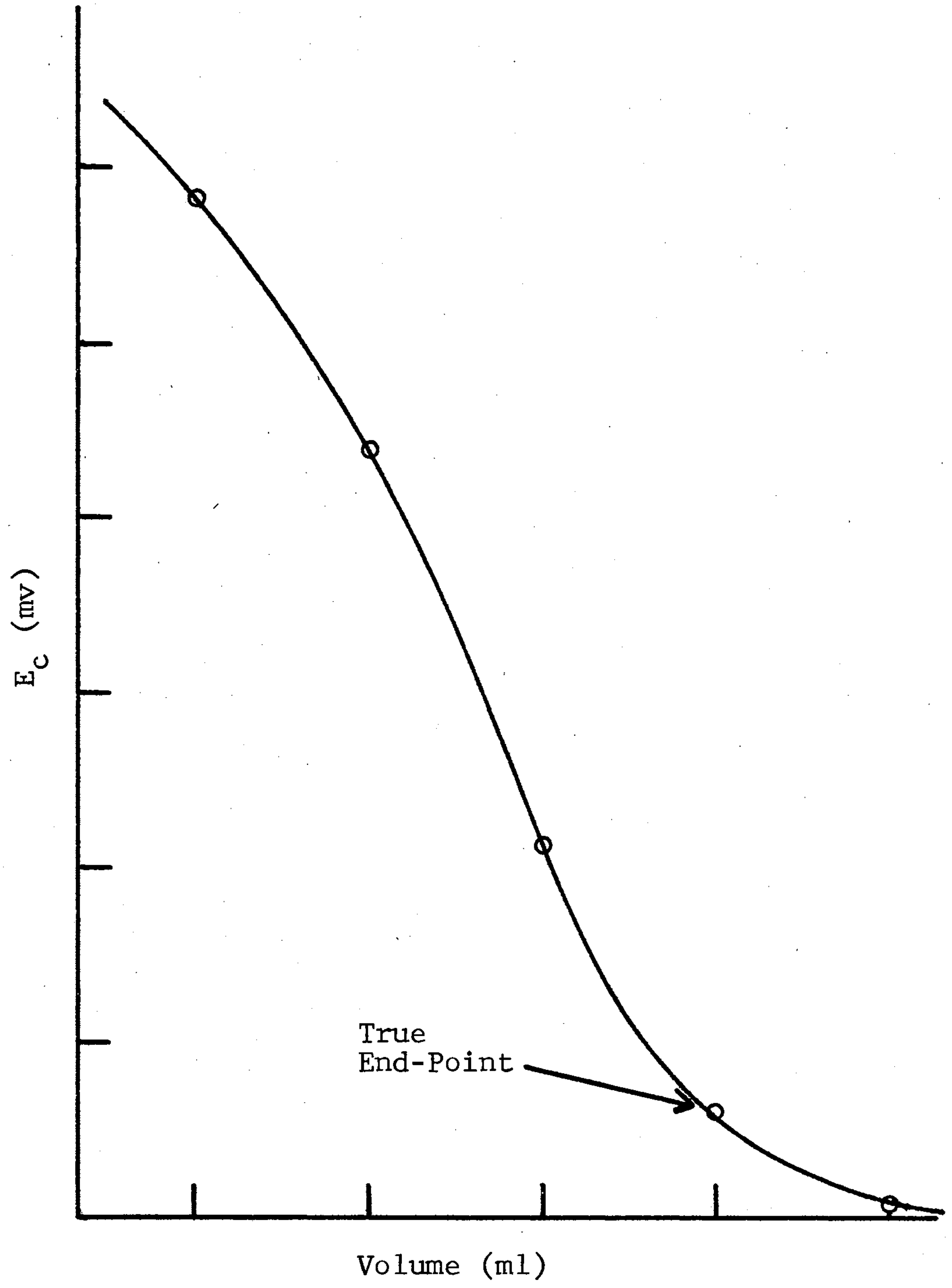

Figure 7. Titration of Bismuth with Phosphate, Showing the Effect of Chloride Interference During a Short Titration Time

