This is to certify that the

thesis entitled

A FEASIBILITY STUDY OF THE SILVER SULFIDE
ION-SELECTIVE ELECTRODE AS A
GEOCHEMICAL EXPLORATION TOOL

presented by

MICHAEL REED SCHOCK

has been accepted towards fulfillment
of the requirements for

Masters degree in Geology

John T. Wilband
Major professor

Date 11/8/78

O-7639

A FEASIBILITY STUDY OF THE SILVER SULFIDE ION-SELECTIVE ELECTRODE AS A GEOCHEMICAL EXPLORATION TOOL

by

Michael Reed Schock

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Geology

1978

ABSTRACT

A FEASIBILITY STUDY OF THE SILVER SULFIDE ION-SELECTIVE ELECTRODE AS A GEOCHEMICAL EXPLORATION TOOL

by

Michael Reed Schock

A literature review was undertaken and the theory of electrode response, interferences, and buffer solutions is described. Standard addition techniques are surveyed and discussed, and a general method derived for volume change corrections in multiple addition potentiometry.

Following investigations of pre-extraction by dithizone, a sulfite-bisulfite buffer system, and a method for silver in photographic fixing solutions, the CAOB solution previously employed for electrode measurements of cupric ion in soils and natural waters was adapted for use. Synthetic solutions 8 N in HNO_3 containing 1.92 ppm silver ion were analyzed with an absolute error of +3.5% and a relative precision (95% c.l.) of ∿6%. It was determined that additional work is necessary to perfect an extraction/pre-filtration step to eliminate unstable potential readings due to solid particles in suspension.

Detailed instructions are given for preparation and modification of the CAOB solution. An appendix of

ion-selective electrode applications in geochemistry includes 59 entries, along with a bibliography of 76 references.

ACKNOWLEDGEMENTS

I would like to extend special thanks to my advisor, Dr. John Wilband. In addition to supplying the primary electrodes, he showed monumental faith and patience in allowing me to pursue this investigation.

I am very appreciative of the interest and enthusiasm of Dr. Stanley Crouch of the Department of Chemistry, who also served on my thesis committee. Dr. Jim Trow was a special friend, and I am greatful for his constant encouragement and attempts to extract some outside financial support.

Enabling this work to be finished was Dr. Philip Malone, Department of Geology, Wright State University, who opened his laboratory facilities to me, provided inspiration for this study, and many discussions of problems. I am also indebted to Dr. Michael Smith of the Wright State Department of Chemistry, who first badgered me into taking analytical chemistry courses as an undergraduate, thus awakening my interest in truly interdisciplinary geochemistry as a career. He also gave valuable suggestions from his own personal experience with electrodes, as well as "super water" and other miscellaneous items.

Last, but not least, are my close friends Sue Leo, Don Carpenter, John Ansted, Jim Dalman, Fred Lawrence, Russ

Harmon, and the local Coca-Cola Bottling Company, who became a bottomless well of moral support and good humor when the skies were the stormiest.

TABLE OF CONTENTS

APPENDICES

LIST OF FIGURES

CHAPTER I

INTRODUCTION AND SCOPE OF STUDY

In view of the absence of articles describing the use of a silver sulfide solid-state membrane electrode for geochemical investigations, this study was devised with the intention of exploring the feasibility of its use in that capacity. Since reasonably accurate and precise laboratory methods presently exist (Rubeska et al., 1967; Slavin, 1968; Ward et al., 1969; Perkin-Elmer, 1971; Nakagawa, 1975; and Minkkinen, 1975, to choose but a few), this study would emphasize the potential of the electrode for use in or near the field, in place of colorimetric techniques.

There are several areas that need to be investigated to determine the potential usefulness of the electrode. One is the linear response range, value of the slope, and the reproducibility of the slope for the buffer medium selected. A suitable decomposition method must be found to liberate the silver, and a buffer must be designed to homogenize variations in the solution matrices from sample to sample, and to eliminate any significant chemical or electrode interference.

Finally, the detection limit of the electrode/buffer system must be investigated. Prior studies have indicated a lower detection limit on the order of 0.01 ppm (0.01 μg/g) under ideal laboratory conditions, for samples which are not buffered with respect to silver activity. The laboratory samples at the low concentrations have also all been at very low ionic strengths.

The general range in silver content to be expected in soils has been reported to be 0.01 to 5 parts per million by Siegel (1974). Without dilutions resulting from decomposition and buffering, the experimentally determined lower detection limit is already nearly reached, so this may possibly provide a very real limit on the applicability of the electrode. The effect of higher ionic strength on the detection limit and the slope needs to be investigated, and could also conceivably be a limitation.

The development of a successful field method for silver analysis using an ion-selective electrode would be a tremendous aid to the exploration geochemist, even though it would by no means replace such laboratory methods as atomic absorption or neutron activation.

Due to the scarcity of information of the application of cation-selective electrodes in general to geochemical systems, and the large number of potentially useful ones, this investigation hopefully will provide useful information for future analytical geochemists working in this field.

CHAPTER II

PREVIOUS WORK

Since the mid-1960s, there has been a substantial rise in applications and use of ion-selective electrodes. This, in part, was due to the development of solid crystal, liquid, and gel exchange membranes, with much greater selectivity than most of their glass forerunners. Electrodes have been especially useful for soil scientists, since they primarily respond to activities of ions in solution, and can be fairly directly applied to cation exchange equilibrium studies (Carlson and Keeney, 1971). Water quality parameters that are defined by activity terms can be more efficiently determined (theoretically) using direct measurement by electrodes (Durst, 1969; Carlson and Keeney, 1971). Continuous and/or automated monitoring of certain chemical constituents in water supplies such as the F^-/Cl^- ratio studies cited by Durst (1969, p. 393), is facilitated by the selective-ion electrode and chart recorder.

Though many cation and anion-sensitive electrodes presently exist, and can sometimes be fabricated upon demand, only several have seen widespread use in geochemical applications.

Probably the most documented application is that of the fluoride ion-selective electrode. This electrode is of the solid variety (using a Eu^{3+}-doped LaF_3 crystal), and was applied to water analysis by Frant and Ross, Jr. (1968). Many water studies have followed (see Appendix G for examples).

Application to fluorine determinations in rocks and minerals has also been greatly studied. Van Loon (1968) fused powdered fluoride-bearing minerals, decomposed the bead, and determined the fluorine concentration using direct potentiometric comparison with standard solutions. Jagner and Pavlova (1972) determined fluorine concentrations in silicate rocks by first sintering powdered samples with sodium carbonate and zinc oxide, and then the sinter was digested for 12 hours in a steam bath. Following leaching with sodium carbonate solution, rinsing, and filtration, a complexing buffer solution was added to adjust the pH, and then the actual concentration in the final solution was determined by multiple standard additions and a Gran plot. Crenshaw and Ward (1975) report a similar procedure, which is an extention of methods of Edmond (1969), Ficklin (1970), and Ingram (1970). They used a sodium carbonate/potassium nitrate flux for sintering, and employed a pH and ionic strength adjustment buffer (TISAB) adapted from Frant and Ross, Jr. (1968). The concentration was determined directly from a known-increment scale on an Orion 407 millivolt meter, following a standard addition. The reported deviation from recommended standard values for the samples tested is substantially greater for the Crenshaw and Ward procedure than that of Jagner and Pavlova.

This may be due to the implicit assumption of true theoretical Nernstian slope in reading directly off of the meter scale, as well as any solution variables.

A slightly different approach to the fusion-analysis of soil and vegetation fluorine has been taken recently by McQuaker and Gurney (1977). Following fusion with NaOH, the pH was adjusted to 8-9 and the samples were filtered to remove most of the Al, Fe, Ca, and Mg as insoluble silicates. Following filtration, the F^- concentration was determined using a TISAB and a single solution calibration procedure. The precision was reported to be 4.1% for soil samples (mean relative standard deviation), and recovery studies showed better than 95% accuracy.

A versatile and simple technique for silicate materials has been presented by Bodkin (1977) for samples of up to 0.4% F in the sample solution. Samples are decomposed by lithium metaborate fusion in a muffle furnace, and the beads are dissolved in 4% (v/v)HNO_3. The buffer system employed is 0.5M in citrate, 0.5M in NaCl and 0.03M in DCTA at a final pH of $\sim$5.5. Numerous samples were analyzed with excellent agreement to "accepted" values. Volatile loss of fluorine was observed when fusions were carried out over gas burners, adding an additional consideration to sample preparation procedures.

Sulfide determinations can be made in water (Orion, 1969), and have been reported by Allum, Pitts, and Hollis (1971) for submerged soils. Many calcium determinations using glass as well as liquid and gel membrane electrodes have been reported, though they are normally subject to some selectivity and pH problems. Woolson, Axley, and Kearney (1970) compared calcium in soil by electrode to atomic absorption values with some success, and Thompson and Ross, Jr. (1966) used an electrode to determine calcium in sea water. Thompson (1966) described a method for magnesium determination in sea water, and another method for calcium analysis in natural water samples was developed by Hulanicki and Trojanowicz (1974) using a constant complexation buffer. Haynes and Clark (1972) used a combination standard addition and potentiometric titration method to determine chlorine in silicate rocks, following fusion of the samples.

Soil scientists have developed quite a few methods using electrodes selective for K^+, NO_3^-, B (as tetrafluoroborate), and Na^+, and several examples are cited by Carlson and Keeney (1971).

Though electrodes specific to many more ions, including potentially geochemically useful ones Cd^{2+}, Cu^{2+}, Ag^+, Pb^{2+}, Zn^{2+}, and Hg^{2+} exist at present, applications or attempts at applications to other geochemical systems are conspicuously absent from the literature.

Suggestion of the application of the Cu^{2+} electrode to soil analysis was made in Carlson and Kenney (1971). The cupric ion-selective electrode was first applied to the analysis of natural waters by Smith (1972) and Smith and Manahan (1973). This was accomplished by the design of a special complexing antioxidant buffer (CAB or CAOB) which simultaneously adjusts pH, ionic strength, keeps dissolved copper ion in the divalent state, ties up iron which might precipitate as hydroxides and oxyhydroxides, and provides a constant weakly-complexed fraction of the cupric ion in the solution. Friederick et al. (1972), suggested the feasibility of the cupric ion-selective electrode for water analysis in geochemical stream surveys in conditions of low interfering ions, but the Smith and Manahan method overcomes virtually all major interferences that would likely be found. Potential interferents Ag^+ and Hg^{2+} would not normally be found in high concentrations in natural waters, nor would interfering anions Cl^- and Br^-.

Schuller (1976) was the first to develop a system to apply the cupric ion-selective electrode to geochemical reconnaissance of soils. This method is a straightforward adaptation of the Smith and Manahan (1973) procedure, and uses the residual acid from the soil digestion as a part of the acetate buffer system. The copper concentration was calculated by standard addition, from a value for the response slope determined experimentally beforehand by a fairly simple multiple addition technique. Though copper concentration trends could be precisely followed compared to atomic absorption values, the electrode values were significantly lower (in the neighborhood of 30%) in most cases. Possible explanations include sample inhomogeneities, the poorer efficiency of the cold 6 M HCl digestion, poor precision and/or reproducibility of the experimentally determined slope value, and surface adsorption on particles in the unfiltered samples. There may also have been problems due to a "suspension effect" at either of the electrode/solution interfaces, analogous to that reported for pH measurements by Feldman (1956).

The silver ion-selective electrode is usually constructed with an Ag_2S solid crystal membrane, and has been used in several chemical studies. Hseu and Rechnitz (1968) first evaluated the Orion 94-16 Ag_2S solid membrane electrode in alkaline solution, at 25 C. This electrode was found to respond in good agreement with the theoretical Nernstian prediction, the experimental slope being determined to be 59.0 mV per decade of Ag^+ activity over a range of pAg^+ of 1 to 4. The pH of the tested solutions was not specified beyond "alkaline" for αAg^+ (Ag^+ activity) measurements. The electrode was found to respond linearly to αS^{2-} with a slope of 29.7 mV (at $\mu = 0.3$ and 0.5 M) per decade αS^{2-} at a pH between 11.4 and 11.8 and for pAg^+ from 2.2 to 7.0. The theoretical Nernst slope is 29.58 mV per decade activity change for divalent ions and 59.16 mV per decade activity change for monovalent ions at 25 C (see Chapter III).

Light and Swartz (1968) extended the investigation of the Orion model 94-16 Ag_2S solid membrane electrode to include temperature coefficients, response time, the effect of oxidizing conditions, and other possible interferences. Buffering the solution for ionic strength and pH (using a background of 1.0 M NaOH), a response slope of 29 mV per decade S^{2-} was determined at 25 C over an unspecified concentration range. No detailed results for detection limits or response slope to αAg^{+} were given, but a summary table stated Nerstian response to αS^{2-} over a pS^{2-} range of 0 to 5 for total sulfide, and a pS^{2-} range of 0 to 20 for free sulfide. The slope was said to be Nerstian toward αAg^{+} over the pAg^{+} range of 0 to 5 for total silver ion, and 0 to 23 for free silver ion. The electrode was further stated to be pH-independent from pH 0 to 14, and the only interference to either ion analysis was Hg^{2+} to silver ion. This interference was somewhat predictable from comparison of the solubility product contants at $\mu = 0.1$ (Ringbom, 1963) for HgS ($pK_{s0} = 51$) and Ag_2S ($pK_{s0} = 48.1$). The nature of this interference is most likely reaction between the Hg^{2+} ions and the sulfide component of the solid membrane, along the lines of the example given by Ross (1969, pp. 82-86). Ross further ascribed the lower detection limit of approximately 10^{-8} m Ag^{+} for "total" silver ion to difficulties arising from adsorption and desorption phenomena at the container and electrode surfaces (ibid., p. 77), and freedom from interference due to strong oxidizing conditions was reaffirmed.

The Light and Swartz (1968) and Hseu and Rechnitz (1968) studies are also summarized in Butler (1969, pp. 177-80).

Durst (1969, pp. 403-6) described Nernstian response down to pAg^+ = 25 M on sample volumes of only 5μL, and suggested that since this was equivalent to a probability of substantially less than one free silver ion in the solution (which was continually buffered in silver-complexing agents), the electrode must have at some point responded to complexed silver ion. He further pointed out that usability as a silver sensor would be limited in basic solutions due to the precipitation of Ag_2O. If silver-complexing agents are used to prevent this precipitation, the use of a standard addition technique is necessary to determine total silver ion concentration.

There have been only a few subsequent applications of the Ag_2S solid membrane electrode, and none of them particularly useful geochemically. Müller, West, and Müller (1969) described the feasibility of determination of silver concentrations down to approximately 10^{-7} M (∿13.5 parts per billion) by direct potentiometry, once again with the Orion 94-16. Their response slope determination was done by addition of small aliquots of $AgNO_3$ solution to 100 ml of 0.1 M $NaNO_3$, and adjusting the sum of added silver ion for volume change. Their electrode showed virtually theoretical response over the range of pAg^+ from 5.92 to 6.92 (about 13 to 130 ppb), at temperatures between 22 C and 28 C. Malfunctioning of the electrode was observed when the Cl^- concentration exceeded about 2.8×10^{-3} M (100 ppm) for an unspecified silver condentration ($<4.6 \times 10^{-7}$ M).

Durst and Duhart (1970) used the Orion 94-16 electrode to monitor silver loss from solution due to adsorption on the container walls. Silver loss was determined by direct potentiometry, comparing the observed potentials to a calibration curve in the silver concentration range of 10^{-6} M to 10^{-7} M. The solutions were simply dissolved $AgNO^3$ in distilled water, with approximately neutral pH.

A method has been published (Orion Applications Bulletin No. 14) that describes a procedure useful for determining total silver ion concentration in photographic fixing bath solutions from 10^{-1} M to 10^{-4} M in silver ion, by standard addition potentiometry. This can be accomplished even though almost all of the silver ion would be tied up in a strong ($\beta_1 = 10^{8.82}$, $\beta_2 = 10^{13.5}$, Ringbom, 1963) thiosulfate complex. Details of the reasons for the concentration limits of the method as well as the precise nature in terms of chemical composition and pH of the fixing solution are not given, and must be inferred. Also, no accuracy or precision data are presented. Lapatnick (1974) used the silver ion-selective electrode to monitor Ag^+ concentration in silver plating baths, with an average error of 2%.

CHAPTER III

THEORY OF ELECTRODE RESPONSE

Glass Membrane Electrodes

There are two main types of ion-selective electrodes quantitatively sensitive to silver ion. One is a glass membrane electrode, which is rendered selective to silver ion by the composition of the glass. Though each manufacturer has its own particular recipe of additives, generally the silver-selective glass membranes have a high Na_2O (11-29%) and high Al_2O_3 (18-19%) content, according to Rechnitz (1967). A reliable method to predict properties of a glass given its composition has yet to be found, and development is still largely a matter of trial and error.

A selectivity constant can be defined for glass electrodes, which is generated simultaneously by the relative mobilities in the glass of the ions under consideration, and their relative ion-exchange constants for aqueous phase/glass interaction (Eisenman, 1969). For convenience, the selectivity ratio of glass membrane electrodes is often expressed for each cation relative to the hydrogen ion. Eisenman has defined a selectivity ratio K for M_1^+ over M_2^+ using the following equation (Rechnitz, 1967):

$$E\left\{\begin{matrix} M_2^+ = 0.1\ M \\ M_1^+ = 0\ \ \ \ M \end{matrix}\right\} - E\left\{\begin{matrix} M_2^+ = 0\ \ \ \ M \\ M_1^+ = 0.1\ M \end{matrix}\right\} = -\frac{RT}{F}\ln K_{M_1^+/M_2^+}$$

where E is the measured cell electromotive force (emf), R is the universal gas constant, F is the Faraday, T is temperature in degrees Kelvin, and M_1^+ and M_2^+ are the only potential-determining cations.

