

Ion-Selective Electrochemical Sensors— Third Report

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United States Department of the Interior • Rogers C. B. Morton, Secretary
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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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INTERMEDIATE REPORT
FOR
ION-SELECTIVE ELECTROCHEMICAL SENSORS

I. INTRODUCTION

Ion-selective electrochemical sensors can be used to economically, rapidly, and continuously monitor the concentrations of a variety of ion constituents in aqueous solutions, particularly brackish, saline, and brine waters. Under an extension of Office of Saline Water Contract No. 14-01-0001-1737, work on the development of such sensors has continued at Texas Instruments. The results of the investigations carried out under this contract prior to the current year have been reported in United States Department of Interior, Office of Saline Water, Research and Development Reports No. 496¹ and No. 619² (hereafter referred to as OSW Reports No. 496 and No. 619) and a paper³ entitled "Ion-Selective Electrochemical Sensors - Fe^{+3} , Cu^{+2} ," published in The Journal of the Electrochemical Society.

The materials approach to developing good ion-selective electrochemical sensors considered both crystalline and amorphous materials. Studies of crystalline materials involved doping single crystals of various calcium compounds and doping several semiconductors such as germanium, silicon, and gallium arsenide. The amorphous materials studies have been limited to doping chalcogenide and oxy-chalcogenide glasses. In general, whatever material is used in the sensor, it must be insoluble in the aqueous solutions it is to measure, and its resistivity should be less than 10^8 ohm-cm. Crystalline materials may show response because of significant conductivity by the ion of interest, because of unique electrochemical properties, or because of an ion exchange reaction. Amorphous material may show response because of ionic conduction in "holes" of the proper size in the glass to accommodate the ion of interest selectively, because of unique electrochemical properties, or because of exchange reactions in the surface.

During the past year, sensors for Fe^{+3} , Cu^{+2} , Ca^{+2} , Mg^{+2} , Na^+ , and $SO_4^{=}$ were investigated. In a few instances the work was of a screening nature and was intended merely to obtain some information concerning conductivity and response of several unique materials not generally available. In most cases, however, detailed materials preparation, resistivity measurements, and sensor response evaluations were made. A major effort was devoted to obtaining a better understanding of the chalcogenide systems and how they function as selective sensors. This study led to the oxy-chalcogenide system which has some promise of being modified to yield a series of selective sensors. The $CuO \cdot As_2S_3$ system has yielded sensors which respond down to 0.1 ppm Cu^{+2} in 3 M KCl and show good response at 0.1 ppm total Cu in sea water. Major effort was also expended on growing doped, crack-free, single crystals of various calcium salts. In the latter part of the year, some good crystals were obtained, but additional work is still required to modify their conductivity.

The previous work on Fe^{+3} sensors¹⁻³ demonstrated that these sensors will respond to Fe^{+3} in the presence of Cu^{+2} . In this report the $(\text{CuO})_{0.15}(\text{As}_2\text{S}_3)_{0.85}$ sensors are shown to have excellent selectivity for Cu^{+2} in the presence of Fe^{+3} . In addition, both sensors have demonstrated the capability of responding in the 0.1 to 1 ppm range and possibly lower. The response appears to be unaffected by large concentrations of Na and/or KCl solutions, as well as many more common divalent ions (Ca^{+2} and Mg^{+2}) found in natural waters. The prospects of obtaining a system, whether direct or indirect, for the detection and monitoring of Fe^{+3} and Cu^{+2} from various corrosion processes such as distillation desalination processes appear excellent. Application of these systems to various pollution control projects also appears worthwhile. In a related project it has been demonstrated that the Fe^{+3} sensor could be used to monitor acid mine drainage waters. Studies of the application of these sensors to monitoring several processes should be accomplished and demonstration programs initiated in the near future. With proper precautions, the usefulness of these ion-selective electrochemical sensors should be limited only by the imagination and ingenuity of the users.

The format of this report will be different from previous reports in this series. Each sensor will be discussed by the ion to which it responds. Included in the discussion of each ion sensor will be sensor materials preparation, resistivity of sensor material, evaluation of materials in ion-selective sensors and mechanistic studies to provide a better understanding of the way the sensor works and some of the precautions necessary to insure its reliable performance.

II. Fe⁺³ SENSORS

A. Material Preparation

The best ion-selective sensor for Fe⁺³ found thus far in this program has been Fe-doped 1173 glass (composition: Ge₉₈Sb₁₂Se₆₀). One of the reasons this material was selected as a basis for doping experiments is that it is readily available in large quantities as a commercial product from Texas Instruments. A second glass composition has reached a similar status, glass #20, which has a composition of Ge₃₃As₁₂Se₆₅. Investigations using this material were undertaken for two reasons: (1) because of the possibility that this material would yield a better sensor that might be extended to ions other than Fe⁺³, and (2) to obtain better understanding of the role of the host material.