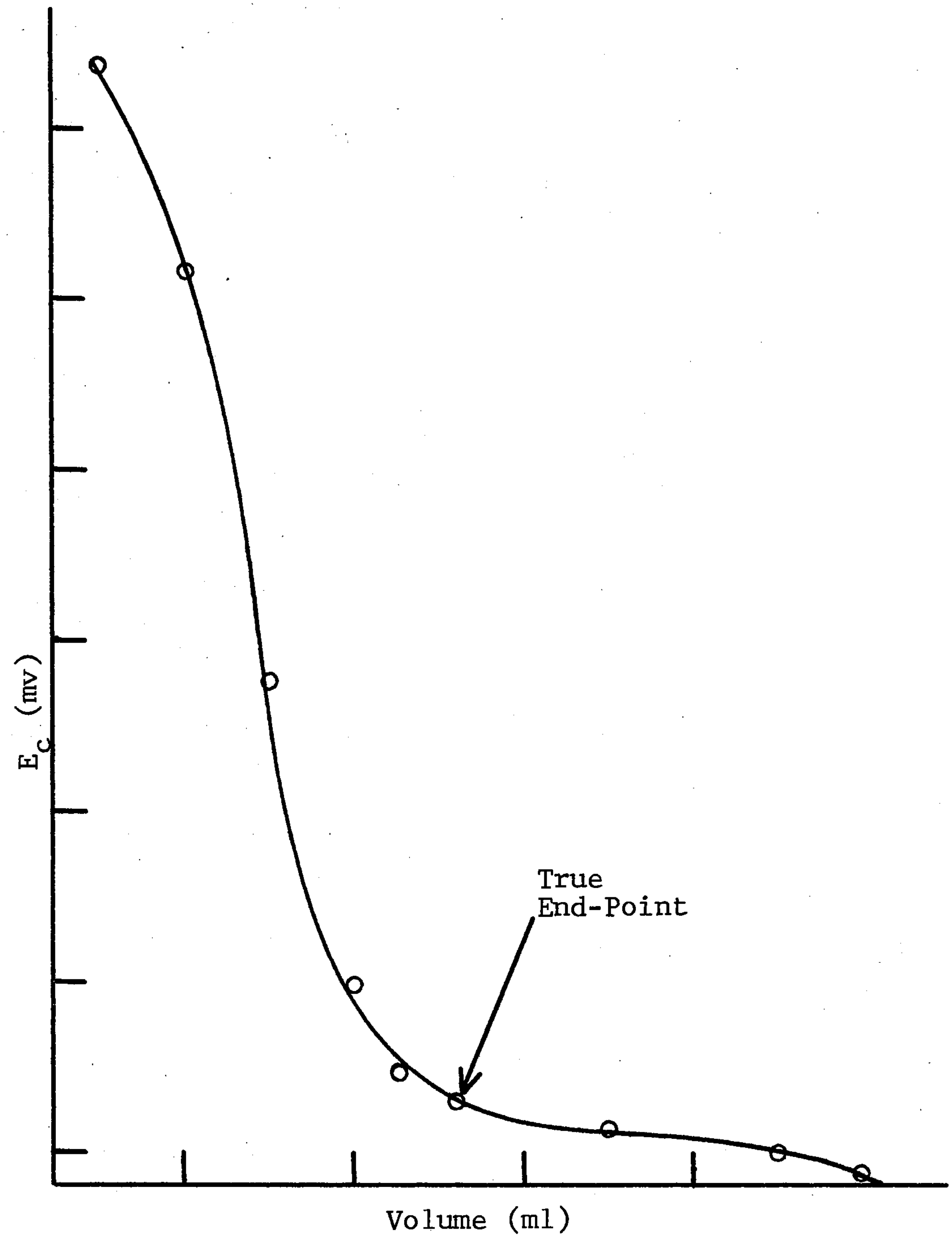

Figure 8. Comparative Titration of Bismuth with Phosphate, Showing the Effect of Chloride Interference during Longer Titrations

stabilized after each incremental addition, the error was even greater. Since bismuth phosphate is soluble in hydrochloric acid , apparently by the formation of chloro complexes, since it is not soluble in nitric acid of similar concentration, the hypothesis was made that even the small leakage of saturated potassium chloride through the porous plug might be sufficient to cause the observed error; particularly since the error seemed to increase with the time used for the titration. This hypothesis was tested using a simple salt bridge made from a U-tube filled with potassium nitrate solution and plugged with cotton to join the titration vessel to an adjoining vessel containing potassium nitrate solution and the reference electrode. The interference immediately disappeared. A more convenient form of salt bridge was constructed and used from that time on. It consisted of a piece of Tygon tubing, plugged at one end with a piece of unfired Vicor (Corning #7930) and filled with potassium nitrate solution. This tube was simply slipped over the bottom end of the reference electrode, forming an extension of the electrode body and removing the necessity for using an adjoining vessel to contain the auxillary salt bridge. This is the bridge that was used for the titrations described in Figures 5 and 6, and it was used for all subsequent work with bismuth solutions. The bridge solution was replaced frequently.

Although the best procedure for phosphate determination will usually be to titrate the phosphate solution with the