In terms of construction, a glass electrode is made from a mixture of oxides of elements of oxidation state +3 or greater with oxides of elements of oxidation state +1 or +2 (Eisenman, 1969). After the mixture is melted and then cooled, a solid is formed in which the most mobile charged species are monovalent cations.

When the bulb of a glass electrode is inserted into an aqueous solution, a layered structure is formed between the external solution to be measured and the internal filling solution. Schematically, it may be represented by (modified from Skoog and West, 1971):

external solution | hydrated gel layer $\sim 10^{-4}$ mm | dry glass ~ 0.1 mm |
hydrated gel layer $\sim 10^{-4}$ mm | internal solution

though there may be in reality more intermediate layers. As the hydrated layers dissolve, additional hydration of the glass takes place, such that the hydrated gel layer maintains a reasonably constant thickness. The rate of hydration is largely a function of the hygroscopicity of the glass and the sample solution (or filling solution), and is mainly responsible for determining the practical lifetime of the electrode.

Metal ions are taken up by the glass in a cation-exchange process, and diffuse into the hydrated layer to some extent. Since tracer experiments failed to show complete migration of tritium from the labeled to unlabeled solutions (Rechnitz, 1967), it was concluded that the current generated must be the rate of some charge-transfer process across the membrane. Further experimentation revealed that the charge is carried by the cationic species of lowest charge available through an interstitial mechanism, wherein each charge carrier only has to move a few atomic diameters before passing on its energy to the next carrier.

When a membrane made of one of these specially-prepared glasses is used to separate an aqueous solution to be measured from an internal filling solution, both of the same salt, a cell potential is developed. This potential can be related to the activity of arbitrary monovalent ion M (αM) in solution.

First, on each side of the glass there will be a half-cell reaction concerning αM at each interface, which may be expressed as:

$$E_1 = k_1 + \frac{RT}{F} \ln \frac{\alpha M_{1o}}{\alpha M_{1g}}$$

$$E_2 = k_2 + \frac{RT}{F} \ln \frac{\alpha M_{1i}}{\alpha M_{1h}}$$

wherein R, T, and F have their usual thermodynamic identities; αM_{1o} and αM_{1i} are the activities in the solutions on the outside and inside of the glass respectively; M_{1g} and M_{1h} the activities in the corresponding gel layers; and k_1 and k_2 are constants relating the respective available sites for M at the gel surfaces (Skoog and West, 1971). The concept of activity and methods for the calculation of activity coefficient is discussed in detail in Hem (1961), Butler (1964), Garrels and Christ (1965), Stumm and Morgan (1970), and Leyendekkers (1971) to cite but a few. Since the calculation methods used in this study solve directly for concentration, the discussion of activity is not undertaken here.

If the exchange equilibrium goes so far to the right that virtually all sites available to it are occupied by M, then αM_{1g} and αM_{1h} should be equal. If, also, there are the same number of exchange sites available in each gel layer, $k_1 = k_2$.

Since the boundary potential, E_b for a membrane is given by

$$E_b = E_1 - E_2$$

where E_1 represents the component at the external solution and gel interface, and E_2 at the internal interface, these two full equations may be substituted, yielding

$$E_b = E_1 - E_2 = \frac{RT}{F} \ln \frac{\alpha M_{1o}}{\alpha M_{1i}}$$

along with the discussed simplifications. Restating, if the two gel surfaces are identical, the potential developed will depend only on M in the external and internal solutions.

If the internal filling solution has a constant composition (and therefore, αM_{1i}), then that term can be removed as a constant, and the overall expression then becomes

$$E_b = \text{Constant} + \frac{RT}{F} \ln \alpha M_{1o}$$

From this equation it can be seen that it is possible under these circumstances to obtain a direct measure of the activity of ion M in an external solution, as soon as a suitable reference electrode is connected to complete a circuit.

In actual practice there are normally several ions which interact in the solution, and which ellicit some electrical response from the membrane. The contributions of these other ionic species are weighted through their selectivity constants.

An example of the adjustment necessary for the case of two cations is displayed in the expression

$$E_b = E_c + \frac{RT}{F} \ln \frac{\alpha M_{1o} + \left[\left({}^{u_2}/_{u_1}\right) K_{1,2}\right] \alpha M_{2o}}{\alpha M_{1i} + \left[\left({}^{u_2}/_{u_1}\right) K_{1,2}\right] \alpha M_{2i}}$$

for the ideal case where n, the ion exchange exponent, = 1. The weighting factor, $\left[({}^{u_2}/u_1)K_{1,2}\right]$ contains terms $({}^{u_2}/_{u_1})$ and $K_{1,2}$, which are the mobility ratio of ions M_2 and M_1 in the membrane, and the ion exchange factor characteristic of the exchange of M_1 and M_2 between the aqueous phase and membrane, respectively (Eisenman, 1969). This weighting factor is sometimes referred to as the "potentiometric selectivity ratio." The mobility may be combined with the ion-exchange equilibrium constant into a "selectivity coefficient." and $\left[({}^{u_2}/u_1)K_{1,2}\right]$ may be replaced by $K\alpha M_2{}^{z_2/z_1}$, where K is the new selectivity coefficient, z_2 is the charge of the interfering ion, and z_1 is the charge on the primary ion of interest. The addition of more activity and selectivity terms enable the equation to be extended to more complicated cases. The above equation is also independent of time, and is therefore applicable as soon as equilibrium at the membrane/ solution interfaces is established (Eisenman, 1969).

Since for these glass membrane electrodes (and any solid ion-exchange types) the overall selectivity is a combination of the ion exchange equilibrium selectivity and the relative mobilities of the ionic species within the exchanger, only several have a combination of these two properties which permit operation with few interferences. The most commonly used glass ion-selective electrodes are for H^+, Ag^+, Na^+ and Li^+.

If the selectivity ratio is very high for one particular ion over the others, the terms for these other ions may be assumed to be negligible, and they may be eliminated from the overall equations. Also, under some circumstances, if their activities are not negligible but are a constant background to the activity change of a single species, the more convenient form

$$E_{obs} = E_{const} + \frac{RT}{ZF} \ln \alpha M^{z}$$

may be used, where E_{obs} is the observed potential, E_{const} is a constant term combining effects of the internal filling solutions, the reference electrode used, liquid junction potentials, the other ionic species in solution, and z and Z are the charge on the species of interest (including sign). The value of this constant tends to very with time, frequently called "potential drift," which makes direct potentiometric measurements more difficult to do accurately than addition techniques, discussed later.

It should also be pointed out that for many reasons, various electrodes will deviate to some degree from the ideal Nerstian slope of RT/ZF. In such cases, an experimentally determined slope, S, may be inserted instead, giving

$$E_{obs} = E_{c} + 2.303S \log \alpha M^{z}$$

under specified temperature, pressure, and solution composition conditions. Curvature of the ideal Nerstian line may also occur due to variations of the liquid junction potential of the reference electrode over wide concentration ranges, as pointed out by Johansson and Edström (1972).

Solid-State Membrane Electrodes

Solid membranes can be made from cyrstalline materials that are ionic conductors at the temperature of use of the electrode. The crystal may be used in the form of a thin disk, providing it is of low solubility in the sample solution, mechanically stable, and chemically inert in the sample solution (Ross, Jr., 1969).

The mechanism of electrical conduction is facilitated by lattice defects. Mobile ions adjacent to the defects are induced to move into the vacancies, which are ideally tailored for specific ions with regard to charge distribution, size, and shape. Normally only one lattice ion is considered to be the mobile one, and usually it is the one with the smallest charge and ionic radius. The very high selectivity of the solid-state electrode is mainly due to this ability to restrict the movement of ions other than the one to be sensed. In some cases, resistivity to electrical conduction can be lowered by "doping" with a divalent cation. In the highly successful LaF_3 membrane electrode, the divalent cation is Eu^{2+}, though the charge is still carried by the F^- ions (Rechnitz, 1967).

The membrane of the silver-sulfide electrode used in this study is a homogeneous Ag_2S solid, in which the only mobile ion is Ag^+. This electrode responds directly to Ag^+ ion in external solution, and responds to S^{2-} activity in the external solution indirectly. The mechanism for S^{2-} sensing appears to be the fixing of Ag^+ activity at the membrane surface by the S^{2-} in solution (Carlson and Keeney, 1971). Cammann and Rechnitz (1976), however, present new evidence that S^{2-} reacts with interstitial silver ion and is also involved in the charge-transfer process.

Certain other solid membrane electrodes, notably the cupric ion-sensitive electrodes, have their membrane pellets made out of a finely divided mix of MS (where MS is the sulfide of any divalent cation, M^{2+}) dispersed in a matrix of Ag_2S, and pressed into a disk. The charge is thought to be carried by the Ag^+ ions. The presence of the considerable amount of Ag_2S means that in solutions containing Ag^+ ions, the electrode also functions as a silver detector, creating an interference. The solubility of many of the metal sulfides in acid solutions provides a lower pH limit to their Nernstian response (Ross, Jr., 1969).

Since no foreign ions can enter the lattice structure, interferences result only from chemical reactions of the ions in solution (method interferences) or at the surface of the crystal (electrode interferences). Because of the different nature of this electrode from the glass-types, the selectivity is much greater, and response should theoretically always be Nernstian. This can be expresssed in fairly simple equations as long as selectivity factors are excluded. A more rigorous look at specific interferences of interest will be taken later.

The observed potential E_{obs} can be related to activity of monovalent ion M^+ in the solution through:

$$E_{obs} = E_c + \frac{2.303\ RT}{F} \log \alpha M^+$$

It should be recognized that the concentration of M^+ in the external solution is the sum of that originally present plus those M^+ ions resulting from the dissolution of the membrane. In most cases the latter contribution is negligible (Parthasarathy et al., 1974).

This assumes as before that the junction potential, if not negligible, can be described within the constant, and that the αM^+ in the internal filling solution (if present) is also fixed and is contained in the constant term. Deviations from the theoretical Nernst factor of $\frac{2.303\ RT}{ZF}$, which is 59.2 mV at 298 K, do often occur in practice, in which case an experimentally determined slope value is substituted.

For the CuS solid state electrode, representative of the mixed-sulfide type, the expression can be derived as follows, based on Ross, Jr. (1969).

If we start with a solution containing cupric ion but not silver ion, the potential at the crystal/solution interface is determined by both

$$2Ag^- + S^{2-} \rightleftarrows Ag_2S(s)$$

and

$$Cu^{2+} + S^{2-} \rightleftarrows CuS(s)$$

for which

$$K_{s0(Ag_2S)} = (\alpha Ag^+)^2(\alpha S^{2-})$$

$$K_{s0(CuS)} = (\alpha Cu^{2+})(\alpha S^{2-})$$

if Ag_2S and CuS are pure solids. Solving for αAg^+

$$\left[\frac{K_{s0(Ag_2S)}}{\alpha S^{2-}}\right]^{\frac{1}{2}} = \alpha Ag^+$$

and substituting for (αS^{2-}), we get

$$\left[\frac{K_{s0(Ag_2S)}}{K_{s0(CuS)}}\ \alpha Cu^{2+}\right]^{\frac{1}{2}} = \alpha Ag^+$$

This may be substituted in the previous full Nernst equation for αM^+, yielding:

$$E_{obs} = E_c + \frac{2.303\ RT}{2F}\log\ \frac{K_{s0(Ag_2S)}}{K_{s0(CuS)}}\ \alpha Cu^{2+}$$

Since $K_{s0(Ag_2S)}/K_{s0(CuS)}$ is a constant, we can further simplify to

$$E_{obs} = E_c + \frac{2.303\ RT}{2F}\log\ \alpha Cu^{2+}$$

where the solubility ratio becomes part of the new constant E_c.

Because Z = 2 for divalent cations, the theoretical Nernst factor becomes 29.6 mV.

The Ag_2S membrane electrode responds to αS^{2-} in solution in a similar indirect manner. We can begin to derive this sensitivity if we start with a sample solution initially containing no silver (I) ion. The Ag_2S membrane will then provide a few Ag^+ ions through its dissolution. This provides a finite silver ion activity, however small it may be. This activity is governed, in the absence of complexing agents, by the sulfide ion activity through the solubility product constant, and can be calculated from

$$Ag^+ = \left[\frac{K_{s0(Ag_2S)}}{\alpha S^{2-}}\right]^{\frac{1}{2}}$$

as before. Substituting again for αAg^+,

$$E_{obs} = E_c + \frac{2.303\ RT}{2F} \log \frac{K_{s0(Ag_2S)}}{\alpha S^{2-}}$$

Since $K_{s0(Ag_2S)}$ is a constant, it can be incorporated into E_c, and moving (αS^{2-}) to the numerator, the form becomes:

$$E_{obs} = E_c - \frac{2.303\ RT}{2F} \log \alpha S^{2-}$$

It has been suggested by Ross, Jr. (1969, ibid., p. 435) that the lower limit of response to αAg^+ of the silver sulfide electrode may be raised by adsorption of silver ion on the membrane surface, but experimental data have not been presented in substantiation for this particular electrode.

Construction of Solid-State Electrodes

Normally, a solid-state electrode consists of an epoxy or inert plastic hollow cylindrical body, in which a sensing wire is passed and connected to the inside of the crystal membrane (Fritz and Schenk, 1974).

It is also possible to have a built-in internal reference electrode immersed in a filling solution. A cation-responsive internal system may use an $AgNO_3$ filling solution (Covington, 1969, and Light and Swartz, 1968). This particular arrangement is used in the popular Orion model 94-16 employed in the studies discussed in Chapter II.

In many cases, the exact mode of internal construction is proprietary information, unless one disassembles the product to find out.

Reference Electrodes

In order to complete an electrical circuit, a reference electrode must be employed having a fixed potential in the analyzed solutions. There are many different kinds described in the chemical literature and manufacturers' brochures, especially with regards to pH measurements (which, in itself, is a cation-selective electrode process). Only practical considerations relating to their use in this investigation will be discussed here.

A conventional single-junction calomel or silver chloride reference electrode is unsuitable for use in analyses for Cu^{2+}, Ag^{+}, and S^{2-}. There are several requirements they do not fulfill, mainly in association with problems stemming from solution leakage.

1. The filling solution should not contain the ion to be measured.

2. No ion in the filling solution may form a complex with the ion to be measured.

3. No ion in the filling solution may form a precipitate with the ion to be measured.

4. No ion in the filling solution may form a precipitate with any ion in the sample solution.

It is likely that in silver, copper, or sulfide determinations in natural waters or geochemical samples, all four of the requirements would be violated. Chloride complexes or precipitates cupric ions and silver ions, which not only remove the ions from availability to be measured, but the precipitates may also clog the electrode membranes, alter the junction potentials, or react with the membranes themselves. Silver (I) ions can leak from the electrode, contaminating the solution to be measured. This gives erroneous concentration information if silver is being determined, and an electrode interference in cupric ion analysis. Mercury (II) ions would possibly form insoluble chlorides or sulfides, clogging the membrane, creating a chemical interference in the solution, or an electrode interference, for both the Ag^+ and Cu^{2+} probes.

These problems can be avoided by employing a double-junction reference electrode, with an inert bridging electrolyte. In this study, double junction electrodes using the original manufacturers' filling solutions were employed. In both cases the internal filling solutions were of KCl, and the external solutions were of KNO_3, which would not interfere with the ions of interest in solution.

Solid-State Electrode Interferences

Interferences fall into two broad types, which are defined by Riseman (1970) as follows. "Method interferences" are those which mask the ion that is sought by making it unavailable to the electrode. "Electrode interferences" are chemical species which either destructively react with the membrane, or which are mistaken by the electrode for the ion being measured. The latter includes common ion(s) adsorbed onto the membrane surface.

Method interferences will not be considered here, since they are so highly variable with the scheme of analysis. They will be considered in the experimental section as they present themselves.

The first set of interferences to be considered is that for the Ag_2S membrane electrode during silver ion analysis.

In order for Nernstian response to hold, the sample solution must be free of species that can react with either component of the membrane. With many types of electrodes, there are several inorganic ions that combine to form more insoluble salts. An example is the interference of SCN^- in solution to the Br^- sensing electrode (AgBr membrane).

If (αSCN^-) exceeds (αBr^-) to the same ratio as the ratio of their solubility products, then the AgBr in the membrane will begin to convert to AgSCN, and the electrode will become a thiocyanate sensing device (Ross, Jr., 1969). A sharp break is seen in a plot of potential versus anion (Br^- or SCN^-) activity.

For the Ag_2S membrane electrode, there are few common interferences of this type, since $K_{s0(Ag_2S)}$ is extremely high ($\sim 10^{-48}$), and the membrane is quite stable. Mercury (II) ion is an interferent when present, since $pK_{s0(HgS)} \sim 51$, but no other cations form sulfides as insoluable as those of silver (I) and mercury (II). The onset of mercuric ion interference may be predicted in general terms from the following proposed reaction:

$$Ag_2S(s) + Hg^{2+} \rightleftarrows HgS(s) + 2Ag^+$$

$$K_{s0(HgS)} = (\alpha Hg^{2+})(\alpha S^{2-})$$

$$K_{s0(Ag_2S)} = (\alpha Ag^+)^2(\alpha S^{2-})$$

$$(\alpha Hg^{2+})/(\alpha Ag^+)^2 = K_{s0(HgS)}/K_{s0(Ag_2S)}$$

$$(\alpha Hg^{2+})/(\alpha Ag^+)^2 \sim 10^{-3}$$

For the copper (II) ion-selective electrode, an analogous procedure will yield the following cation interference ratios, using data from Ringbom (1963):

$$(\alpha Ag^+)^2/(\alpha Cu^{2+}) \sim 10^{-14}$$

$$(\alpha Hg^{2+})/(\alpha Cu^{2+}) \sim 10^{-17}$$

Smith and Manahan (1973) also report that due to the "relative solubilities of copper (II) sulfide and iron (III) sulfide" ferric ion may be expected to interfere when $[Fe^{3+}]/[Cu^{2+}] = 0.1$.