Samples of Fe-20 glass were prepared using Fe wire in a manner similar to that employed with 1173.¹ Pieces of bulk glass were weighed and placed in a quartz ampule along with the appropriate amount of Fe wire. The ampule was evacuated, sealed, and placed in a rocking furnace. Reaction time varied from 20 hours to 70 hours at 700°C to 900°C. The samples were then quenched and annealed for several hours. Slices were cut from the resulting glass cylinder and fabricated into sensors of both electrode and membrane configurations.

Some of the #20 glass samples were quite good. Undoped samples were also prepared for comparison. The excellent results obtained for the 1173 glass and the #20 glass prompted the decision to prepare glass compositions containing the constituent elements of the two base systems (with the exception of Sb, which is a very poor glass-former) in an attempt to identify the factors important in the electrochemical activity. Glasses based on Se, As-Se, and Ge-Se were prepared. As before, both undoped and Fe-doped materials were prepared. In some cases, the iron doping was carried out using Fe₂Se₃ instead of iron wire. Resistivity measurements of the Fe-doped #20 glass exhibited considerable variation with preparation procedure. Several additional samples were made with 2%, 4%, and 6% Fe.

Table I lists the chalcogenide samples prepared for Fe⁺³ during this report period.

Other undoped chalcogenide glasses were investigated. These samples were prepared for another, unrelated program. Tests were performed to gain further information concerning the mechanisms of these materials as ion-selective electrochemical sensors. The specific samples were chosen because their resistance was less than 10⁷ ohms. The materials tested were

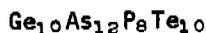


Table I
Chalcogenide Sensor Materials
Prepared for Fe⁺³ Sensor Studies

<u>Sample</u>	<u>Dopant</u>	<u>Mole %</u>	<u>Comments</u>
# 20 glasses*	Fe (wire)	2	22 hours at 700°C; quenched at 500°C and annealed 70 hours at 175°C.
Se	Fe (wire)	2	2.8 hours at 740°C; quenched at 500°C and annealed at 175°C.
Se	Fe (wire)	2	8.2 hours at 740°C, 2.0 hours at 750°C; quenched at 500°C, annealed at 175°C.
Se	Fe ₂ Se ₃	2	6.7 hours at 740°C.
Ge ₃₀ Se ₇₀	Fe ₂ Se ₃	1	6.0 hours at 740°C.
Ge ₁₅ Se ₈₅	Fe ₂ Se ₃	1	5.5 hours at 740°C.
# 20	Fe (wire)	2	22 hours at 700°C; annealed 23 hours at 175°C.
# 20	Fe (wire)	2	68.5 hours at 700°C; annealed 3.5 hours at 175°C.
As ₄₀ Se ₆₀	None	0	4.7 hours at 700°C.
As ₄₀ Se ₆₀	Fe (wire)	2	19 hours at 700°C, 2 hours at 175°C.
# 20	Fe (wire)	2	16 hours at 900°C; quenched at 700°C, annealed 2.7 hours at 175°C.

Table I
(continued)

<u>Sample</u>	<u>Dopant</u>	<u>Mole %</u>	<u>Comments</u>
# 20	Fe (wire)	4	16 hours at 900°C; quenched at 700°C, annealed 3 hours at 175°C.
# 20	Fe (wire)	6	16 hours at 900°C; quenched at 700°C, 2.8 hours at 175°C.
Ge ₁₅ Se ₈₅	Fe (wire)	2	18 hours at 900°C; cooled to 700°C; air-quenched, annealed 2.5 hours at 175°C.

* # 20 glass is 33 mole % Ge, 12 mole % As, and 55 mole % Se.

Ge₇Te₁₃ (crystal)
Sn₁₈AsSe (crystal)
GeAs₁₅Te₄

All these materials were made into electrode configuration sensors.

B. Resistivity of Fe⁺³ Sensor Materials

Resistivity measurements on material prepared for Fe⁺³ sensors were made according to the procedure outlined in OSW Report #496.¹ These measurements are summarized in Table II

No resistivity measurements could be obtained with the doped pure Se glasses because of the low melting point of the material. These samples were badly deformed during the contact evaporation step. The other glasses have much higher melting points and can easily withstand the temperature reached during evaporation of gold contacts.