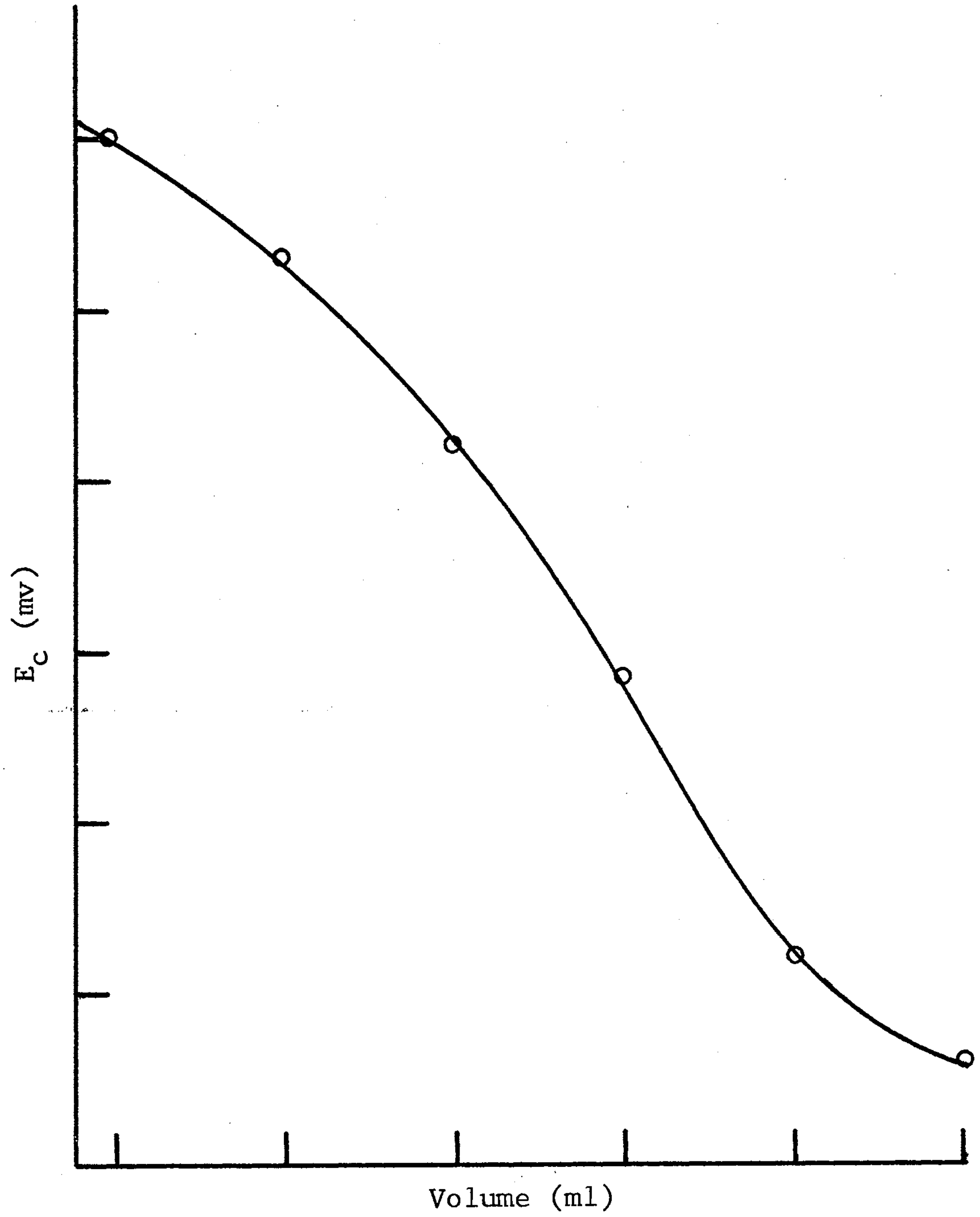

Figure 9. Titration of Bismuth with Phosphate, Direct Plot

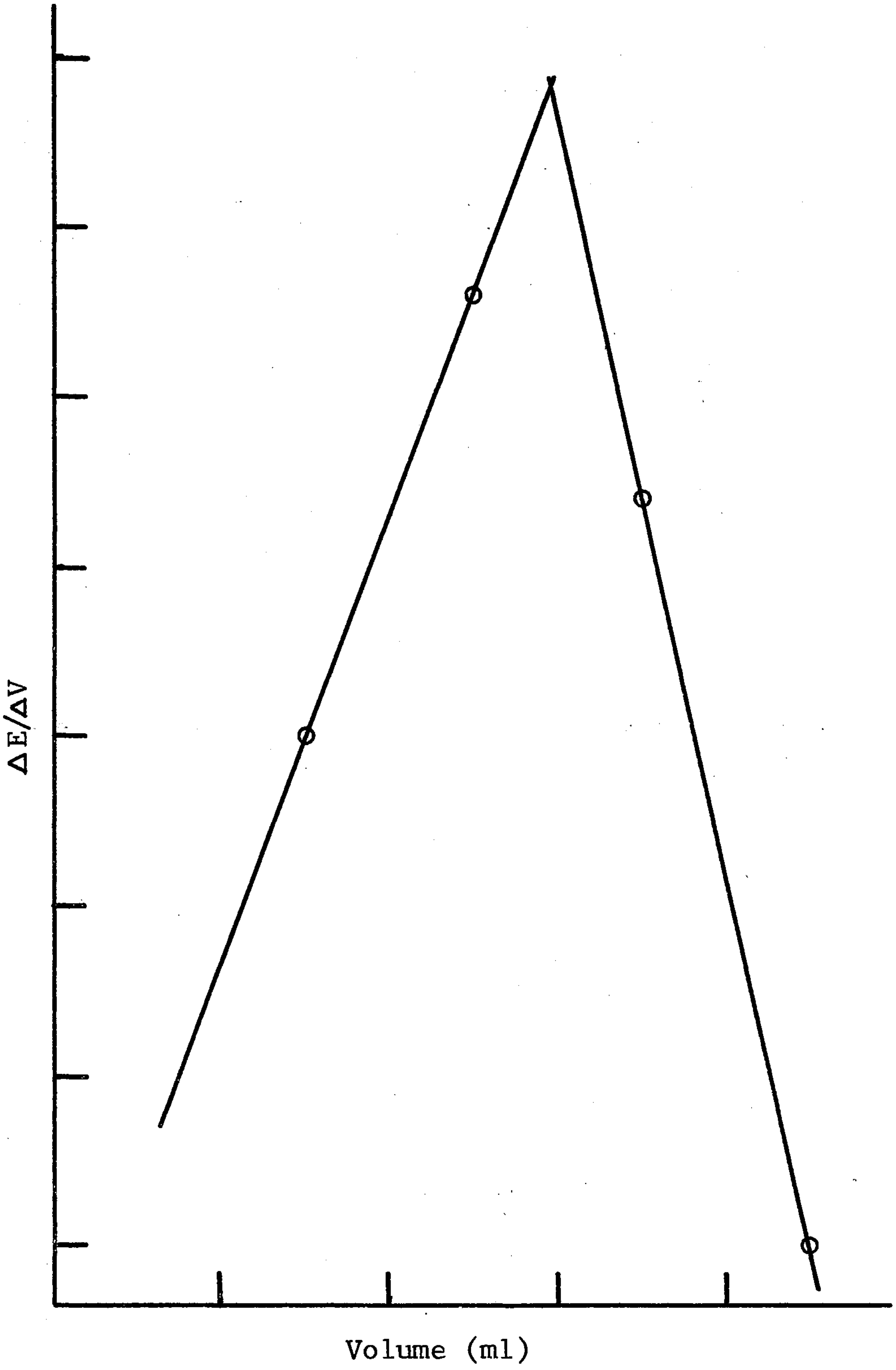

Figure 10. Titration of Bismuth with Phosphate, First Derivative Plot near the Inflection Point

bismuth nitrate solution, it is also entirely possible to use phosphate for the titrant. Figures 9 and 10 show the result of one such titration. The bismuth concentration was approximately 10^{-3} molar, and the inflection point on the first plot is apparent but a bit difficult to locate precisely. Figure 10 shows a plot of the rate of change of potential with volume of titrant near the inflection point, thus locating the inflection point more precisely.

Bismuth Amalgam Electrodes

The results of the studies on the billet electrodes emphasize the difficulty in making the electrode generate the same potential day after day, even under conditions as nearly ideal as it is possible to make them. The problem was attributed to variations in the surface of the electrode. Many billet electrodes were made and a variety of methods were used for making the surface uniform. Some of the billets were mechanically polished with a file, followed by fine emery paper; some were etched in concentrated nitric acid. In each case, the potential of the electrode changed very rapidly when it was first immersed in the solution, but, after finally stabilizing, it performed satisfactorily for titration but was never very reproducible. Billets were anodized in phosphoric acid solution to try to build a layer of bismuth phosphate, but this simply resulted in oxygen evolution, as was anticipated. Some billets were cleaned and coated with bismuth metal by electrodeposition, but the coating was finely divided and black and not very adherent. No improvement in electrode performance was observed with these "bismuthized bismuth" electrodes; in fact, they required more time to stabilize than did the plain metal billets. The elaborate precautions employed in the making of the electrode described in Figure 4 resulted in the most nearly reproducible surface, but it was still not sufficiently reproducible for use in direct potentiometry.