Using solubility ratios is a highly simplistic approach, and should normally be considered to be a rough predictive tool, since actual solubilities are controlled to a great extent by the common ion effect and complexation equilibria involving other species in the solution. The reported K_{s0} values and those calculated from free energy data also vary by several orders of magnitude, making experimental and theoretical quantitative agreement highly fortuitous. Adsorption of sensed ions onto the membrane as previously cited may also be responsible for raising the estimated detection limit based on these K_{s0} considerations by as much as 10-12 orders of magnitude.

A variation of this electrode interference is the creation of a solid precipitate that can clog the membrane. An example would be the formation of AgCl precipitate when making silver additions to solutions containing free chloride ions in the appropriate amounts. In addition to removing the silver from the solution, surface adsorption on the membrane inhibits the accurate measurement of ionic potentials at the solution/membrane interface, or impedes the movement of ions in the membrane itself. Tarnishing was observed by Müller, West, and Müller (1968) for solutions of unspecified $[Ag^+]$ ($<4.6 \times 10^{-7}$M) having $[Cl^-] = 2.8 \times 10^{-3M}$ at $\mu = 0.1$.

The CuS-Ag_2S membrane electrode is also subject to a form of interference due to conversion of part of the Ag_2S phase to 2AgCl by the following reaction (Ross, Jr., 1969):

$$Ag_2S(s) + Cu^{2+} + 2Cl^- \rightleftarrows 2\ AgCl(s) + CuS(s)$$

For the above reaction,

$$K_{RXN} = \frac{(\alpha AgCl)^2(\alpha CuS)}{(\alpha Ag_2S)(\alpha Cu^{2+})(\alpha Cl^-)^2}$$

Substituting the K_{s0} expressions

$$K_{RXN} = \frac{(\alpha Ag^+)^2(\alpha Cl^-)^2(\alpha Cu^{2+})(\alpha S^{2-})\ K_{s0(Ag_2S)}}{K^2_{s0(AgCl)}\ K_{s0(CuS)}(\alpha Ag^+)^2(\alpha S^{2-})^2(\alpha Cu^{2+})(\alpha Cl^-)^2}$$

which simplifies to

$$K_{RXN} = \frac{K_{s0(Ag_2S)}}{K^2_{s0(AgCl)}K_{s0(CuS)}}$$

This implies that, to prevent the reaction from proceeding to the right,

$$(\alpha Cu)(\alpha Cl)^2 < \frac{K_{s0(Ag_2S)}}{K^2_{s0(AgCl)}\ K_{s0(CuS)}}$$

Should the activity product exceed the value on the right, the silver sulfide at the membrane surface would theoretically become converted to silver chloride, and the electrode would abruptly change function to a chloride ion detector. Similar problems with other ions are possible.

Another major type of electrode interference to be considered is that due to the oxidation or reduction potential existing in the solution. While using the cupric ion-selective electrode, sulfide or sulfide species in equilibrium at the electrode surface may become oxidized, resulting in electrode instability (Smith, 1972). The ferric ion is thus a dual interferent; first, because of its ability to form an insoluble sufide at the electrode surface, and also because of its behavior as a moderately strong oxidizing agent. This is particularly important in natural water samples, in which Fe^{2+} is easily oxidized through atmospheric contact. The mixed $CuS\text{-}Ag_2S$ membrane is also easily oxidized in 0.1 M $HClO_4$, according to Johansson and Edstrom (1972).

The Ag_2S membrane is reportedly not sensitive to redox couples in solution, including Fe^{3+} and nitric acid, according to both Butler (1969) and Swartz and Light (1968).

Some membranes with higher solubilities may also show a pH limitation. This is due to an increased rate of membrane dissolution attributed to the formation of HS^- and H_2S in the solution under oxidizing conditions (Ross, Jr., 1969). The usable pH range is reported to be 0 to 14 for the Ag_2S membrane by Light and Swartz (1968), but this does not consider the effects of the pH on the silver species in the solution. The theoretical pH range for the mixed $CuS\text{-}Ag_2S$ membrane is also reported to be 0 to 14, but is subject to the limitations imposed by the formation of insoluble copper hydroxides, phosphates, carbonates, etc. (Orion, 1968).

Strong complexing agents in solution (e.g., formation or stability K values very large) for one of the membrane components have a tendency to raise the lower detection limit of the electrode. This is done mainly by increasing the solubility of one or more of the membrane components in the test solution. The electrode "sees" this as an increase of that species in the solution. This has been documented for F^- analysis using the LaF_3 membrane electrode in solutions containing citrate by Ross, Jr. (1969), and for the cupric ion-selective electrode in solutions containing Na_2EDTA by Smith (1972). Butler (1969) states that the Ag_2S membrane electrode is free from interference by strong complexing agents such as thiosulfate and iodide. Durst (1969) shows that that particular electrode may to a degree respond to complexed silver ion, and laboratory results presented later in this report indicate that contrary to Butler (1969), the lower level of detection for Ag^+ is raised by high levels of thiosulfate in the solution. By definition, this should constitute an electrode interference.

A problem with almost all electrode measurements, though possibly not technically always an interference, is that of long-term potential drift. This is likely due to changes in components of the "constant" term of the response equation, rather than in sensitivity to the ion being measured (Smith, 1972). Changes of ±10 mV are not uncommon from day to day in identically prepared standard solutions. The length of time for these changes to take place is highly variable, and it is gradual rather than abrupt. Frequent restandardization is often necessary when direct potentiometric analyses are being conducted.

Colloids and suspensions in the solution may cause a variable modification of the liquid junction potential or the true membrane potential of both the indicator electrode and the reference electrode when the particles are highly charged. This effect was pointed out for pH measurement by Feldman (1956), and may be extended to ion-selective electrode operation by analogy. Using the ion-selective electrode in organic solutions may necessitate changes in the internal and reference electrode filling solutions.

Johansson and Edström (1972) extensively tested the Orion model 94-29 cupric ion-selective electrode to see the effects on the theoretical Nernst response and electrode stability of the topography of the membrane surface. Their results showed that deviations from the Nernst slope could result from spots, cracks, and pits on the crystal surface. Membranes with pits produced calibration lines having slopes of less than the theoretical values by approximately 1-13 millivolts. The potential readings were also less stable, and the electrodes had longer equilibration times. Dislocations on the surface were also found to be areas of rapid corrosion and etching. The authors suggested that to maintain nearly theoretical response, the electrode should be frequently diamond-polished and treated with silicone oil. These results should prove applicable to other solid-state membrane electrodes.

CHAPTER IV

STANDARD ADDITION TECHNIQUES

Introduction

There are several important problems with direct potentiometric analysis, which render it highly unsuitable for geochemical application.

First, the measured potential is a combination of many factors that are difficult to evaluate at the necessary levels of precision and accuracy. These include the contributions from the liquid junction potential, the true potential of the reference electrode in the solution being analyzed, and the potential of the ion-selective electrode itself. The latter is a combination of several internal contributions discussed in Durst (1969) and in many other papers on the developed potentials of glass and solid-state ion-selective electrodes.

Secondly, the results are in terms of activities, which means that when concentration is the variable of interest, precise and accurate data on solution composition and activity coefficients must be obtained for each sample solution analyzed.

There is additionally an inherent limitation in the precision attainable to direct potentiometric analyses stemming from the logarithmic nature of the Nernst equation. This is pointed out by Skoog and West (1971) and Durst (1969, p. 376), who show that the resulting error in reported activity is approximately ±4% for univalent ions, and ±8% for divalent ions per millivolt uncertainty in observation. These few difficulties render this technique highly unsuitable for all but the most sophisticated laboratory environments, and makes it very time-consuming for routine analyses.

Calibration curve techniques can be applied to some natural water situations. Once again, however, the ionic strength of the samples and standards must be the same, and similar electrolyte and complexing agent backgrounds must be assured. This is in addition to simple variables such as temperature, pH, and stirring rate.

A total ionic strength adjustment buffer (TISAB) can sometimes be used to overcome most of the difficulties for simple systems, but matrices present from soil, rock, and vegetation samples are highly complex, and often unpredictable with the necessary certainty. Because of potential drift, calibration curves should also be prepared frequently, and this adds time to the overall analytical procedure.

A variation on this theme is the bracketing of samples with standard solutions, analogous to the commonly accepted practice for pH measurements. McQuaker and Gurney (1977) offer a "single solution" method providing a constant ionic background and temperature. This reportedly allows more accurate blank determinations, linear calibration curves, and enhanced sensitivity and accuracy of the concentration values.

The most suitable techniques for samples with complex and/or highly variable backgrounds are single and multiple standard addition, otherwise known as "known increment" methods. Each of the two have special advantages and disadvantages, depending on the exact circumstances of the problem. Standard addition techniques are presently the only reliable methods to determine the concentration of an ion when complexing agents are present.

Single Standard Addition

The major prerequisite for the single standard addition method is that the response slope, whatever it may be, is known accurately and is reproducible with high precision for a given set of conditions. The technique involves adding an aliquot of a standard solution of the ion of interest to a known volume of sample, and using the resulting change in the measured emf of the solution coupled with the known slope to calculate the original concentration of that ion.

There are several other practical requirements which, depending on the sample composition, may or may not dictate solution pre-treatment before the actual analysis.

1. The addition of standard must not change the activity coefficient of the species of interest. For

practical situations this implies that the ionic strength of the solution must remain constant, and that the junction potentials of the electrodes must not change.

2. If complexing agents are present in the original solution, the fraction of the species of interest complexed must not change after the addition, and the complexing ligand identity should be as constant as possible.

3. The response of the electrode must be linear and equal to the previously determined slope value between the unknown activity and the sensed ion's activity after the standard addition.

4. Electrode interferences are not present in the original sample, or are eliminated by sample pre-treatment.

The following is a derivation of the equations that will enable the concentration calculation to be made.

For a solution containing the species of interest, X, the observed potential (E_o) can be described by

$$E_o = K + \frac{2.303\ RT}{ZF} \log \phi_x \gamma_x C_x \qquad \text{(IV-1)}$$

where R, T, Z, and F retain their previous meanings, 2.303 is the natural logarithm to base-10 logarithm conversion factor, K is the combined constant term (previously E_c), C is the total concentration (of X), γ_x is the activity coefficient for ion X, and ϕ_x is a term correcting for the availability of X due to complexation. If there is no complexation, ϕ_x is unity.

We can substitute an empirically determined value for the slope, S, when the electrode responds in a non-theoretical (but reproducible) manner. This results in

$$E_o = K + S \log \phi_x \gamma_x C_x \qquad \text{(IV-2)}$$

When an aliquot of standard is added, the new observed potential (E_1) is expressed by

$$E_1 = K' + S \log \left[C_x + \left(\frac{C_s V_s}{V_x + V_s} \right) \right] \gamma_x' \phi_x' \qquad \text{(IV-3)}$$

In this equation, ϕ_x' and γ_x' are the same as above (but for the new concentration of X), V_x is the volume of standard added, C_s is the concentration of the standard solution, V_x is the original solution volume, and K' is the new catch-all constant. At this point, several adjustments can be made to simplify the situation.

First, if the ionic strength of the solution can be assumed to remain constant $\gamma_x' = \gamma_x$. If the sample is pretreated so that complexing agents (if present in the first place) are in excess, the available fraction of ion X is not changed, and the ϕ_x and ϕ_x' terms are equal. Combining these simplifying stipulations, the change in observed potential (ΔE) may be seen to be

$$\Delta E = E_1 - E_o \qquad \text{(IV-4)}$$

or,

$$\Delta E = S \log \left[\left[C_x + \left(\frac{C_s V_s}{V_x + V_s}\right)\right](C_x)^{-1}\right] \qquad \text{(IV-5)}$$

At this point, if it is possible to make V_s negligible with respect to V_x (say, less than 1%), then the equation can be simplified and solved as follows, with substitution of $\Delta C = \frac{C_s V_s}{V_x}$:

$$(\Delta E/S) = \log \frac{C_x + \Delta C}{C_x}$$

$$\text{antilog } (\Delta E/S) = 1 + (\Delta C/C_x)$$

$$C_x = \Delta C \left[\text{antilog } (\Delta E/S) - 1\right]^{-1} \qquad \text{(IV-6)}$$

If it is not possible to assume V_s is negligible with respect to V_x, then the general form may be derived from (IV-6).

$$\Delta E = S \log \left[\frac{C_x V_x}{V_x + V_s} + \frac{C_s V_s}{V_x + V_s}\right](C_x)^{-1} \qquad \text{(IV-7)}$$

$$\text{antilog } (\Delta E/S) = \frac{V_x}{V_x + V_s} + \frac{C_s V_s}{C_x V_x + C_x V_s}$$

$$\frac{V_x + V_s}{C_s V_s}\left[\text{antilog } (\Delta E/S) - \frac{V_x}{V_x + V_s}\right] = C_x{}^{-1}$$

or

$$C_x = \frac{C_s V_s}{V_x + V_s}\left[\text{antilog } \frac{\Delta E}{S} - \frac{V_x}{V_x + V_s}\right]^{-1} \qquad \text{(IV-8)}$$

By evaluation of the above equations, a practical consideration that arises is that the relative uncertainty of the emf measurements is the largest when ΔE is small.

This leads to the analytical objective of the largest possible ΔC consistent with maintaining constant ionic strength, relative complexation, and staying in a region of constant slope. A rule of thumb often suggested is that the addition solution should be approximately 100X as concentrated in the ion of interest as the unknown solution. This probably comes from the idea of using 100 mL solutions and trying to double (approximately) the concentration of the sought ion.

The use of micropipettes facilitates the delivery of negligibly small volumes of standard solutions. When microliter-range additions are made, there is a danger of large errors in concentration being propagated if the delivery device is at all worn. These should be recalibrated before use for the most accurate results.

A nomograph has been developed by Karlberg (1971) based on similar equations for single and multiple standard additions, as well as analate addition. The slope need not be theoretical, but must be between $56/|Z|$ and $62/|Z|$. The ΔE value also must be in the range of 0 to 65 mV, and the volume ratio V_s/V_x must be between 0.5 and 100.

It may also be pointed out that for a series of routine analyses, V_s and V_x may be constant and can therefore be numerically combined into a factor. In addition, S should be constant. By fixing these values, and setting $\Delta C = 1$, a table of values may be easily generated by computer or programmable calculator so that ratios of $C_x/\Delta C$ may be obtained by direct comparison with ΔE values for any particular case. ΔC_x can then be easily solved for, since ΔC is a known quantity.

Orion Research Incorporated has generated such a table for 298 K and the theoretical slope, and is available upon request (see Bibliography).

The form of equation most useful for the generation of the tables would be:

$$C_x/\Delta C = \left[\text{antilog } (\Delta E/S)-1\right]^{-1} \qquad \text{(IV-9)}$$

Methods for determining S by dilution and multiple additions are described by Orion (1970) and Schuller (1976), and a computer least-squares method is described in Smith (1972).

Multiple Standard Addition

Multiple standard addition, as pointed out by Orion (1970) relies on the same essential prerequisites concerning ionic strength, complexing agents and absence from interferences as single standard addition, but has an added utility. The slope value need not be known beforehand, though it must be constant throughout the region to be analyzed. When experimental S values are imprecise, this method may be employed instead. The drawback to this procedure, as can be seen from the descriptive equations, is that potential errors can be very large for even small reading errors of 0.1 mV or less. Thus error propagation becomes especially large as $\Delta E_2/\Delta E_1 \rightarrow 2.0$. This problem may be somewhat lessened by the use of digital millivolt meters. It is also necessary in the following development to stipulate that the additions be of equal volumes and concentrations, and that the volumes of the additions be negligible with respect to that of the sample solution (Orion, 1970). A later modified derivation will demonstrate a method for volume correction, but solution composition requirements are still the same.

Starting as before, E_1 is the observed potential after the addition to the unknown solution with potential E_o. The symbol ΔC represents $\frac{C_s V_s}{V_x}$, the amount of the standard addition.

$$E_o = K + S \log C_x \qquad \text{(IV-10)}$$

$$E_1 = K + S \log (C_x + \Delta C) \qquad \text{(IV-11)}$$

The difference, $\Delta E_1 = E_1 - E_o$, is then:

$$\Delta E_1 = S \log \frac{C_x + \Delta C}{C_x} \qquad \text{(IV-12)}$$

If a second, equivalent addition of ΔC is made, this E_2 will result

$$E_2 = K + S \log (C_x + \Delta C + \Delta C) \qquad \text{(IV-13)}$$

and a ΔE_2 may be defined as $E_2 - E_o$, giving:

$$\Delta E_2 = S \log \frac{C_x + 2\Delta C}{C_x} \qquad \text{(IV-14)}$$

It is then possible to compare the ratio $R = \Delta E_2/\Delta E_1$, which is expressed by:

$$R = \Delta E_2/\Delta E_1 = \left[\log\left(\frac{C_x + 2\Delta C}{C_x}\right)\right]\left[\log\left(\frac{C_x + \Delta C}{C_x}\right)\right] \quad \text{(IV-15)}$$

This eliminates the slope term S. It introduces the problem that C_x can not be solved for explicitly in terms of R. By successive approximations using a computer (Orion, 1970, and Lawrence, 1976) or a programmable calculator, tables can be constructed of R versus C_x. One manner in which this can be done is by fixing $\Delta C = 1$, and then selecting ratios of $C_x/\Delta C$ and inserting that fraction or multiple of ΔC for C_x in the equations. Two examples follow.

For $C_x/\Delta C = 0.01$, the equation to be solved becomes:

$$R = \left[\log\left(\frac{0.01 + 2}{0.01}\right)\right]\left[\log\left(\frac{0.01 + 1}{0.01}\right)\right]^{-1}$$

$$R = 1.149$$

This is interpreted as meaning that a solution which contains C_x at a concentration 0.01 times that of each of the additions will have a ratio $\Delta E_2/\Delta E_1$ of 1.149.

For $C_x/\Delta C = 10.0$,

$$R = \left[\log\left(\frac{10 + 2}{10}\right)\right]\left[\log\left(\frac{10 + 1}{10}\right)\right]^{-1}$$

$$R = 1.913$$

Therefore, if the original sample solution was 10X as concentrated in the ion of interest as each addition volume of

C was, the resulting ratio of potential changes should be 1.913/1.

The first step following sample analysis is to calculate the observed R value. If a table has been generated, values for R can be directly correlated with $C_x/\Delta C$ ratios. For direct calculation in the field or laboratory, values of $C_x/\Delta C$ are fed into the program and subsequently iterated by hand until the R displayed mathces the R observed. This procedure takes substantially less than a minute with very little practice.

The algebra becomes more complicated when the volumes of the standard additions can not reasonably be neglected, though the final calculation is not really more difficult. Should the simplification be impossible, the first concentration increment becomes

$$\Delta C_1 = \frac{C_s V_s}{V_x + V_s}$$

(forcing a dilution of C_x also) and then for a second equal volume of standard ΔC_2 must be:

$$\Delta C_2 = \frac{C_s V_s}{V_x + V_s + V_s}$$

Since there are now two volumes of standard solution added, the second concentration increment is not as great as the first. These considerations yield the new formulae

$$E_1 = E + S \log \frac{C_x V_x + C_s V_s}{V_x + V_s} \qquad \text{(IV-16)}$$

$$E_2 = K + S \log \frac{C_x V_x + C_s V_s + C_s V_s}{V_x + V_s + V_s} \qquad \text{(IV-17)}$$

Once again, it is desired to be able to fix ratios of $C_x/\Delta C$, but there are now two different ΔC's. In this case, C_s can be fixed as equal to 1, and three constants can be employed to solve for the unknown concentration in spite of the unequal dilutions.

$$\Delta C = \frac{C_s V_s}{V_x} \qquad \text{(IV-18)}$$

$$A = \frac{V_x}{V_x + V_s} \qquad \text{(IV-19)}$$

$$B = \frac{V_x}{V_x + 2V_s} \qquad \text{(IV-20)}$$

Substituting;

$$E_1 = K + S \log \left[C_x + \Delta C\right] + S \log A \qquad \text{(IV-21)}$$

$$E_2 = K + S \log \left[C_x + \Delta C\right] + S \log B \qquad \text{(IV-22)}$$

$$E_0 = K + S \log C_x \qquad \text{(IV-10)}$$

Combining (IV-10) and (IV-21) gives

$$\Delta E_1 = S \log \frac{C_x + \Delta C}{C_x} + S \log A \qquad \text{(IV-23)}$$

and combining (IV-10) and (IV-22) yields

$$\Delta E_2 = S \log \frac{C_x + 2\Delta C}{C_x} + S \log B \qquad \text{(IV-24)}$$

Finally, (IV-15) becomes

$$R = \frac{\Delta E_2}{\Delta E_1} = \frac{\log \left[(C_x + 2\Delta C)(C_x)^{-1} \right] + \log B}{\log \left[(C_x + \Delta C)(C_x)^{-1} \right] + \log A}$$

For simplicity of calculation, this can be further reduced to

$$R = \frac{\log [1 + (2\Delta C/C_x)] + \log B}{\log [1 + (\Delta C/C_x)] + \log A} \qquad \text{(IV-25)}$$

As the volumes V_s and V_x are known, A and B can be calculated, and it is not appreciably harder to numerically evaluate (IV-25) than (IV-15) . Once again, it is not possible to solve for C_x explicitly, and the ratio $C_x/\Delta C$ must be found by successive approximations after setting $\Delta C = 1$.

To illustrate, take a hypothetical case where the sample volume (including buffer) is 50 mL, the concentration of the standard solution is 100 ppm, and the standard addition volumes are each 1.0 mL. The experimentally observed $R = 1.895$.

$$\Delta C = \frac{(100 \text{ ppm})(1.0 \text{ mL})}{(50 \text{ mL})} = 2.0 \text{ ppm}$$

$$A = \frac{(50 \text{ mL})}{(50 \text{ mL}) + (1.0 \text{ mL})} = 0.98$$

$$B = \frac{(50 \text{ mL})}{(50 \text{ mL}) + (2.0 \text{ mL})} = 0.96$$

After fixing $\Delta C = 1$ and iterating equation (IV-25) it is found that $C_x/\Delta C = 10.0$, enabling C_x to be calculated by

$$(C_x/\Delta C)(\Delta C) = C_x$$

$$(10.0)(2.0 \text{ ppm}) = 20 \text{ ppm}$$

One should be aware of the limitations imposed upon the accuracy of R by the precision of the ΔE_2 and ΔE_1 determinations, and the number of significant figures reported for C_x should be adjusted accordingly.

The use of a multiple addition technique to evaluate the effects of interfering substances in systems of controlled composition, and in detecting the presence of interferences at solid state electrodes is discussed by Smith (1972).

CHAPTER V

ELECTRODE BUFFER SYSTEMS

General Considerations

Buffer systems for ion-selective electrodes may serve any one or combination of several functions. The most typical are:

1. Ionic strength adjustment,
2. pH adjustment,
3. Constant levels of complexing agents, and
4. Interference suppression.

Since electrodes respond to ionic activities in solutions, when concentrations are sought, either of two conditions must be fulfilled. The ionic composition of the standard and sample solutions must be known so that activity coefficients can be calculated, or the ionic background must not change from solution to solution. Even when standard addition methods are employed, the addition must not change the activity coefficient of the sought ion. This can fairly easily be accomplished for addition methods by mixing into the solution an inert, non-interfering electrolyte, to "swamp" any inhomogeneities between samples. It is also possible, for ions present in high concentrations, to dilute the solution to a very low ionic strength, effectively raising the activity coefficients to a high value. In either case, care must be taken not to lower the activity of the ion of interest below the detection limit of the electrode.

In cases where the speciation of the sought ion is adversely affected by pH, or if the response of the electrode varies with pH, a buffer may be designed to fix the hydrogen ion activity at an appropriate value. Consideration must be given to the equilibria involved in each particular circumstance, so there can be little in terms of specific guidelines. As with typical pH buffers in analytical chemistry, these solutions are mainly composed of fairly high concentrations of a weak acid and its conjugate base that do not take part in interfering reactions (Butler, 1964). A method for the calculation of the concentrations necessary for a selected pH, and the buffer index for a chosen simple single system is given in Appendix 1.

Complexing agents may be added to a solution either to decomplex ions from other ligands, to provide a constant complexed fraction, or both. The greatest danger here is that the solubility of the sensor membrane must not be affected.

Interference suppression is also variable with the individual case. Interferences may sometimes be eliminated (if possible at all) by complexation of the interfering ions, or by removing the ion sought from a competing species by substitution or weak complexation. Conditions in the solution that are too oxidizing may often be remedied by the addition of a suitable reducing agent, and vice versa (though the addition of oxidizing agents are quite uncommon). These agents may be used to oxidize or reduce other potential reducing or oxidizing agents, such as Fe^{2+} ion during copper determinations in groundwater. They may also be used to inhibit precipitation of compounds by the fixing of valence states.

Examples of how these four functions have been accomplished in practice follow.

Previous Applications

One of the first applications of a multi-faceted buffer system was the "Total Ionic Strength Adjustment Buffer" (TISAB) developed by Frant and Ross, Jr. (1968) for F^- determinations.

First, the ionic strength of the water samples can be fixed by adding an equal volume of TISAB which compositionally is 1.75 M, according to Light (1968).

Through the acetic acid-sodium acetate conjugate system formed through the dissociation of acetic acid, titration with NaOH, and dissociation of sodium citrate, the pH of the sample can be held fairly close to the optimum for electrode performance of 5. This avoids hydroxide interference, and stays in the region of reasonably large buffer index. It also keeps sample-to-sample variations small.

The citrate in the system serves to complex Fe^{3+} and Al^{3+}, which prevents them from binding the fluroide ion in the solutions. The use of larger amounts of citrate than recommended by Frant and Ross, Jr. (1968) was investigated by Crenshaw and Ward (1975) with essentially poor results for most samples.

Smith (1972) and Smith and Manahan (1973) devised a complexing antioxidant buffer (CAOB or CAB) to use in trace cupric ion analyses with the CuS solid-state membrane electrode.

The pH can be fixed around 5 using an acetic acid-sodium acetate conjugate pair. Potassium hydroxide was incorporated into this system to provide acid neutralizing capacity without resorting to a very high acetate concentration. The acetate is also a mild complexing agent for copper (II) ion, and serves to fix the level of complexation in the solution.

The fluoride ion from the dissociation of sodium fluoride mainly serves to complex Fe^{3+} ion, an interferent to the electrode in that form, and also to prevent the precipitation of $Fe(OH)_3 \cdot XH_2O$ from groundwater samples.

Ferric ion and other oxidizing agents are prevented from interfering by the addition of formaldehyde. Hydoxylamine hydrochloride and ascorbic acid were investigated for this purpose, but were found unsuitable by Smith (1972).

The ionic strength adustment is made by a combination of all of the ionic species present from the buffer, though mainly from dissociation of the sodium fluoride.

Both of the aforementioned cupric ion-selective electrode investigations showed the unsuitability of Na_2EDTA as a buffer system, arising mainly from erroneously high calculated Cu^{2+} concentrations. This was attributed to the increased solubility of the electrode membrane. Phosphate buffer systems produced annoying metal phosphate precipitates, and were therefore also unsuitable.

Schuller (1976) modified the CAOB to the following specifications, for direct use with 0.1 g soil samples decomposed with 1 mL of 50% (v/v) HCl in distilled deionized water.

1. 17.17 g sodium acetate
2. 63.5 mL 1.00 N KOH
3. 0.84 g sodium fluoride
4. 2.0 mL 1.00 M formaldehyde

These reagents are then diluted to 1.00 liter with deionized distilled water. After soil digestion, 50 mL of this buffer is added directly into the container, and the cupric ion concentration determined.

The unique aspect of Schuller's pH 5 buffer system is that the acid component of the acetic acid-acetate conjugate pair is contributed by the HCl used for the sample decomposition.

Present Application

From the literature cited previously concerning possible interferences to silver determinations, a buffer system must be designed around the following criteria:

1. The pH range should not be too low (intermediate sulfide interferences at the membrane), nor above 9 (precipiation of silver oxyhydroxides or hydroxides).

2. Hg^{2+} ion should be absent or prevented from interacting in the sample solution with the electrode membrane or sulfur species present.

3. Chloride ion should be absent or prevented from interfering.

4. Precipitation from the solution should be inhibited.

5. Sample variations should be minimized to enable the use of a single or multiple standard addition technique to determine concentration of silver ion.

Another benefit may accrue if a system could be devised that would enable the determination of more than one ion of interest to the exploration geochemist, either simultaneously or successively, in the same solution.

Though it cannot be said with absolute certainty that it would be impossible, it is reasonable to say that it is most difficult to separate Hg^{2+} ion from Ag^+ ion in prospective samples without complicated ion-exchange or extraction procedures. Since the standard reduction potential for Ag^+ is less than that of Hg^{2+}, it would be virtually impossible to selectively reduce the mercury species to a non-interfering form. It is likely, however, that there will be few instances where Hg^{2+} ion is present to the extent that it would interfere significantly, and if it should be present, it may in fact also be geochemically significant. It is suggested that at least a spot test be employed in conjunction with silver determinations if there is a reasonable possibility of the presence of ionic mercury.

Chloride ion should not present particular difficulties with most reconaissance samples, since they would likely have undergone substantial leaching by water. Chlorine bound in silicate lattices would not be liberatated by the HNO_3 cold-digestion method suggested. Reagents, however, must be chloride-free. Ion-exchange purification of water to be used must be done with resins in OH^- and H^+ forms.

It can be seen that the modified CAOB of Schuller (1976) meets most of the essential requirements for silver ion analysis, as well as for the cupric ion. The buffer capacity is large enough to assure reasonable homogeneity, and to resist changes due to the acidity of the added silver standard(s). It also keeps the pH well below the level of silver hydroxide precipitation. The acetate ion, so long as the concentration is kept fairly low, will serve to keep a constantly complexed fraction of ions in solution. The formaldehyde would stabilize and homogenize the redox potentials of the solutions, and offset any residual oxidizing potential left over from the HNO_3. The sodium fluoride again fixes ionic strength and serves to complex ferric ion which is likely present in weathered soils and sediments. In any case, agents such as NaF and formaldehyde do not provide any adverse effects, even if not essential.

The use of a slight modification of the existing CAOB would also enable successive determinations of cupric ion and silver ion concentrations in each sample, providing the copper additions were done first. This is because silver (I) ion is an interferent to the cupric sulfide electrode.

Decomposition would be done in this case by the addition of a small amount of concentrated HNO_3, instead of 6N HCl. Any field method must of necessity be a compromise of effectiveness for the purpose at hand and ease of use. Rubeska et al. (1967) successfully employed cold extraction of silver from sulfide minerals by digesting powdered rock samples overnight with concentrated HNO_3.

The buffer composition may easily be adjusted to compensate for any change in the molarity of the acid used. Nitric acid also is preferable because of the formation of insoluble silver chloride. Though possibly not the optimum reagent for copper extraction, it should nonetheless prove adequate for this purpose.

Detailed preparation instructions are given in Appendix 2 for a modified CAOB. Due to the general semi-quantitative nature of these buffer solutions, there is some latitude for additional experimentation.

CHAPTER VI

EXPERIMENTAL RESULTS

Instrument and Equipment Notes

The special instruments used in this investigation were an Orion Model 401 Specific Ion Meter, a Sensorex S800Ag silver monoprobe, and a Sensorex S701RD refillable double-junction reference electrode employing standard gelled filling solutions Sensorex S-18 and S-19. A Misco Model 1902 λ Pipettor was used for the first two sections of this study. All volumetric glassware was pyrex glass and of class-A tolerance. Sample solutions were placed in 50 mL Teflon beakers while measurements were being made, except as noted in the cupric-ion electrode study.

Initial Electrode Response Check

The response of the electrode was observed by preparing replicate freshly-diluted solutions of a stock $AgNO_3$ standard. This was made by dissolving the appropriate amount of analytical reagent grade salt in deionized double-distilled water and acidifying to between pH 1 and 2 with concentrated HNO_3. The potentials were observed in magnetically stirred solutions after the meter reading became constant, usually in about two minutes. The concentration range covered was between 0.001 ppm and 100 ppm, which corresponds to approximately 9 x 10^{-9} to 9 x 10^{-4}M (See Appendix 6). The potential was observed to be essentially constant below 10^{-7}M as is shown in Figure 1. The slope was calculated to be 58 mV per decade by the linear regression formula found in Draper and Smith (1966), with a standard error for the slope of 4.7 mV. This is slightly lower than the theoretical slope, but is quite acceptable. The linear response was also observed to begin at a similar value as that reported previously in the literature. The poor precision of the slope determination probably stems from the use of separate solutions, rather than a dilution technique as such as those described by Orion (1970) and Schuller (1976).

Thiosulfate Complexing Buffer Medium

The first approach to the problem of finding a suitable buffer solution was an attempt to adapt the procedure used for silver in photographic fixing baths by Orion (Applications Bulletin 14). No details were given on the chemical composition of the baths, so several thiosulfate concentrations were experimented with. A sodium sulfite-bisulfite pH buffer was also investigated at various concentrations.