In an early design of a bismuth billet electrode, a small piece of the metal was fastened into the end of a polypropylene tube with epoxy resin glue, and electrical contact on the inside of the tube was made with a platinum wire and a pool of mercury. This proved immediately to be unsatisfactory because, during the first series of tests, the mercury broke through the bismuth disc and fell into the reaction vessel. Examination indicated that the mercury had simply dissolved a major portion of the bismuth disc. Experiment quickly confirmed that bismuth is, indeed, rather soluble in mercury, so the mercury connector was not used again, being replaced with solder.

Very late in the study (indeed, after this dissertation was nearly finished) this ability of bismuth to form an amalgam came to mind as a possible solution to the problem of a reproducible electrode surface. A saturated bismuth amalgam was at hand from the previous experiments, so a new electrode was quickly constructed to test it.

The first test electrode body was simply a polypropylene funnel with the stem bent sharply up. The amalgam was poured into the funnel to fill it to just above the apex of the cone, and electrical contact with the voltmeter was made through a platinum wire inserted through the turned-up funnel stem. A few milliliters of the phosphate test solution in 0.10 M nitric acid were poured into the funnel on top of the amalgam, and the salt bridge of the reference electrode contacted the test solution. Between tests, the used solution was removed with a suction tube and the surface of the amalgam was wiped dry with a strip of filter paper. Later, a more compact and more easily handled temporary electrode was made, utilizing a polypropylene thistle tube instead of the funnel. Comparative tests showed no interference in this electrode by the chloride ions from the reference electrode porous plug, so the potassium nitrate salt bridge was removed. If the test conditions required extremely small volumes of test solution or required that the reference electrode remain in the solution for a long time, the potassium nitrate bridge might prove to be necessary.