The first solution examined was a buffer composed of 20 mL of .08 M sulfite buffer and 5 mL of 0.1 M sodium thiosulfate, all in aqueous solution. The sulfite-bisulfite component was prepared by mixing 20 mL of 1.99 N NaOH and

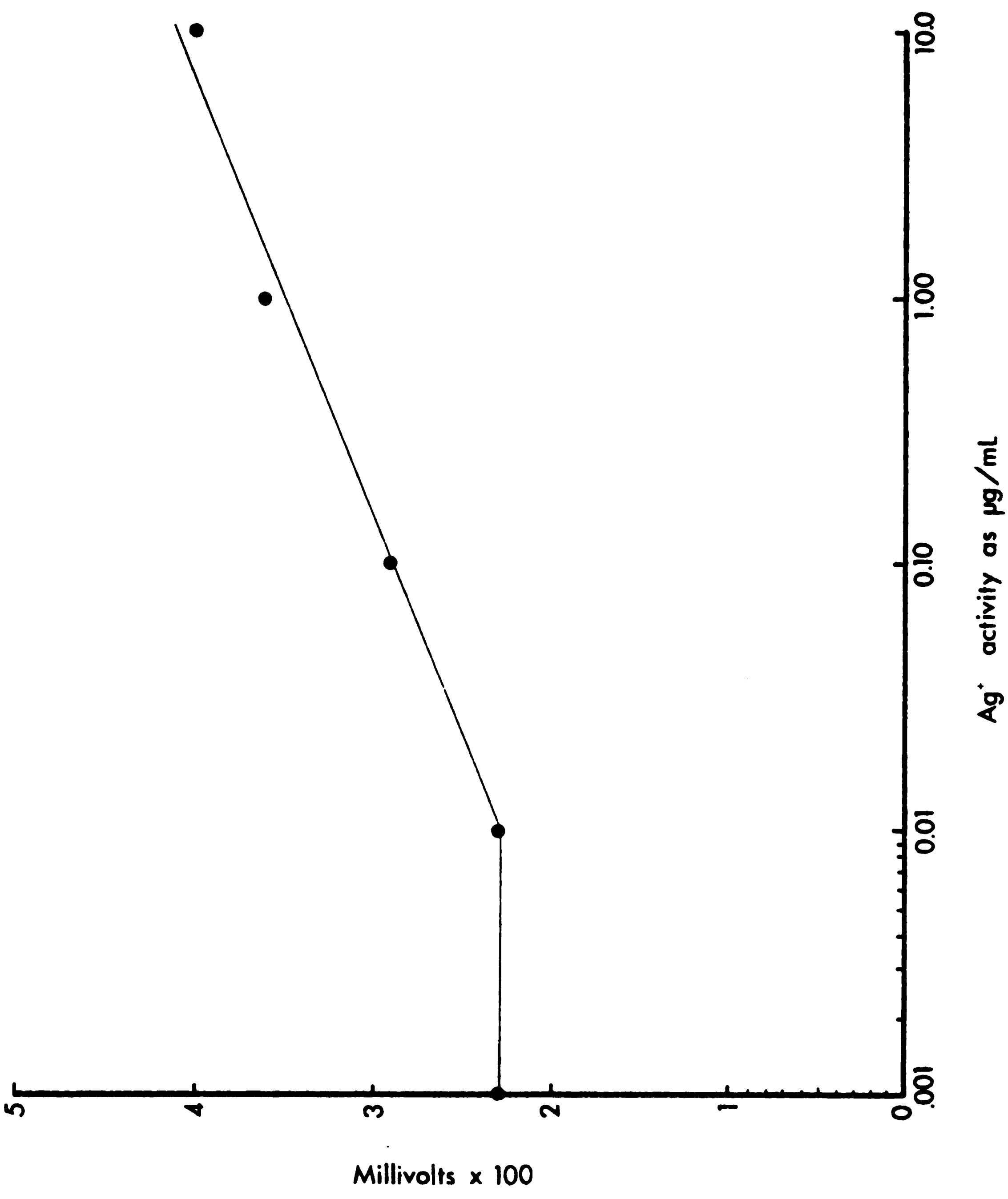

Figure 1. Observed potential vs. Ag^+ activity for $AgNO_3$ in pure water.

8.325 g $NaHSO_3$ in a 1000 mL volumetric flask, brought to volume with double distilled-deionized water. The 0.1 M thiosulfate solution was prepared by dissolving 12.414 g of the salt in a 500 mL volumetric flask, brought to volume with the high purity water.

After these two solutions were pipetted into the Teflon beaker, a 1.0 mL aliquot of silver ion standard solution was added and the initial potential observed. The concentrations in the final solution are 0.06 M for the sulfite-bisulfite buffer, and 0.02 M for the thiosulfate. Two 104.1 ± .10 μL additions were then made of a 1300 ppm silver standard. The concentration of the spike was then calculated by the formulae for double additions. The means of duplicate analyses are shown in Figure 2, compared with the actual concentrations of the spikes. As can be seen, the relative errors are highly significant.

A buffer was then prepared that was 1.0 N in $NaHSO_3$, 0.5 N in NaOH, and 0.1 M in sodium thiosulfate. At least 3 replicate determinations were made at each silver concentration, using a similar procedure to above. Better precision was obtained for this batch, but the errors were still unacceptable up to about 100 ppm silver ion concentration, where the accuracy improves to within 3%. These results are plotted in Figure 3.

The mistakenly high values calculated below approximately 2 ppm are very serious for geochemical survey work.

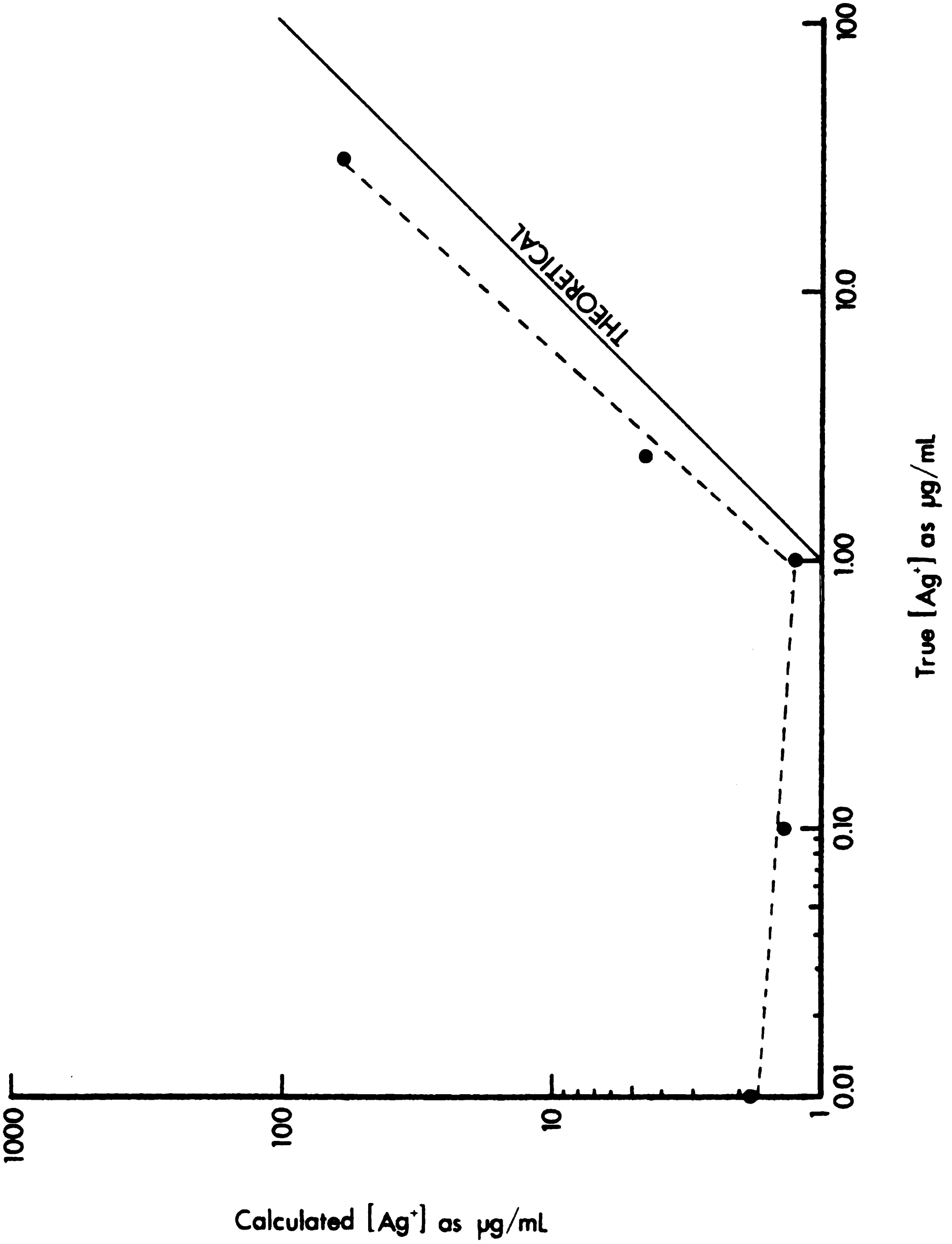

Figure 2. Spike recovery from a 0.06 M sulfite-bisulfite and 0.02 M thiosulfate buffer.

Fig

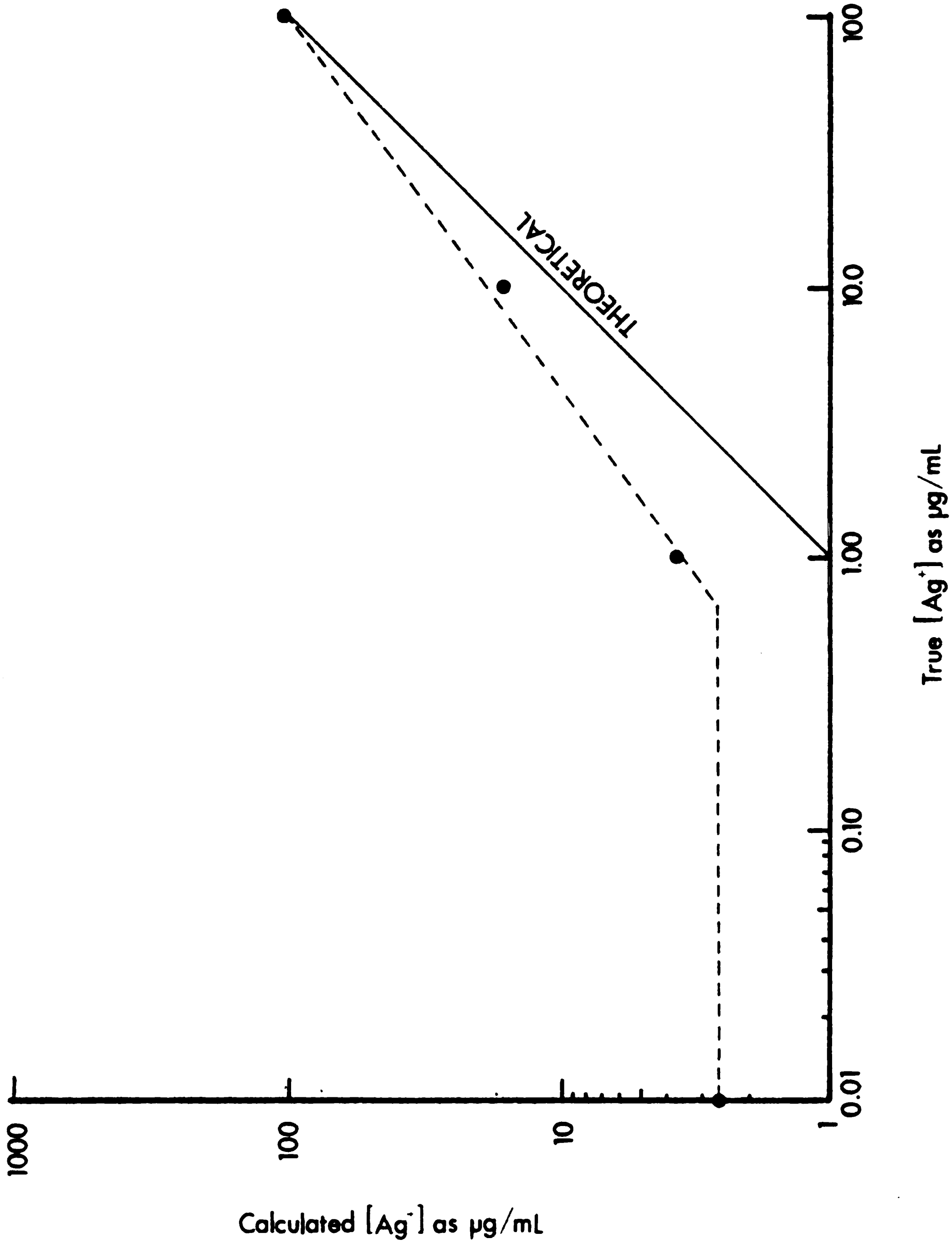

Figure 3. Spike recovery from a 0.8 M sulfite-bisulfite and 0.02 M thiosulfate buffer.

Sample analyses from soils containing no silver mineralization would be reported as containing ∿3 ppm (or more), making this procedure useless.

The raising of the detection limit by approximately three orders of magnitude is similar to the problem encountered by Smith (1972) for cupric ion determinations in EDTA and acetic acid media. Erroneously high concentration values were previously reported for some fluoride analyses when large amounts of citrate were used by Crenshaw and Ward (1975). No mechanism for this effect has been rigorously developed. It may possibly be qualitatively ascribed to the small increase in the equilibrium concentration of dissolved components of the electrode membrane at the interface, due to its complexation-enhanced solubility. A rough caluclation of the solubility of Ag_2S in 0.1 M thiosulfate medium indicates that the electrode membrane solubility is still approximately fifteen orders of magnitude or more smaller than the detection limit, though the solubility has been significantly raised. Some of the error may also be atributed to response of the electrode toward complexed silver ion, as indicated by Durst (1968).

The effect of the pH buffer component without the thiosulfate was examined, and is summarized in Figure 4. This part of the system alone increases the detection limit to $\sim 10^{-5}$ M or ∿1 ppm. Significant reductions in strength of the pH buffer are not possible because of the small reagent

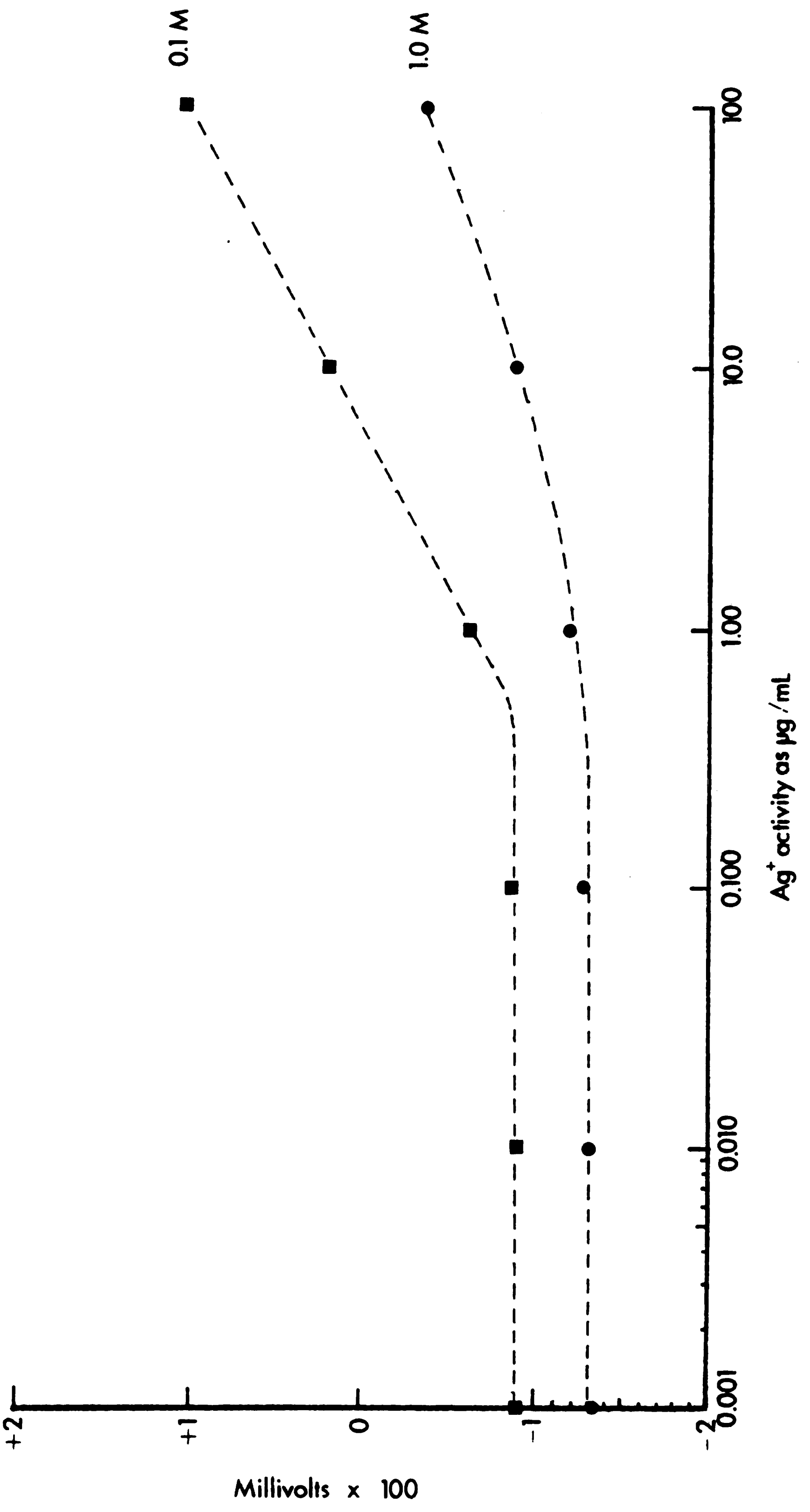

Figure 4. Effect of sulfite-bisulfite buffer concentration on electrode response to Ag^+.

volume and high acid concentration anticipated for soil or rick analysis.

This line of approach was then abandoned. As this was a feasibility study, no attempt was made to determine the detailed behavior or mechanism of the interferences.

Dithizone Pre-Extraction Investigation

At this time, it was decided to take a novel approach to the problem.

Because of the selectivity of certain organic complexing agents, a pre-extraction step offers several potential advantages.

1. Some potentially interfering ions may be removed.
2. The dilution loss would be somewhat lessened, since larger soil and sediment samples could be used than for direct measurement.
3. Determinations theoretically could be made in a simpler aqueous phase than the concentrated buffers normally employed for electrode studies.

To see if this type of scheme was practical for general geochemical survey purposes, the well-behaved Orion 94-29A cupric-ion selective electrode and Orion 90-02-00 double-junction reference electrode with standard filling solutions were used. Thus far, no articles on this general type of technique using ion-selective electrodes have been found in the literature. This was possibly the first attempt at adapting pre-extraction to electrode analysis.

Because of its selectivity and easy availability, the organic chelating agent dithizone was investigated for the extraction, though measurements must ultimately be made in the aqueous phase. Geiger and Sandell (1953) described the copper (II) equilibria in dithizone solutions prepared with CCl_4 as the solvent. Uses and properties of dithizone for trace metal analysis were described in detail by Sandell (1959). Separations of silver, mercury, and copper using dithizone are covered by Friedeberg (1955), relying upon pH and masking agent variations.

Two main problems present themselves for this type of approach. First, the ion of interest must be separated from the organic phase complexes and be put into the aqueous phase. Secondly, that aqueous medium must be suitable for stable electrode operation.

Most of the useful masking agents are themselves strong complexing agents, and would likely cause a chemical interference at the electrode or in the solution. By adjusting only the pH of the extraction medium to ~ 2, Cu^{2+}, Ag^{+}, and Hg^{2+} can be separated from most other metals. Unfortunately, the latter two interfere with the cupric ion selective electrode, and the last one interferes with the silver sulfide membrane electrode. Since synthetic samples were used for the feasibility study, the problem was put off for further consideration (if necessary) at a later date.

Tedious decomposition methods for metal dithizonates such as evaporation of the organic phase followed by oxidizing acid or furnace decomposition of the residual organic matter were ruled out as unnecessarily complicated for a survey method. This investigation centered on finding a simpler procedure.

Many reagents were examined in a largely trial-and-error process. Sandell (1959) suggested several oxidizing substances in the context of interferents to colorimetric procedures, but most were not readily available. Several other common oxidizing agents were then examined for their effect.

Though there certainly are other substances and/or concentrations that will decompose 1 X 10^{-3}% dithizone in CCl_4, the following were found to be useful:

1. 30.6% H_2O_2 in basic solution
2. 1:1 (v/v) 6 N H_2SO_4 to 6 N HNO_3
3. 6 N HNO_3

These solutions turned the dithizone phase to pale straw yellow color or clear. No noticeable effect was detected for 6 N H_2SO_4, and HCl shifts the extraction equilibria at that normality; it does not alter the basic structure of the dithizone. Tests were done by adding 1 mL of the oxidizing agent to 3 mL of dithizone which had previously extracted a 1 mL aliquot of 100 ppm Cu^{2+} standard solution.

Two batches of pH 5 CAOB were prepared from Schuller (1976) such that one was identical and was used with an aliquot size of 50 mL; the other had the acetate and KOH concentrations correspondingly adjusted to enable only 15 mL of the buffer to neutralize the 6 millimoles of acid that would be present. A pK_a of 4.65 was also used in the calculation procedure, instead of 4.75.

Numerous recovery experiments were tried, using 6 N HNO_3 as the oxidizing agent. A three-neck 250 mL distillation flask was used for the studies, with two of the necks slightly enlarged to accommodate the Orion electrodes. The flask was set in a beaker on a magnetic stirring plate, and a Teflon magnetic stirring bar was inserted into the flask. The dithizone solution, acid, and buffer were added into the flask by pipet through the central neck.

A 1.0 mL aliquot of various concentrations of copper standards was extracted for 5 minutes with 0.001% dithizone solution in a test tube with a plastic cap having a Teflon liner. Following the settling out of the organic phase, 3.0 mL of the dithizonate were taken out and transferred to the flask. The acid was then added, and the mixture was allowed to stir until the organic phase became pale straw yellow or colorless. Then the buffer was added, followed by insertion of the electrodes. Copper standard additions were then made, and the spike calculated by double addition when possible.

The electrode suffered from extreme drift during almost all of the individual tests. The drift was normally continuously negative, but not always. The formaldehyde concentration was increased ten-fold without effect.

Because of the drift problem, this line of research was abandoned. The reason for the drift is not known. It may possibly be due to residual oxidizing conditions in the solution caused by the HNO_3, or to interactions of the electrode membrane with unknown products of the dithizone decomposition. The latter may contain sulfur in some form.

Modified CAOB Investigation with Silver Ion

The third major thrust of the research was an investigation of the response of the silver ion-selective electrode in a buffer of similar composition to that of the previous studies with the cupric-ion selective electrode. Since silver forms a slightly-soluble salt and series of complexes with acetate ion, the buffer must contain a low enough level of acetate ion so that the ion activity product of the silver and acetate ions does not exceed the value of K_{s0} for silver acetate. The value for K_{s0} is given by Butler (1964) as $10^{-2.40}$.

"Unknown" silver solutions were prepared by mixing 1.00 mL of 100 ppm Ag^+ standard (from $AgNO_3$ in double distilled deionized water, acidified to pH 2 with HNO_3), 1.00 mL 8 N HNO_3, and 50 mL of CAOB (the same solution as the last section) in a Teflon 50 mL beaker. A Teflon magnetic stirring bar was added, and several sheets of paper filter disks were placed under the beaker on the stirring plate as heat insulation from the motor.

Standard additions were made by 1.00 mL class-A volumetric pipets, using the same 100 ppm standard solutions. The electrodes were allowed to equilibrate to a standard potential reading (about five minutes). The meter was then set on the expanded millivolt scale, and the needle zeroed at mid-scale. After each addition, the solution was allowed to equilibrate for one to two minutes before reading the new potential.

The spike concentration and associated uncertainty can be determined as follows. The delivery precision of class-A volumetric ware may be taken from Skoog and West (1969) as

	s	s_r
1.00 mL pipet	±0.006 mL	0.6%
10.0 mL pipet	0.02	0.2
50.0 mL pipet	0.05	0.10
100.0 mL volumetric pipet	0.08	0.08

where s is the standard deviation and Sr is the relative standard deviation (variance). The uncertainty in the analytical balance used may be taken to be ±0.0001 g.

The error in the preparation of the stock standard may be estimated by considering the weighing uncertainty plus that in the volume of the 100.0 mL flask. For the weight of the silver nitrate

$$\left(\frac{0.0001\ \text{g error}}{0.1575\ \text{g AgNO}_3}\right) \text{X } 100 = 0.0635\%\ s_{r1}$$

Including the volume error, the total error from this step would be

$$s_{r2} = \left[(0.06)^2 + (0.08)^2\right]^{\frac{1}{2}}$$

The dilution of this stock standard to the working 100 ppm solution introduces errors additionally from the pipet and volumetric flask:

$$s_{r3} = \left[(0.10\%)^2 + (0.2\%)^2 + (0.08\%)^2\right]^{\frac{1}{2}} = 0.24\%$$

The error in the final spike concentration, delivered by two 2.00 mL pipet aliquots into a solution whose initial volume was a delivery from a 5.00 mL pipet plus 1.00 mL of 6 N HNO_3 can then be estimated by

$$s_{r4} = \left[(0.24\%)^2 + 2(0.6\%)^2 + (0.20\%)^2\right]^{\frac{1}{2}} = 0.887\%$$

(extra digits were carried throughout the computations)

The true "unknown" concentration in each of the four determinations made was then

1.92 ± 0.017 ppm

Calculation of the "unknown" concentration was done by the double addition technique described previously. The constants calculated for the iterations were:

$$\Delta C = \frac{(100\ \text{ppm})(1.00\ \text{mL})}{(52.0\ \text{mL})} = 1.923\ \text{ppm}$$

$$A = \frac{52.0\ \text{mL}}{52.0\ \text{mL} + 1.00\ \text{mL}} = 0.981$$

$$B = \frac{52.0\ \text{mL}}{52.0\ \text{mL} + 2.00\ \text{mL}} = 0.963$$

The following were experimental data used to calculate the results:

TRIAL	ΔE_1	ΔE_2	R	C_x	$C_x \Delta C$
1.	22.5 mV	35.6 mV	1.582	1.050	2.019 ppm
2.	19.1 mV	29.9 mV	1.565	0.952	1.831 ppm
3.	17.2 mV	27.2 mV	1.581	1.044	2.008 ppm
4.	17.3 mV	27.5 mV	1.590	1.095	2.106 ppm

Using the standard equation for the 95% confidence limits from Fritz and Schenk (1974)

$$\bar{x} \pm \frac{t_{0.95}s}{n} = \frac{(2.132)(0.115)}{4} = 0.123$$

the experimental value of the spike was:

2.0 ± 0.12 ppm

The relative precision at that internval can then be calculated to be 6.2%, the absolute error of the mean +3.5%. The recovery was well within the 95% confidence limit and the precision of the spike.

Several attempts were made to make silver measurements of actual 1.0 g soil samples dried and sieved through nylon plankton netting, but the particulate matter made the potential unstable, rendering precise and accurate readings impossible.

CHAPTER VII

RECOMMENDATIONS FOR FURTHER RESEARCH

While the use of organic chelating agent extraction and separation appears to be a potentially useful method, the more conventional CAOB procedure would seem to be the easiest approach to make initially productive.

Two facets of the CAOB method need some further work. A more detailed investigation of the response of a freshly polished silver sulfide electrode would seem to be in order, especially in the region of 0.01 to 1.0 ppm. This is particularly important, since geochemically significant silver concentrations may likely lie in many instances around 0.5 ppm or even below, according to Chaffee (1976). The reproducibility of the slope and precision estimates should first be obtained to see if it would be possible to use the more simple single addition method. The possibility of any special or systematic errors resulting from the use of double addition in this region should also be investigated, since emphasis that technique has been largely ignored in the literature. This problem is not encountered in the cupric ion determinations, since there is virtually always much more copper (II) ion in the soil, sediment, or water than the detection limit of the electrode.

A general approach worth investigating would be the overnight cold digestion of the sample with 16N HNO_3 as suggested by Rubeska et al. (1967), followed initially by dilution with an equal volume of double distilled deionized water. Some of the solution could then be withdrawn into a volumetric syringe through a small membrane filter. A known volume of the sample solution could then be transferred to the measuring beaker after the removal of the filter apparatus. Small, circular plastic filter holders are available, which could be adapted to connect in-line to the syringe. Filtration must be performed on the suction step so that the volume of the solution to be transferred is known accurately (no particulate matter distorting the volume reading). The syringes should probably be transparent so that volume corrections can be made for air bubbles. They must also be readily cleaned for repeated use.

Fusion techniques have been employed successfully by several investigators, especially for fluorine analyses. Though too complicated for field use, they might prove a useful laboratory procedure providing solid residue could be eliminated (or minimized).

The soil or sediment sample size must also be investigated, to try to determine the optimum balance between the availability of enough silver (if there) to show an anomaly after dilution, and filter clogging.

One intriguing possibility of the organic extraction procedure is the prevention of extraction of Hg^{2+} by the use of a suitable masking agent. One such may be 1,2-diaminocyclohexanetetraacetic acid (DCTA), which has a log K_{ML} = 23.3 for Hg^{2+}, but does not form complexes with Ag^+, according to data in Ringbom (1963).

Suggestions for additional investigations of the extraction technique must, however, center on finding the specific cause(s) of the electrode drift. This may require additional investigation of suitable reducing agents, or a technique to remove the organic phase entirely from contact with the aqueous phase during analysis. This may be possible through the use of a container with a stopcock and drain in the bottom, or even some other method entirely.

In either case, further investigation would seem to be well warranted based on this feasibility study. With comparatively little additional expense and effort, a reasonably precise and accurate field method for silver ion alone, or both cupric and silver ion simultaneously, may be possible.

APPENDICES

APPENDIX 1

ELEMENTARY pH BUFFER EQUILIBRIA EXPRESSIONS

ELEMENTARY pH BUFFER EQUILIBRIA EXPRESSIONS

A useful definition for a buffer solution is one which resists change in pH. There are many different ways of designing buffer solutions. Universal buffers operate over the entire pH range, but for electrode work a buffer is normally designed to hold all samples close to a predetermined pH value. This is most efficiently done by designing a solution that contains a fairly large concentration of a weak acid and its conjugate base.

To be strictly correct, activities of the species involved must be used in the buffer equilibria expressions. However, the resulting error is not critical for this application, and concentrations will be used here.

A detailed derivation of buffer equilibria is given in many analytical chemistry texts, and will not be repeated here. Several of those texts are listed in the Bibliography.

For a simple single conjugate weak acid and base pair, the most useful expressions are

$$[H^+] = \frac{C_{HA}}{C_A} K_a \qquad (1)$$

(otherwise known as Henderson's equation) and

$$pH = pK_a + p\left[\frac{C_{HA}}{C_A}\right] \qquad (2)$$

In these equations, pH = -log $[H^+]$, and C represents the analytical concentration of a substance, which may be defined as the total number of moles of a pure substance added per liter of solution (independent of ultimate speciation). It can be seen that when the desired pH is fixed, the ratio of salt to acid necessary can be calculated, since K_a is known. It can also be seen that when $C_{HA}/C_A = 1$, the resulting pH is equal to $-\log K_a = pK_a$.

Two examples of how to use the buffer equations in practice follow.

Example 1

What will be the pH of an acetic acid-sodium acetate buffer in which $[HAc] = 1 \times 10^{-2}M$, and $[NaAc] = 1.5 \times 10^{-2}M$? The pK_a is given by Ringbom (1963) as 4.65 at $\mu = 0.1$.

First, since the acetic acid is the only source of acid,

$$C_{HA} = [HAc] - 1.0 \times 10^{-2}M, \text{ and}$$

$$C_A = [NaAc] = 1.5 \times 10^{-2}M.$$

Then, from equation 1 and taking the antilog of the pK_a,

$$[H^+] = \left(\frac{1.0 \times 10^{-2}M}{1.5 \times 10^{-2}M}\right)(2.24 \times 10^{-5})$$

$$[H^+] = 1.49 \times 10^{-5}$$

$$pH = 4.83$$

Example 2

It is desired to make a buffer with pH = 5 using only acetic acid and sodium acetate, similar to that used by Smith and Manahan (1973). How much of each reagent should be mixed to make exactly 1 liter of buffer, if the overall acetate concentration is to be 0.01 M?

First, using equation 2, and $pK_a = 4.65$,

$$(5.0 - 4.65) = p\left[\frac{C_{HA}}{C_A}\right] = 0.35$$

$$\frac{C_{HA}}{C_A} = 0.45$$

If $C_A = 0.01$ M, then

$$C_{HA} = (0.45)(0.01) = 0.0045 \text{ M}$$

Since the formula weight for sodium acetate (anhydrous) is 82.04 g mol^{-1}, and since glacial acetic acid is normally about 17 M,

$$(0.01 \text{ mol L}^{-1} \text{ NaAc}) \text{ X } (1 \text{ L}) \text{ X } (82.04 \text{ g mol}^{-1}) = 0.82 \text{ g NaAc}$$

and

$$(1000 \text{ mL}) \text{ X } (0.0045 \text{ mmol mL}^{-1}) \text{ X } (1000/17) \text{ mLmmol}^{-1}$$
$$= 0.26 \text{ mL glacial acetic acid.}$$

APPENDIX 2

CALCULATION OF BUFFER CAPACITY

CALCULATION OF BUFFER CAPACITY

The buffer capacity can be considered to be a measure of a solution's ability to resist change in pH due to the addition of strong acid or strong base. The most convenient mathematical form is the reciprocal of the slope of a neutralization curve, and is expressed by

$$\beta = -\frac{dC_A}{dpH} = \frac{dC_B}{dpH} \qquad (3,\ 4)$$

This is called the "buffer index," and a large value of β indicates a good buffer. The quantity C_B is the concentration of strong base added in mol L^{-1}, and C_A is the concentration of strong acid added in mol L^{-1}. Though it will not be derived here, the buffer index β is an additive property of all of the acid-base couples present in the solution, as is shown by Bruckstein and Kolthoff (1959).

For a simple buffer system consisting of a weak monoprotic acid HA and its conjugate salt XA in aqueous solution, the following equation can be derived, according to Butler (1964):

$$\beta = 2.303 \left[\frac{K_w}{[H^+]} + [H^+] + \frac{C\ K_a\ [H^+]}{\left(K_a + [H^+]\right)^2} \right] \qquad (5)$$

In this equation, C represents the initial analytical concentration of the weak acid system ($C = [HA] + [A^-]$). The buffer index then can be directly calculated when the pH of the buffer is known, as is the usual case.

If the differentials of the defining equations are approximated by small changes (Δ), the amount of pH change can be easily calculated.

Example

What is the pH change brought about in 1.0 L of a buffer solution that is 1.0×10^{-2} M in acetic acid and 1.0×10^{-2} M in sodium acetate by the addition of 1.0 mL of 8N HNO_3?

From equation 2 of Appendix 1, $pH = pK_a = 4.65$, using the same Ringbom (1963) pK_a value.

The buffer index can then be calculated by equation (5), with

$$C = (1.0 \times 10^{-2} \text{ moles of HAc}) + (1.0 \times 10^{-2} \text{ moles of NaAc})$$
$$= 2.0 \times 10^{-2} \text{ moles}$$

total of weak acid components. Converting the values to powers of 10, the buffer index is calculated to be

$$\beta = (2.303)\left[\frac{10^{-14}}{10^{-4.65}} + 10^{-4.65} + \frac{10^{-1.70}\ 10^{-4.65}\ 10^{-4.65}}{\left(10^{-4.65} + 10^{-4.65}\right)^2}\right]$$

$$= (2.303)\ 10^{-2.30}$$

$$= 10^{-1.94}$$

$$= 1.16 \times 10^{-2}$$

Rearranging equation (3), approximating the differentials by Δ , and assuming that HNO_3 dissociates completely yielding 8 millimoles of H^+ (which is C_A)

$$\Delta\ pH = - \left(\frac{8.0 \times 10^{-3}}{1.16 \times 10^{-2}}\right)$$

$$= - 0.69$$

Therefore, the final pH after the addition will be approximately:

$$pH = 4.65 - 0.69 = 3.96$$

The more millimoles of acid or base added, the more inaccurate the resulting pH estimate will be.

APPENDIX 3

PREPARATION AND MODIFICATION OF THE CAOB

PREPARATION AND MODIFICATION OF THE CAOB

The components of the original CAOB of Schuller (1976) were previously described in Chapter V. The purpose of this section is to show how to either prepare a similar solution, or to modify it slightly to suit new experimental conditions. There are many equally useful ways to modify any or several of the components, so this is intended only as a guide.

Overview

The sodium acetate component must meet two simultaneous requirements:

1. The concentration must be adequate to maintain suitable buffer capacity when it reacts with the residual digestion acid to form an acetic acid-sodium acetate conjugate pair, and

2. The dissociated acetate ion must be low enough in concentration so that the ion activity product of acetate ion and silver ion does not exceed the solubility product constant for silver acetate.