During a test, the surface of the electrode becomes coated by a fine white film which is wiped off by the filter paper each time the test solution is changed. Stirring is neither necessary nor desirable during a test. The test solution is simply poured into the cell on the amalgam, the reference electrode lowered into place, and the millivolt meter turned on. The instrument used here was the same Fisher Accumet Model 320 described earlier, used in the expanded mode. The potential is read as soon as the needle movement has stopped. Initial movement is smooth and rather rapid, but it slows as the stability point is reached. With phosphate concentration greater than 10^{-3}, stability is usually reached in less than a minute; often in only a few seconds. With solutions more dilute than 10^{-3}, more time is required for stability, even up to three or four minutes. With solutions whose concentration is near 10^{-5}, the initial movement of the electrode response is sometimes even in the "wrong" direction; that is, toward a negative potential versus the saturated calomel electrode. This quickly reverses, however, and normal stability is attained. The more dilute the solution, the more time is required to attain stability, as a general rule. All of these observations tend to suggest that the electrode is of the second class, forming the film of bismuth phosphate anew with each measurement, but this hypothesis needs further testing.

Table III lists the results of many replicate measurements, made in various sequence, in the cells described above. These data are plotted in Figure 11, showing a very nearly Nernstian response over a wide range of concentration. The slope is approximately 21.1 mv per decade of concentration compared to the theoretical slope of 19.7 mv per decade which is predicted by the Nernst Equation for a three-electron half-reaction. This difference is probably within the limits of experimental error for this series of determinations.

TABLE III

RESPONSE OF A BISMUTH AMALGAM ELECTRODE TO CHANGES IN PHOSPHATE ION CONCENTRATION

Phosphate Concentration	Electrode Response, in Mv
1×10^{-1} M	86.1; 87.0; 93.5
1×10^{-2} M	69.5; 66.0
1×10^{-3} M	46.6; 48.0; 46.2
1×10^{-4} M	24.6; 25.2; 27.2
1×10^{-5} M	20.0; 16.5

Over a long period of time, or with electrodes made with different amalgams, standardization with a known solution may prove to be necessary, as in the case of the glass electrode. This standardization might be necessary because electrodes made of different amalgams might have different bismuth activity in the amalgam. Small drift in an individual electrode with time and use might also be anticipated, for the same reason, but such drift has not been observed during the relatively short time of these tests.

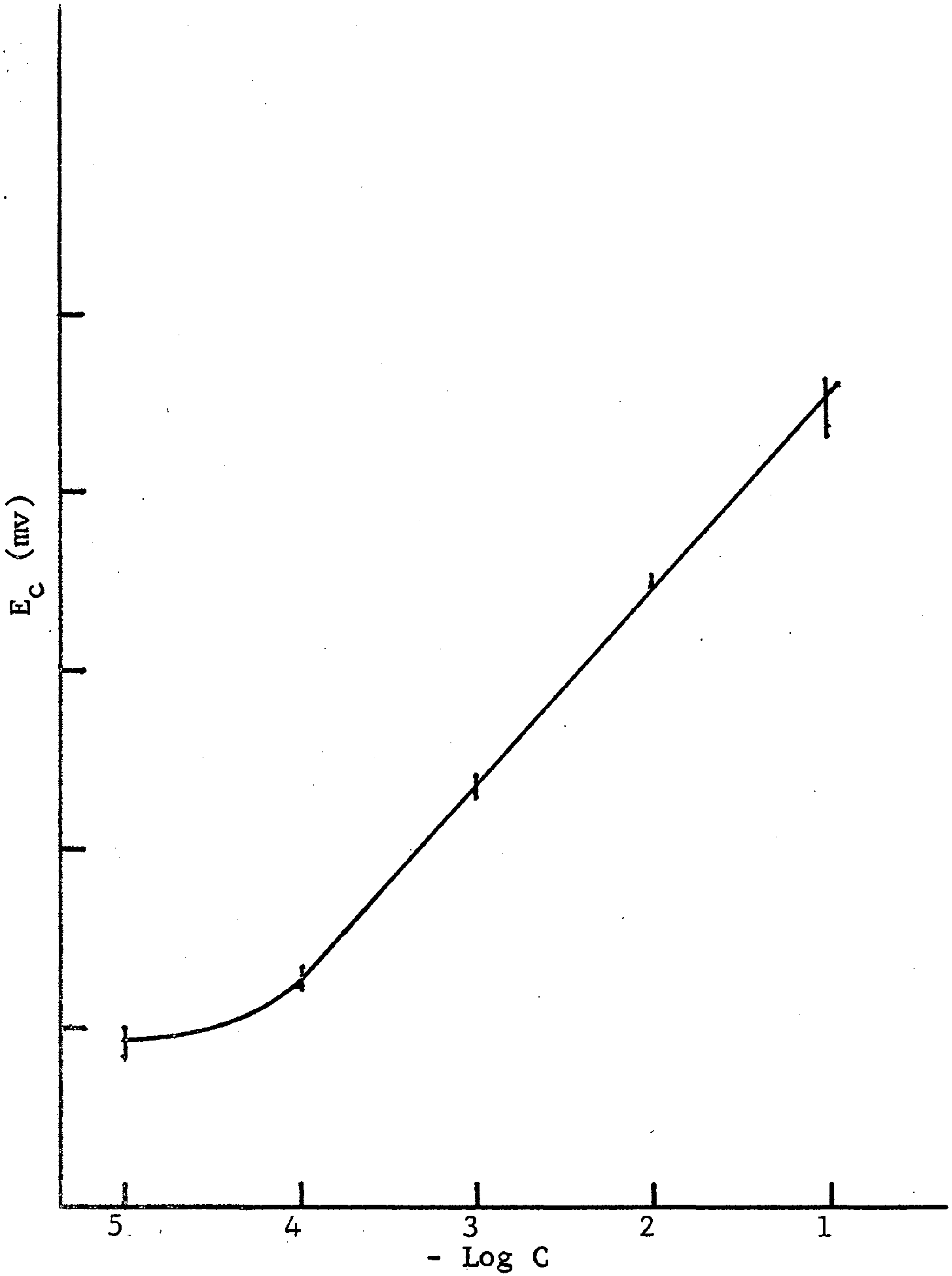

Figure 11. Potential of a Bismuth Amalgam Electrode as a Function of the Phosphate Concentration

Studies of these amalgam electrodes are still in progress. Among the items of design under study are the optimum concentration of bismuth in the amalgam and the physical design of the electrode itself. A dipping cup electrode might be easier to clean between tests, simply by rinsing it with the new test solution. The dipping cup electrode might also make it possible to leave the film undisturbed on the surface of the amalgam from test to test. This would provide very interesting and perhaps very significant data about the nature of the electrode response which could lead to the extension of both its response range and its range of applications. A flow-through electrode, for continuous monitoring, is also on the agenda for testing. The report of the development of these bismuth amalgam electrodes promises to be a publication in its own right.

CHAPTER V

DISCUSSION AND CONCLUSIONS

Membranes Containing Phosphate Salts

The factors mentioned in Chapter III concerning the low mobility of the phosphate ions did not predict a high probability of success for this series of experiments. Indeed, Ross (43) says, "It is probably safe to say that only small univalent ions can have sufficient mobility in a crystal lattice at room temperature." However, Pungor and his co-workers (37) had reported an electrode made with manganese (III) phosphate suspended in silicone rubber. Its further development was not reported. These same workers had also reported in 1964 (36) that phosphate interfered with the action of a membrane containing barium sulfate and sensitive to sulfate ions. Rechnitz (39) evaluated a membrane containing bismuth phosphate and found it to be unstable, although somewhat responsive. The possibility that such electrodes could be made seemed great enough to justify the time and effort.

High resistance across paraffin membranes, such as was found in this study, seems to be characteristic of these membranes. If the membrane is thin enough or loaded heavily enough with crystals to reduce this resistance, its mechanical strength and integrity are lost. Shatky (45) attempted to overcome this difficulty by incorporating gauze into a membrane containing calcium oxalate. The resulting membrane was strong enough, and it would concuct, but it was not selective.

A similar difficulty was encountered with the membranes whose matrix was epoxy resin. This material had sufficient mechanical strength to allow a very thin membrane to be formed without using gauze. The dielectric constant of the epoxy is high, however, and the resistance of the membrane remained too high for measurement until it became so thin that it leaked. It was hoped that a continuous crystal-to-crystal contact could be established from one face of the membrane to the other, allowing some ion mobility. Evidence of such mobility was not observed, however. This may be because the epoxy resin effectively "wet" the individual crystals and isolated them, or it may simply be that the phosphate ions are not, in fact, sufficiently mobile in the crystal.

In the hope that the mobility of the ions would be much greater in the glass than in the crystal, several glasses were made, but they were so unstable and so soluble that it proved to be impossible to make meaningful measurements with them.

With these results, the conclusion becomes almost inescapable that useful phosphate sensitive electrodes cannot be made by the present techniques for making heterogeneous membrane electrodes. The ions are simply too immobile in their crystals.

Ion Exchange Membranes

An ion-exchange membrane consisting of tiny beads of anion-exchange resin in an inert matrix is comparable in many ways to the heterogeneous membranes containing crystals. When this resin is converted to the phosphate form, it is, in effect, a series of crystals in which the anion is held relatively loosely. Covington (8) has summarized the results of many workers to show that this type of electrode can be made sensitive to sulfate, chloride, hydroxide, hydrogen, potassium, zinc, and nickel. The conclusion of Pungor and his co-workers was that these electrodes were sensitive only to ion valence type and not to individual ions (38). Phosphate sensitive membranes were not mentioned.