The potassium hydroxide is a strongly basic component which mainly serves to contribute acid neutralizing capacity to augment the sodium acetate. It secondarily contributes K^+ to help maintain constant ionic strength.

The sodium fluoride is a strong electrolyte, and provides high ionic strength through dissociation. In most forseeable cases, its concentration would need no adjustment.

The formaldehyde is a reducing agent, and the concentration originally was empirically determined. Though the mechanism of its action is not fully known, its concentration is likely not critical beyond several percent.

The following buffer solution is designed to be used in a 50.0 mL aliquot, and will neutralize 8 millimoles of acid to a pH of approximately 4.6. The sodium acetate concentration is adjusted to neutralize 3 millimoles of the acid, and the KOH should neutralize the other 5 millimoles. The quantities were calculated assuming a pK_a for acetic acid of 4.65. If it is desired to make a buffer of pH 5 instead, as in the Schuller (1976) and Smith and Manahan (1973) studies, it is suggested that the ratio of acetate to acid molarity be 2.24/1 rather than 1.8/1 used previously, as a result of the suppressed ionization of acetic acid at higher ionic strengths.

Preparation of the Buffer

The following solutions and/or reagents should be prepared or obtained and transferred quantitatively in the indicated amounts to a 1000 mL volumetric flask. Following this, the contents should be brought to volume with distilled deionized water, making sure that the solution is at room temperature when the last drops are added. The solution should then be thoroughly mixed and transferred to a clean polyethelene storage bottle. The amounts of reagents may simply be adjusted to suit different volumetric flask sizes.

1. Standardized Potassium Hydroxide (KOH), (0.10 N final):

If commercially purchased 1.00 N KOH is available, pipet 100 mL into the 1000 mL volumetric flask, and go on to the next step. Carbon dioxide must be excluded as much as is possible. Ultimately, after long storage, the solution may have to be carefully boiled in a suitable container to chive off dissolved CO_2. The solution must then be re-standardized.

To prepare and standardize this reagent, first boil approximately 1 liter of distilled deionized water to drive off dissolved carbon dioxide, and keep the water covered while cooling to minimize atmospheric contact. When the water is cooled, quickly weigh 28.06 g of KOH pellets (weight corrected for impurities, when assay is given) into a scrupulously cleaned beaker. Transfer slowly to a 500 mL volumetric flask previously filled with 100 mL of CO_2-free distilled and deionized water, using a powder funnel. Swish the solution in the flask by hand during the transfer process, so that the pellets do not stick to the bottom or sides of the flask. The reaction is highly exothermic, so the transfer cannot be done too fast, but the pellets are very hygroscopic and tend to stick together quickly. When all of the pellets are out (some may have to be prodded with a clean glass rod), rinse the residue out of the beaker with many volumes of CO_2-free water, 5 or 10 mL at a time, and transfer to the 500 mL mixing flask. When that is done, add CO_2-free water to the flask until an inch or so below the line. Stopper lightly and let cool to room temperature, which may be quite a while. Bring to the mark with water after cooling, mix thoroughly, and transfer to a tightly capped polyethelene storage bottle.

Before use, the solution must be standardized to determine its true normality. The following special materials will be needed for this step:

(1) Several (at least 4) 125-mL Erlenmeyer flasks, and a Teflon stirring bar for each

(2) Phenolphtalein indicator (liquid)

(3) An accurate 10 mL buret, with a Teflon or plastic stopcock

(4) A ring stand and buret clamp

(5) A magnetic stirring plate

(6) A drying oven

(7) A dessicator and fresh dessicant

(8) Potassium hydrogen phtalate, $KHC_8H_4O_4$, commonly abbreviated "KHP."

(9) A 250 mL beaker or large watchglass for drying of the KHP. First, dry 10 g of the KHP in the drying oven at 110 C for about 2 hours, and let cool to constant weight in the dessicator. Weigh at least 4 portions of the KHP, approximately 1 g each, recording the exact weights. Place each of these portions in a separate labelled Erlenmeyer flask, making sure the transfer is quantitative. Rinse down the sides of the flasks with about 50 mL of CO_2-free distilled and deionized water. The water does not take part in the reaction, so the volumes in each flask need only to be about the same for accuate comparison of relative indicator colors. The KHP dissolves slowly, and may need to be stirred or gently (!) heated.

When ready for titration, fill the buret with KOH and cap lightly. Add the Teflon stirring bar (if not done previously) and 2 or 3 drops of phenolphtalein. The solution should be clear and titrated until the first sign of lasting magenta color. A fuzzy endpoint is a sign of CO_2 contamination.

If the KOH is close to 1.0 N, the endpoint should be reached at 5 mL for a 1.0 g quantity of KHP, which is 204.23 mg meq^{-1}. The exact normality of the KOH for each separate titration is given by

$$N_{KOH} = \frac{(\text{mg KHP})(\text{mL KOH to endpoint})}{204.23\ \text{mg/meq}}$$

and the appropriate methods to calculate confidence limits of precision can be found in analytical chemistry texts such as Fritz and Schenk (1974) and Skoog and West (1969).

After standardization, the appropriate aliquot to pipet into the buffer solution preparation flask can be calculated from

$$\text{mL KOH} = \frac{100}{(\text{calculated normality})}$$

Make sure that the stock solution is tightly closed at all times, and never use a container with a glass stopper. The top should never be left open when the solution is not immediately being transferred.

Restandardization should be done every couple of weeks.

2. <u>Sodium acetate component (6.0×10^{-2} M final)</u>:

Weigh and quantitatively transfer to the 1000 mL volumetric preparation flask 8.165 g of $NaC_2H_3O_2.3H_2O$ (136.08 g mol^{-1}) or 4.922 g of $NaC_2H_3O_2$ (82.03 g mol^{-1}).

3. Sodium fluoride component (2.0×10^{-2} M final):

Weigh and quantitatively transfer to the 1000 mL preparation flask 0.840 g of NaF (41.99 g mol^{-1}).

4. Formaldehyde component (2×10^{-3} M final):

Pipet 2.0 mL of a standard 1.00 M formaldehyde solution, if available. If not, the molarity must be estimated from the density and molecular weight information on the individual reagent bottle. Typical 37% formaldehyde solution should require about 0.025 mL to be added for buffer preparation. The volume is not highly critical.

APPENDIX 4

PREPARATION AND STORAGE OF SILVER SOLUTIONS

PREPARATION AND STORAGE OF SILVER SOLUTIONS

There exists in the literature a large number of papers concerning the significant loss of silver ion through adsorption on container surfaces. This adsorption is a function of silver concentration, the matrix of the silver solution, the nature of the container itself, and several external variables such as light and temperature. The exact experimental conditions in the many articles vary, and all should be examined that are accessible to anyone doing quantitative work with silver solutions. Several important articles will be summarized here.

Struempler (1973) prepared 0.5 ppb silver solutions from $AgNO_3$, acidified them to pH 2 and 4.5, and examined them in borosilicate glass, polypropylene, and polyethelene containers. He also stored the solutions in both light and darkness, and stored the solutions for 36 days. Little silver was adsorbed at pH 2 on either borosilicate glass or polyethelene. At pH 4.5 losses began immediately on both container types, becoming 10 - 25% within 4 days, and increased thereafter linearly with time. Upon acidification, desorption began occurring. Complete loss resulted within 4 days using polypropylene containers. Desorption was not observed after acidification of solutions stored in polypropylene.

Erratic behavior of aged silver was observed and discussed, but generally the significant results of this study indicate that silver standard solutions should be acidified to approximately pH 2 and should not be stored for more than a day or two. The standards should probably be stored in polyethelene, since glass containers tend to allow trace metals to be leached from the walls, including silver.

Durst and Duhart (1970) looked at the adsorption low on Pyrex, Vycor, Teflon (FEP), and Pyrex coated with Desicote. For a time period of up to 10 days, the smallest losses were found when using Teflon, Vycor, and Polyethelene. Teflon was recommended for short-period ($\sim$1 day) storage, but none were considered satisfactory beyond that period. The use of a complexing ligand was highly recommended, but is unfortunately risky in trace-level electrode studies.

The use of complexing ligands was examined by West, West, and Iddings (1966), and sodium thiosulfate was found to be quite useful. There are many detailed results given in this paper, but polyethelene was found to be safe for up to 8 hours at 1 ppm silver concentration without complexation. The pH study revealed more adsorption at pH 4 than at pH 7 and pH 9, in contradiction to other studies.

Robertson (1968) recommended the acidification to pH 1.5 and storage in polyethelene to prevent silver loss from sea water samples.

Combining the results of the various papers, all silver stock standards used in this study were prepared daily from AR grade $AgNO_3$, and were acidified to between pH 1 and 2 with HNO_3. A rule of thumb is that two drops from a disposable pipet should lower the pH properly in 100 mL of water, but the amount should be tested on the water being used before the standards are prepared.

Solutions were transferred immediately to polyethelene storage bottles that had been initially pre-soaked with 5% HNO_3 for a week, and rinsed after each subsequent use with dilute acid cleaning solution and distilled and deionized water. Working standards were diluted immediately before use, and were discarded immediately thereafter.

APPENDIX 5

CLEANING PROCEDURES

CLEANING PROCEDURES

To insure as little contamination as possible, before the study was commenced all volumetric glassware (exclusive of pipets), beakers, and stirring bars were first cleaned with hot or boiling acid cleaning solution (ACS) prepared by mixing concentrated HNO_3 and H_2SO_4 in a 1 to 3 (v/v) ratio. This was the same cleaning solution used by Smith (1972), and is analogous to the traditional dichromate solution. According to Adams (1972) the oxidizing power normally due to the alkalai dichromate in sulfuric acid solution is now provided by the nitric acid, and it substantially lessens the availability of trace metals (particularly chromium) for adsorption after treatment.

Following this washing, the containers were rinsed copiously with deionized water, prepared by passing tap water slowly through a mixed-bed ion-exchange column (H^+ and OH^- form). After this rinse, all containers underwent a final rinse with double distilled deionized water, prepared by quartz distilling once-distilled water, and passing the redistillate through three mixed-bed exchange columns (H^+ and OH^- forms) and a molecular sieve column. This water was stored in a closed polyethylene vat, and all tubing used was polyethylene or a non-contaminating plastic.

In between uses, volumetric flasks were soaked overnight in concentrated ACS, and rinsed as above. Other containers were rinsed with ACS before the water rinses.

Pipets were initially cleaned with a concentrated solution of sodium dichromate dissolved in concentrated sulfuric acid with a few milliliters of deionized water. Following thorough water rinsing, the pipets were cleaned with the concentrated acid cleaning solution and rinsed as above. Subsequently, pipets were left to soak in a 1:1 solution of ACS with double distilled and deionized water between uses.

APPENDIX 6

SOME CONCENTRATION EQUIVALENTS FOR Ag^+

SOME CONCENTRATION EQUIVALENTS FOR Ag^+

Parts Per Million	Moles Per Liter
1.0×10^{-3}	9.3×10^{-9}
1.0×10^{-2}	9.3×10^{-8}
1.1×10^{-2}	1.0×10^{-7}
1.0×10^{-1}	9.3×10^{-7}
1.1×10^{-1}	1.0×10^{-6}
1.0	9.3×10^{-6}
1.1	1.0×10^{-5}
1.0×10^{1}	9.3×10^{-5}
1.1×10^{1}	1.0×10^{-4}
1.0×10^{2}	9.3×10^{-4}
1.1×10^{2}	1.0×10^{-3}
1.0×10^{3}	9.3×10^{-3}
1.1×10^{3}	1.0×10^{-2}
1.0×10^{4}	9.3×10^{-2}
1.1×10^{4}	1.0×10^{-1}
1.0×10^{5}	9.3×10^{-1}
1.1×10^{5}	1.0

$1\ \mathrm{mol}\ L^{-1}\ Ag^+ = 107{,}874\ \mathrm{ppm}\ Ag^+$

APPENDIX 7

APPLICATIONS OF ION-SELECTIVE ELECTRODES TO GEOCHEMICAL SYSTEMS

APPLICATIONS OF ION-SELECTIVE ELECTRODES TO GEOCHEMICAL SYSTEMS

This is a compilation approximately through October 1977 of articles on applications of ion-selective electrodes to diverse systems of geochemical interest not cited elsewhere in this thesis. No claim is made that this list is complete, though it is extensive.

References are listed alphabetically by major element determined.

Ammonia

Thomas, R. T., Booth, R. L. (1973), Selective electrode measurement of ammonia in water and wastes: Environ. Sci. and Tech., 7, 523.

Bromide Ion

Savenko, V. S. (1976), Utilization of bromide ion-selective electrodes in geochemical investigations: Oceanology (U.S.S.R.), 16, 473.

Chlorine

Herman, W., Weiss, D. (1973), Determination of chlorides in rocks using the chloride ionically selective electrode after pyrolysis: Silikaty c., 2, 125.

Hipp, B. W., Langdale, G. W. (1971), Use of solid-state chloride electrode for chloride determinations in soil extracts: Soil Sci. and Plant Anal., 2, 237.

Copper (II)

Jyo, Akinori, Hashizume, Takao, Ishibashi, Nabuhiko (1977), Ligand interference preventive buffer in determination of copper (II) by a cupric ion selective electrode: Anal. Chem., 49, 1868-1869.

Ogelsby, G. B., Duer, W. C., Millero, F. J. (1977), Effect of chloride ion and ionic strength on the response of a copper (II) ion-selective electrode: Anal. Chem., 49, 877.

Fluoride and Fluorine

Anfalt, Torbjorn, Jagner, Daniel (1971), A standard addition method for the potentiometric determination of fluoride in sea water: Anal. Chim. Acta, 53, 13-22.

Baker, R. L. (1972), Determination of fluoride in vegetation using the specific ion electrode: Anal. Chem., 44, 1326.

Bloxam, T. W. (1968), A rapid method for the determination of fluoride in silicate rocks: Chem. Geol., 3, 89-94.

Clements, R. L., Sargeant, G. A., Webb, P. J. (1971), The determination of fluorine in rocks and minerals by a pyrohydrolytic method: Analyst, 96, 51.

Crosby, N. T., Dennis, A. L., Stevens, J. G. (1968), An evaluation of some methods for the determination of fluoride in potable waters and other aqueous solutions: Analyst, 93, 643.

Evans, L., Hoyle, R. D., Macaskill, J. B. (1970), An accurate and rapid method of analysis for fluorine in phosphate rocks: New Zealand J. of Sci., 13, 143.

Hallsworth, Alan S., Weatherell, John A., Deutsch, Dan (1976), Determination of subnanogram amounts of fluoride with the fluoride electrode: Anal. Chem., 48, 1660-1664.

Ingram, B. L., May, I. (1971), Determining fluoride in rocks with a specific ion electrode: U.S. Geol. Surv. Prof. Paper 750-B, B-180.

Kauranen, Pentti (1977), The use of buffers in the determination of fluoride by an ion-selective electrode at low concentrations and in the presence of aluminium: Anal. Letters, 10, 451-465.

Ke, P. J., Reigier, L. W. (1971), Determination of fluoride in soils by a nonfusion distillation pF method: J. Fish. Res., 28, 1055.

Kesler, S. E., VanLoon, J. C., Bateson, J. H. (1973), Analysis of fluoride in rocks and an application to exploration: J. Geochem. Exploration, 2, 11-17.

Kosov, A. Ye., et al. (1976), Potentiometric determination of fluorine in seawater: Oceanology (U.S.S.R.), 16, 467-469.

Larsen, S., Widdowson, A. E. (1971), Soil fluorine: J. Soil Sci., 22, 210.

Phuphatana, Amorn, Carlson, Ernest H., Manus, Ronald W. (1976), The fluoride ion-selective electrode as applied to fluorospar deposits in Southwest Texas and Southern Illinois: Econ. Geol., 71, 661-664.

Pluger, W. L., Friedrich, G. H. (1972), Determination of total and cold-extractable fluoride in soils and stream sediments with an ion-sensitive fluoride electrode: Proceedings of the Fourth International Geochemical Exploration Symposium, London, 1972, 421-427.

Pouget, R. (1971), Measuring fluorine in geological materials: Chim. Anal., 53, 479 (in French).

Tanikawa, S., Kirihara, H., Shiraishi, N. (1975), Masking ability of various complexing agents for aluminum in the fluorine determination with a fluoride ion-selective electrode: Anal. Letters, 8, 879-883.

Troll, Georg, Farzaneh, Abbas, Cammann, Karl (1977), Rapid determination of fluoride in mineral and rock samples using an ion-selective electrode: Chem. Geol., 20, 295-305.

Warner, T. B. (1971), Normal fluoride content of seawater: Deep-Sea Res., 18, 1255.

Warner, T. B., Bressan, D. J. (1973), Direct determination of less than 1 part-per-billion fluoride in rain, for an aerosols with an ion-selective electrode: Anal. Chim. Acta, 63, 165.

Wilkness, P. E., Warner, T. B., Carr, R. A. (1971), Some aspects of the geochemistry of fluorine, iron and manganese in coastal waters and in fresh-water springs on the southeast coast of Hawaii: Marine Geology, 11, 39.

Windom, H. L. (1971), Fluoride concentration on coastal and estuarine waters of Georgia: *Limn. and Oceanog.*, 16, 806.

Gold

Weiss, D. (1972), The iodide-ion selective electrode as a cationic sensor for the determination of gold: *Z. Anal. Chem.*, 262, 28.

Halide Concentration

Jagner, Daniel, Aren, Kerstin (1970), A rapid semi-automatic method for the determination of the total halide concentration in sea water by means of potentiometric titration: *Anal. Chim. Acta*, 52, 491.

Lerman, A., Shatkay, A. (1968), Dead Sea brings degree of halite saturation by electrode measurements: *Earth Planet. Sci. Letters*.

Ion-Exchange Studies

Busenberg, E., Clemency, C. V. (1973), Determination of the cation exchange capacity of clays and soils using an ammonia electrode: *Clays and Clay Minerals*, 21, 213.

Fertl, W., Jessen, F. W. (1969), Cation replacement studies of hetero ionic bentonitic clay fractions using specific ion glass electrodes: *Clays and Clay Minerals*, 17, 1.

Iron (III)

Fung, Y. S., Fung, K. W. (1977), Determination of iron (III) with a copper selective electrode: *Anal. Chem.*, 49, 497.

Nitrate

Bremner, J. M., Bundy, L. G., Agarwal, A. S. (1968), Use of a selective ion electrode for the determination of nitrate in soils: *Anal. Letters*, 1, 837.

Bunton, N. G., Crosby, N. T. (1969), The determination of nitrate in waters and effluents using a specific ion electrode: *Water Treat. Exam.*, 18, 338.

Chalk, P., Keeney, D. R. (1971), Nitrate and ammonium contents of Wisconsin limestones: *Nature*, 229, 42.

Keeney, D. R., Byrnes, B. H., Genson, J. J. (1970), Determination of nitrate in waters with the nitrate selective electrode: *Analyst*, 93, 383.

Langmuir, D., Jacobson, R. L. (1970), Specific-ion electrode determination of nitrate in some freshwaters and sewage effluents: *Environ. Sci. and Tech.*, 4, 835.

Mack, A. R., Sanderson, R. B. (1971), Sensitivity of the nitrate-ion membrane electrode in various soil extracts: *Can. J. Soil Sci.*, 51. 95.

Mahendrappa, M. K. (1969), Determination of nitrate nitrogen in soil extracts using a specific ion activity electrode: *Soil Sci.*, 108, 132.

Mertens, J., Massart, D. L. (1973), The determination of nitrate in mineral waters by potentiometry and ultraviolet spectrophotometry: *Bull. Soc. Chim. Belg.*, 82, 179.

Milham, P. J., Awad, A. S., Paull, R. E., Bull, J. H. (1970), Analysis of plants, soils, and waters for nitrate by using an ion-selective electrode: *Analyst*, 95, 751.

Morie, G. P., Ledford, C. J., Glover, C. A. (1972), Determination of nitrate and nitrite in mixtures with a nitrate ion electrode: *Anal. Chim. Acta*, 60, 397.

Myers, R. J. K., Paul, E. A. (1968), Nitrate ion electrode method for soil nitrate nitrogen determination: *Can. J. Soil Sci.*, 48, 369.

Oien, A., Selmer-Olsen, A. R. (1969), Nitrate determination in soil extracts with the nitrate electrode: *Analyst*, 94, 888.

Potterton, S., Shults, W. D. (1967), An evaluation of the performance of the nitrate-selective electrode: *Anal. Letters*, 1, 11.

Sommerfeldt, T. G., Milne, R. A., Kozub, G. C. (1971), Use of the nitrate specific ion electrode for the determination of nitrate nitrogen in surface and ground water: *Comm. Soil Sci. Plant Anal.*, 2, 415.

Potassium

Lal, S., Christian, G. D. (1970), Response characteristics of the Orion potassium ion selective electrode: *Anal. Letters*, 3, 11.

Sodium

Savenko, V. S. (1977), Use of sodium-selective electrodes in marine geochemical studies: *Oceanology* (U.S.S.R.), 17, 43-45.

Sulfate

Goertzen, J. O., Oster, J. D. (1972), Potentiometric titration of sulfate in water and soil extracts using a lead electrode: *Soil Sci. Soc. Proc*., 36, 691.

Miscellaneous Applications

Kester, D. R., Pytkowicz, R. M. (1969), Sodium, magnesium, and calcium sulfate ion-pairs in seawater at 25 C: *Limn, and Oceanog*., 14, 686.

Koryta, Jiri (1977), Theory and applications of ion-selective electrodes, part II: *Anal. Chim. Acta*, 91, 86 pp.

Midgley, Derek (1977), Interpretation of non-ideal calibrations of ion-selective electrodes: *Anal. Chem*., 49, 1211.

Reynolds, R. C., Jr. (1971), Analysis of Alpine waters by ion electrode methods: *Water Resources Res*., 7, 1333.

Riseman, J. M. (1969), Measurement of inorganic water pollutants by specific ion electrode: *Am. Lab*., 1, 32.

Roberson, C. E., Hem, J. K. (1968), Activity product constant of cryolite at 25 C and one atmosphere using selective-ion electrodes to estimate sodium and fluoride activites: *Geochim. Cosmochim. Acta*, 32, 1343.

Tanji, K. K. (1969), Solubility of gypsum in aqueous electrolytes and affected by ion association and ionic strengths up to 0.15M and at 25 C: Environ. Sci. Technol., 3, 656.

Westcott, C. C. (1977), Ion-selective measurements by Gran plots with a Gran ruler: Anal. Chim. Acta, 86, 269-271.

BIBLIOGRAPHY

BIBLIOGRAPHY

Adams, P. B. (1972), Glass containers for ultrapure solutions, Ch. 14 in Ultrapurity: Methods and Techniques (Morris Zeif and Robert Speights, editors), Marcel Dekker.

Allum, A. I., Pitts, G., and Hollis, J. P. (1971), Sulfide determination in submerged soils with an ion-selective electrode: Soil Science, 114, 456-467.

Bates, Roger G. (1973), Determination of pH: Theory and Practice, 2nd ed., 479 pp, Wiley-Interscience.

Bodkin, J. B. (1977), Determination of fluorine in silicates by use of an ISE following fusion with lithium metaborate: Analyst, 102, 409-413.

Buffle, J., Parthasarathy, N., Haerdi, W. (1974), Study of the behaviour of solid-state membrane electrodes, Part II: Anal. Chim. Acta, 68, 253-266.

Bruckenstein, Stanley, and Kolthoff, I. M. (1959), Acid-base strength and protolysis curves in water, Ch. 12, in Treatise on Analytical Chemistry (I. M. Kolthoff, P. J. Elving, and E. B. Sandell, editors), The Interscience Encyclopedia.

Buck, Richard P. (1976), Ion selective electrodes: Anal. Chem., 48, 23R-39R.

Butler, James Newton (1964), Ionic Equilibrium: A Mathematical Approach, 547 pp, Addison-Wesley.

Butler, James Newton (1969), Thermodynamic studies, Ch. 5. in Ion-Selective Electrodes (Richard A. Durst, editor), 452 pp, Nat. Bur. Std. Special Publication 314.

Cammann, Karl, and Rechnitz, G. A. (1976), Exchange kinetics at ion-selective membrane electrodes: Anal. Chem., 48, 856-862.

Carlson, R. M., and Keeney, D. R. (1971), Specific-ion electrodes: techniques and uses in soil, plant, and water analysis, in Instrumental Methods for Analysis of Soils and Plant Tissue, 39-64.

Chaffee, Maurice A. (1976), Geochemical exploration techniques based on distribution of selected elements in rocks, soils, and plant, Mineral Butte copper deposit, Pinal County, Arizona, *U.S. Geol. Surv. Bull*. 1278-D, 55 pp.

Covington, Arthur K. (1969), Reference electrodes, Ch. 4 in *Ion-Selective Electrodes* (Richard A. Durst, editor), 452 pp. Nat. Bur. Std. Special Publication 314.

Crenshaw, George L., and Ward, F. N. (1975), Determination of fluorine in soils and rocks by known-increment addition and selective-ion electrode detection, in New and Refined Methods of Trace Analysis Useful in Geochemical Exploration, *U.S. Geol. Surv. Bull*. 1408, 77-84.

Draper, N. R., and Smith, H. (1966), *Applied Regression Analysis*, 407 pp, John Wiley and Sons.

Durst, Richard A. (1969), Analytical techniques and applications of ion-selective electrodes, Ch. 1 in *Ion-Selective Electrodes* (Richard A. Durst, editor), Nat. Bur. Std. Special Publication 314, 452 pp.

Durst, Richard A., and Duhart, Benjamin T. (1970), Ion-selective electrode study of trace silver ion adsorption on selected surfaces: *Anal. Chem*., 42, 1002-1004.

Edmond, C. R. (1969), Direct determination of fluoride of phosphate rock samples using the specific ion electrode: *Anal. Chem*., 41, 1327-1328.

Eisenman, George (1969), Theory of membrane electrode potentials: an examination of the parameters determining the selectivity of solid and liquid ion exchangers and of neutral ion-sequestering molecules, Ch. 1 in *Ion-Selective Electrodes* (Richard A. Durst, editor), Nat. Bur. Std. Special Publication 314, 452 pp.

Feldman, Isaac (1956), Use and abuse of pH measurements: *Anal. Chem*., 28, 1859-1866.

Ficklin, Walter H. (1970), A rapid method for the determination of fluoride in rocks and soil, using an ion-selective electrode, *U.S. Geol. Surv. Prof. Paper* 700-C, C186-C188.

Frant, M. S., and Ross, J. W., Jr. (1968), Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplied: *Anal. Chem*., 40, 1169-1171.

Friedenberg, Harald (1955), Separation and determination of microgram quantities of silver, mercury, and copper with dithizone: Anal. Chem., 27, 305-306.

Friedrick, G. H., Plüger, W. L., Hilmer, E. F., and Abu-Abed, I. (1972), Flameless atomic absorption and ion-sensitive electrodes as analytical tools in copper exploration, in Geochemical Exploration 1972, The Institute of Mining and Metallurgy, London, 435-443.

Fritz, James S., and Schenk, George H. (1974), Quantitative Analytical Chemistry, 3rd ed., 689 pp, Allyn and Bacon.

Garrels, Robert M., and Christ, Charles L. (1965), Solutions, Minerals, and Equilibria, 450 pp. Freeman, Cooper, and Company.

Haynes, Simon J., and Clark, Alan H. (1972), A rapid method for the determination of chlorine in silicate rocks using ion-selective electrodes: Econ. Geol., 67, 378-382.

Hem, John D. (1961), Calculation and use of ion activity, U.S. Geol. Surv. Water-Supply Paper 1535-C, 17 pp.

Hseu, Tong-Ming, and Rechnitz, G. A. (1968), Analytical study of a sulfide ion-selective membrane electrode in alkaline solution: Anal. Chem., 40, 1054-1060. Correction ibid. (1968), 40, 1661.

Helanicki, Adam, and Trojanowicz, Marek (1974), Direct potentiometric determination of calcium in waters with a constant complexation buffer: Anal. Chim. Acta, 68, 155-160.

Ingram, Blanch L. (1970), Determination of fluoride in silicate rocks without separation of aluminum using a specific ion electrode: Anal. Chem., 42, 1825-1827.

Jagner, Daniel, and Pavlova, Violeta (1972), A standard addition titration method for the determination of fluorine in silicate rocks: Anal. Chim. Acta, 60, 153-158.

Johansson, Gillis, and Edström, Kerstin (1972), Studies of copper (II) sulphide ion-selective electrodes: Talanta, 19, 1623-1632.

Karlberg, Bo (1971), Nomograph for known addition methods in analysis with ion selective electrodes: Anal. Chem., 43, 1911-1913.

Lapatnick, Leonard N. (1974), Application of ion-selective electrodes to the analysis of silver-plating baths: Anal. Chim. Acta, 72, 430-433.

Lawrence, Fred W. (1976), Department of Geology, University of South Florida, Tampa, Florida, personal communication.

Leyendekkers, J. V. (1971), Single ion activities in multicomponent systems: Anal. Chem., 43, 1835-1843.

Liberti, Arnaldo, Mascini, Marco (1969), An ion determination with ion-selective electrodes using Gran's plots: Anal. Chem., 41, 676-679.

Light, Truman S. (1969), Industrial analysis and control with ion-selective electrodes, Ch. 10 in Ion-Selective Electrodes (Richard A. Durst, editor), Nat. Bur. Std. Special Publication 314, 452 pp.

Light, Truman S., and Swartz, James L. (1968), Analytical evaluation of the silver sulfide membrane electrode: Anal. Letters, 1, 825-836.

McQuaker, Neil R., and Gurney, Mary (1977), Determination of total fluoride in soil and vegetation using an alkalai fusion-selective ion electrode technique: Anal. Chem., 49, 53-56.

Minkkinen, Pentti (1975), A method for the correction of the background absorption in silver analysis of calcareous samples: At. Abs. Newslett., 14, 71-72.

Müller, Doris Clegg, West, Philip W., and Müller, Ralph H. (1969), Determination of silver ion in parts per billion range with a selective ion electrode: Anal. Chem., 41, 2038-2040.

Nakagawa, H. M. (1975), Atomic absorption determination of silver, bismuth, cadmium, cobalt, copper, nickel, lead, and zinc in calcium- and iron-rich geologic materials, in New and Refined Methods of Trace Analysis Useful in Geochemical Exploration, U.S. Geol. Surv. Bull. 1408, 85-96.

Orion Research Incorporated (1974), *Bibliography, Orion Specific Ion Electrodes*, and addendum, 21 pp.

Orion Research Incorporated, Determination of silver in photographic fixing solutions, *Applications Bulletin No. 14*, date unknown.

Orion Research Incorporated (1969a), Determination of total sulfide content in water, *Applications Bulletin No. 12*.

Orion Research Incorporated (1970), Faith, slope, and charity, *Newsletter/Specific Ion Electrode Technology*, Vol. 2, Nos. 7 and 8. Also, ibid., Vol. 2, Nos. 9 and 10.

Orion Research Incorporated (1968), *General Catalog*, 24 pp.

Orion Research Incorporated (1969b), Know-how on known addition, *Newsletter/Specific Ion Electrode Technology*, Vol. 1, No. 2.

Perkin-Elmer Corporation (1971), Analysis of sulfide minerals, *Analytical Methods for Atomic Absorption Spectrometry*, GC3-GC4.

Parthasarathy, N., Buffle, J., Monnier, D. (1974), Study of the behaviour of solid-state membrane electrodes, Part I: *Anal. Chim. Acta*, 68, 185-196.

Rechnitz, G. A. (1967), Ion-selective electrodes: *Chem. and Eng. News*, 45, 146-158.

Ringbom, Anders (1963), *Complexation in Analytical Chemistry*, 395 pp, Interscience Publishers.

Riseman, Jean M. (1970), Specific ion electrodes-versatile new analytical tools: *Water and Sewage Works*, 117, IW12-IW18.

Robertson, D. E. (1968), The absorption of trace elements in sea water on various container surfaces: *Anal. Chim. Acta*, 42, 533-536.

Ross, James W., Jr. (1969), Solid-state and liquid membrane ion-selective electrodes, Ch. 2 in *Ion-Selective Electrodes* (Richard A. Durst, editor), Nat. Bur. Std. Special Publication 314, 452 pp.

Rubeska, I., Sulcek, Z., and Moldan, B. (1967), The determination of silver in sulphide minerals by atomic absorption spectrophotometry: *Anal. Chim. Acta*, 37, 27-32.

Sandell, E. B. (1959), Colorimetric Determination of Traces of Metals, 3rd ed., 1032 pp, Interscience.

Schuller, Rudolph M. (1976), The Cupric Ion-Selective Electrode as a Geochemical Reconnaissance Tool, unpublished M.S. thesis, Department of Geology, Wright State University, Dayton, Ohio.

Selig, Walter (1973), Microdetermination of fluoride using Gran's plots: Mikrochim. Acta wien , 87-100.

Siegel, Frederic R. (1974), Applied Geochemistry, 353 pp, Wiley-Interscience.

Skoog, Douglas A., and West, Donald M. (1969), Fundamentals of Analytical Chemistry, 2nd ed., 835 pp, Holt, Rinehart, and Winston.

Skoog, Douglas A., and West, Donald M. (1971), Principles of Instrumental Analysis, 710 pp, Holt, Rinehart, and Winston.

Slavin, Walter (1968), Atomic Absorption Spectroscopy, 307 pp, Interscience Publishers.

Smith, Michael James (1972), The Chemistry of Copper and Algal Growth, Ph.D. dissertation, Department of Chemistry, University of Missouri, Columbia, Missouri.

Smith, Michael J., and Manahan, Stanley E. (1973), Copper determination in water by standard addition potentiometry: Anal. Chem., 45, 836-839.

Struempler, Arthur W. (1972), Adsorption characteristics of silver, lead, cadmium, zinc, and nickel on borosilicate glass, polyethelene, and polypropylene container surfaces: Anal. Chem., 45, 2251-2254.

Stumm, Werner, and Morgan, James J. (1970), Aquatic Chemistry, 583 pp, Wiley-Interscience.

Thompson, M. E. (1966), Magnesium in sea water: an electrode measurement: Science, 153, 866-867.

Thompson, M. E., and Ross, J. W. (1966), Calcium in sea water by electrode measurement: Science, 154, 1643-644.

Van Loon, J. C. (1968), The rapid determination of fluoride in mineral fluorides using a specific ion electrode: Anal. Letters, 1, 393-398.

Ward, F. N., Nakagawa, H. M., Harms, T. F., and Van Sickle, G. H. (1969), Atomic-absorption methods of analysis useful in geochemical exploration, U.S. Geol. Surv. Bull. 1289, 45 pp.

West, Foymae Kelso, West, Philip W., and Iddings, Frank A. (1966), Adsorption of traces of silver on container surfaces: Anal. Chem., 38, 1566-1570.

West, Foymae Kelso, West, Philip W., and Iddings, Frank A. (1967), Adsorption characteristics of traces of silver on selected surfaces: Anal. Chim. Acta, 37, 112-121.

Woolson, E. A., Axley, J. H., and Kearing, P. C. (1970), Soil calcium determination using a calcium specific ion electrode: Soil Science, 108, 279-281.

dsh