In this study being reported, the electrode potential in pure potassium phosphate solution showed a response of about 30 millivolts per decade, suggesting that the species being sensed is the divalent ion. In such a solution, all three species are present and the monovalent ion predominates in number, but the selectivity of the membrane would be expected to be greater for the more highly charged ion. This selectivity is not apparently sufficient, however, to overcome the mass effect of increasing the total ion concentration. Under these conditions, the membrane displays little or no selectivity.

Bismuth Metal Electrodes

A metal in contact with its ions in solution establishes an electrical potential between the metal and the solution which is a function of the particular metal involved, the temperature, and the activity of the ions in the solution. When a reference electrode of constant potential is used to complete the cell, the measured potential can be expressed by a form of the Nernst Equation:

$$E_c = K + (RT/nF)\ \ln \left[M^{n+}\right]$$

E_c is the observed potential of the cell, in volts, K is a constant which includes the standard electrode potential, the reference electrode potential, and the sum of the junction potentials resulting from assembling the cell, and all other terms are standard.

For a bismuth electrode at 25° C, the equation can be written:

$$E_c = K + 0.0197\ \log \left[BiO^{+}\right]$$

If this measured cell potential is plotted against the log of the bismuth ion activity, the equation predicts that the result would be a straight line with the intercept at K and a slope of almost twenty millivolts per decade of molar activity.

As was predicted by the nature of the bismuth metal in Chapter III and confirmed by the experimental data of Chapter IV, the value of K is not usually constant from experiment to experiment or from electrode to electrode. The pertinent variable is apparently the surface condition of the electrode. During the course of the study, many shapes and types of billets were made and evaluated in an attempt to achieve a more constant value for the cell constant. Exposure to the solution often caused small changes on the surface. This meant that changing the solution level, from stirring or from titrant addition, exposed a slightly different surface to the solution and caused the potential to vary significantly. The electrode described in Figure 4 was designed specifically to minimize this source of variation. This billet was used for many titrations, both macro and micro, and gave uniformly excellent results at concentrations above 10^{-4} molar phosphate. The variations in end-point potential noted in Chapter IV seem to reflect differences in the electrode surface but do not detract from its sensitivity. It is possible that a stable billet electrode could be standardized, much as a glass electrode is standardized, and then be useful for direct potentiometry. This possibility is being investigated as part of the continuing study on direct potentiometry with amalgam electrodes.

With the bismuth dissolved in mercury to make an amalgam, linear Nernst plots have been observed over a range of nearly five decades of phosphate concentration.

It seems likely that these electrodes are responding as electrodes of the second class; that is, as a bismuth electrode coated with bismuth phosphate. In the absence of bismuth ion from another source, such an electrode responds directly to the phosphate ion concentration. It is limited by the solubility product constant of bismuth phosphate, which is very low.

Conclusion

The conclusion of this study is that phosphate sensitive membrane electrodes of the Pungor type are probably not feasible. Ion-exchange membranes are not sufficiently selective to be very useful. Bismuth metal billets are certainly useful for end-point detection for titrations in acid solutions and, with standardization, they hold some possibility of usefulness for direct potentiometry. The amalgam electrodes are certainly useful for direct potentiometry and, with the proper changes in physical form, should be equally useful for titrations.

With regard to the thesis stated at the beginning of Chapter I, the conclusion is that phosphate can, indeed, be determined by the use of an ion-selective electrode.

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APPENDIX

This Appendix is a paper prepared for publication of the results of the research reported in the body of this dissertation. Because of its position as an Appendix, the references to Figures and Bibliography are keyed to the main body of the dissertation. The size and form of the figures will be somewhat different for the publisher's format.

Potentiometric Determination of Phosphate Using a Bismuth Billet Electrode.

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Summary: A bismuth billet electrode was constructed and tested for its usefulness as an end-point detector in the volumetric titration of phosphate with bismuth nitrate in nitric acid medium. Volume-potential curves were obtained which show the inflection point at the stoichiometric end point. Interference was experienced from arsenate, iodate, and chloride ions. The experimental parameters of the electrode structure are described. The prospect and direction of future work with bismuth amalgam electrodes is indicated.

INTRODUCTION

In recent years, the development and use of specific-ion electrodes has grown apace. The work of Pungor (36) (37)(38), Ross (43), Rechnitz (39)(40)(41), Eisenman (11), Durst (10), and others is well known in this field and is thoroughly reviewed and summarized to 1969 in the symposium papers which were edited by Durst (10). Since that time, however, the work of evaluation and testing is proceeding rapidly by workers like Baum (3), Carr (5)(6), Ridden (42), and Levins (28).

Much activity has been directed toward making a useful phosphate ion sensitive electrode by using a heterogeneous membrane, but so far without very much success. The aim of this work was to build a bismuth electrode and use it to determine inorganic orthophosphate, either by titration or by direct potentiometry, or both.

Experimental

Chemicals. All chemicals were of analytical reagent grade. Stock solutions of both bismuth nitrate and potassium dihydrogen phosphate were prepared in 0.10 M HNO_3. Other concentrations were prepared by dilution with the dilute acid. The bismuth used was Bismuth Metal Lumps, Fisher Scientific Co. catalog number B-316, marked 99.98% pure.

Apparatus. Potentiometric measurements were made on a Fisher Accumet Model 320 Expanded Scale Research pH Meter, used in the expanded mode. A Heath EU-20B Servo Recorder, equipped with a variable speed chart drive, recorded the performance of the electrode over extended periods. The reference electrode was a Fisher Saturated Calomel Electrode having a porous plug liquid junction at the bottom.

Procedure for Titration. The indicator electrode was prepared for titration by protecting all of the billet, except one prepared area, from contact with the solution. To accomplish this, the electrode was built as indicated in Figure 4. The bismuth metal was fused in a porcelain crucible and cast into a cylindrical mold made by rolling thin sheet aluminum. The mold stood on a porcelain plate during casting, causing the bottom of the cast cylinder to be smooth and bright. This surface was the active surface of the electrode. After cooling, the aluminum sheet, to which bismuth does not adhere, was unrolled and a copper wire was soldered to the upper end of the cylinder. The sides of the cylinder were liberally coated with Dow Corning Silicone Grease, a piece of polypropylene tubing whose outside diameter was approximately equal to that of the cast billet was slipped down over the wire to the top of the billet, and then the entire assembly was enclosed in a piece of heat-shrink tubing (Chemical Rubber Company) which was then shrunk firmly into place. The polypropylene tube, which carries the copper connecting wire and forms the upper body of the electrode, was then poured full of beeswax. The electrode was prepared for use by soaking in some of the phosphate solution until its potential ceased changing.

The reference electrode was modified for use by placing a salt bridge containing 0.10 M KNO_3 between the porous plug and the reaction solution. The bridge consisted of a piece of Tygon tubing closed at one end with a piece of unfired Vicor (Corning # 7930), filled with the bridge solution, and slipped over the bottom of the reference electrode.

Titrations were carried out manually, with magnetic stirring after each addition, but the stirring was then stopped until the electrode had completely stabilized and had been read. This precaution was probably not absolutely necessary, but it seemed to give somewhat more reproducible results. The electrode potential was read when the line on the strip-chart recorder straightened out after each increment of titrant had been added.

Discussion

Results. The four curves shown in Figures 5 and 6 illustrate the results obtained with this electrode. These titrations were made at different times and with different concentrations of solution, and it is noteworthy that the potential of the electrode at the equivalence point is not the same for any two of them, although the inflection point is at the stoichiometric end-point in each case. This is apparently due to small changes in the surface characteristics of the electrode from time to time and in different solutions. A freshly acid-etched electrode surface is very unstable for several hours; its potential drifting slowly but surely. In earlier parts of these experiments, a simple bismuth billet, unprotected, was used much like a silver wire can be used. The results varied sharply and were very unreliable. After a stable reading had been obtained, if the level of the reaction mixture rose a bit on the billet, the potential changed very significantly. This led to the rather elaborate design to protect the sides of the billet from the solution; even from capillary seepage. Experiment proved even this precaution to be necessary but, when observed, to be effective. There is reason to think that the chemical characteristics of the electrode surface change from time to time and from solution to solution, probably because of the deposit of bismuth phosphate on the surface.

The need for the potassium nitrate salt bridge became evident during these titrations. In small volumes of solutions, the electrode would never really stabilize if the bridge were not used, but it would promptly do so if the chloride ions were kept out of the solution. Bismuth phosphate is soluble in hydrochloric acid at this concentration and, if chloride ions are leaking into the reaction vessel during a relatively long titration time, using phosphate as the titrant, the end-point comes prematurely. The longer the titration time, the more premature the apparent end-point. Figures 7 and 8 show the kind of results which led to the use of the salt bridge.

The high acidity of the reaction solutions is necessary because of the ease with which bismuth ion hydrolyzes. The precipitation reaction seems to be:

$$BiO^{+} + H_2PO_4^{-} \rightleftharpoons \underline{BiPO_4} + H_2O$$

The high acidity is also useful in preventing many interferences. Bismuth phosphate is the only common phosphate not soluble at this pH, but bismuth arsenate and bismuth iodate also precipitate at this pH and will interfere if arsenates or iodates are present.

<u>Conclusion</u>. This bismuth billet electrode has given very good results when used under the conditions described here

as an indicator electrode for the titration of phosphate with bismuth nitrate solution. The lack of complete reproducibility of the electrode surface leaves something to be desired, however, and a preview of further developments is appearing in the early tests of a bismuth amalgam electrode. The amalgam electrode has a much better surface and is demonstrating Nernstian response to phosphate over a wide concentration range, apparently as an electrode of the second class. Its development is continuing and will be reported later.

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