Various slices from the doped #20 glasses were tested because the doping process yielded a glass that appeared inhomogeneous. Resistivity measurements did not confirm this observation. There was a considerable variation in resistance between preparations. As pointed out below, low resistance may be a necessary condition for good sensors; but it is not sufficient in itself. However, as discussed in the sensor evaluation section, the sensor dissolves, and no further work was attempted.

One idea behind doping a solid material with a specific ion to measure that ion's activity in aqueous solution is based on the mercury amalgam concentration cell. In that system, the ion of interest is dissolved in some form into mercury to form a mercury amalgam or solid solution. The activity of that ion in an aqueous solution in contact with the amalgam is measured according to the change in potential given by the expression:

$$E = E_0 - \frac{RT}{nF} \ln \frac{a^+(\text{solution})}{a^+(\text{amalgam})} ,$$

where $a^+(\text{solution})$ is the activity in solution related to concentration and $a^+(\text{amalgam})$ is the activity in the solid solution, which is, of course, fixed.

By analogy, the chalcogenide glasses may be serving as the amalgam. The potential generated should be independent of the resistivity of the material and should indicate the effect on the bulk properties of the material relative to electrochemical activity. However, such information is masked by the experimental difficulties of measuring the potential when the electrode is a nonconductor. The high resistivity is a complicating factor for the glass system, not necessarily a fundamental limitation. A new method of evaluation must be devised to separate the electrochemical potential effects from the resistivity complication.

An obvious physical solution to the problem is to mount the electrodes in such a way that the electrode thickness can be substantially lowered by polishing. A second method is to identify a glass doping agent, if possible, which will lower the bulk resistivity but at the same time remain electrochemically inactive.

Table II
Specific Resistivities of Fe⁺³ Sensor Material
at 20 V dc and Ambient Temperature

<u>Sample</u>	<u>Resistivity (Ω-cm)</u>
2% Fe-Se	Sample melted
1% Fe-Ge ₃₀ Se ₇₀	6×10^{10}
1% Fe-Ge ₁₅ Se ₈₅	2×10^{10}
2% Fe-Ge ₁₅ Se ₈₅	4×10^{10}
As ₄₀ Se ₆₀	6.2×10^1
2% Fe-As ₄₀ Se ₆₀	1.8×10^6
2% Fe-20* A	
Slice #2 (bottom)	2.5×10^{10}
Slice #19 (top)	2.8×10^{10}
2% Fe-20* B	4.8×10^9
2% Fe-20* C	
Slice #3 (bottom)	1.5×10^2
Slice #7	7.8×10^2
Slice #15	3.2×10^2
4% Fe-20*	1.2×10^3
6% Fe-20*	4.2×10^1

* #20 glass (composition: Ge₃₃As₁₂Se₅₅).

Identification of the factors important in these doped 1173 and 20 glass systems may well lead to other systems which show the same performance for other ions. An understanding of the successful systems is essential.

One approach to obtaining more information about the chalcogenide systems themselves is to study some undoped system which has acceptable conductivity $< 10^8 \Omega\text{-cm}$. Additional measurements of undoped samples of other chalcogenide glasses were made with a General Radio Impedance Bridge, Model No. 1650A. In this instance the resistance of the actual sensor element was measured. The samples varied slightly in thickness, but all were between 30 and 50 mils thick and 0.5 cm in diameter. Resistance data are presented in Table III. Other samples of chalcogenide glasses were merely screened to assure that their resistances were below $10^7 \Omega$.

C. Sensor Evaluation

The first preparation and initial test of a 2% Fe-20 glass sensor yielded good results. A typical response is shown in Figure 1. The open circles represent decreasing concentration of Fe^{+3} , and the solid circles indicate increasing concentration. The slope as calculated by a computer program for least square fitting of the points to the best straight line yielded a slope of 76 millivolts (mV)/decade with a standard error of 4 mV/decade. However, these sensors tended to lose their activity rapidly and became almost inactive within 24 to 48 hours after a fresh surface was prepared. The initial activity loss appears as poor response at the low concentrations. This was true with minor variations for the 2, 4, and 6% Fe-20 sensors. In addition, an effect of stirring was noted. Measurements made in stirred solutions resulted in lower slopes and in some instances approached 59 mV/decade.

Since germanium is a component of sensors based on both 1173 and #20, and to provide a better understanding of the operation of these electrodes, a germanium sensor was fabricated and tested. The response of one of these electrodes is shown in Figure 2. The slope is a rather high 105 mV/decade with a standard error of less than 5 mV/decade. These results might explain some of the deviations from the 59 mV/decade observed in other Ge-containing sensors. Additional work to understand the Ge electrodes was warranted.

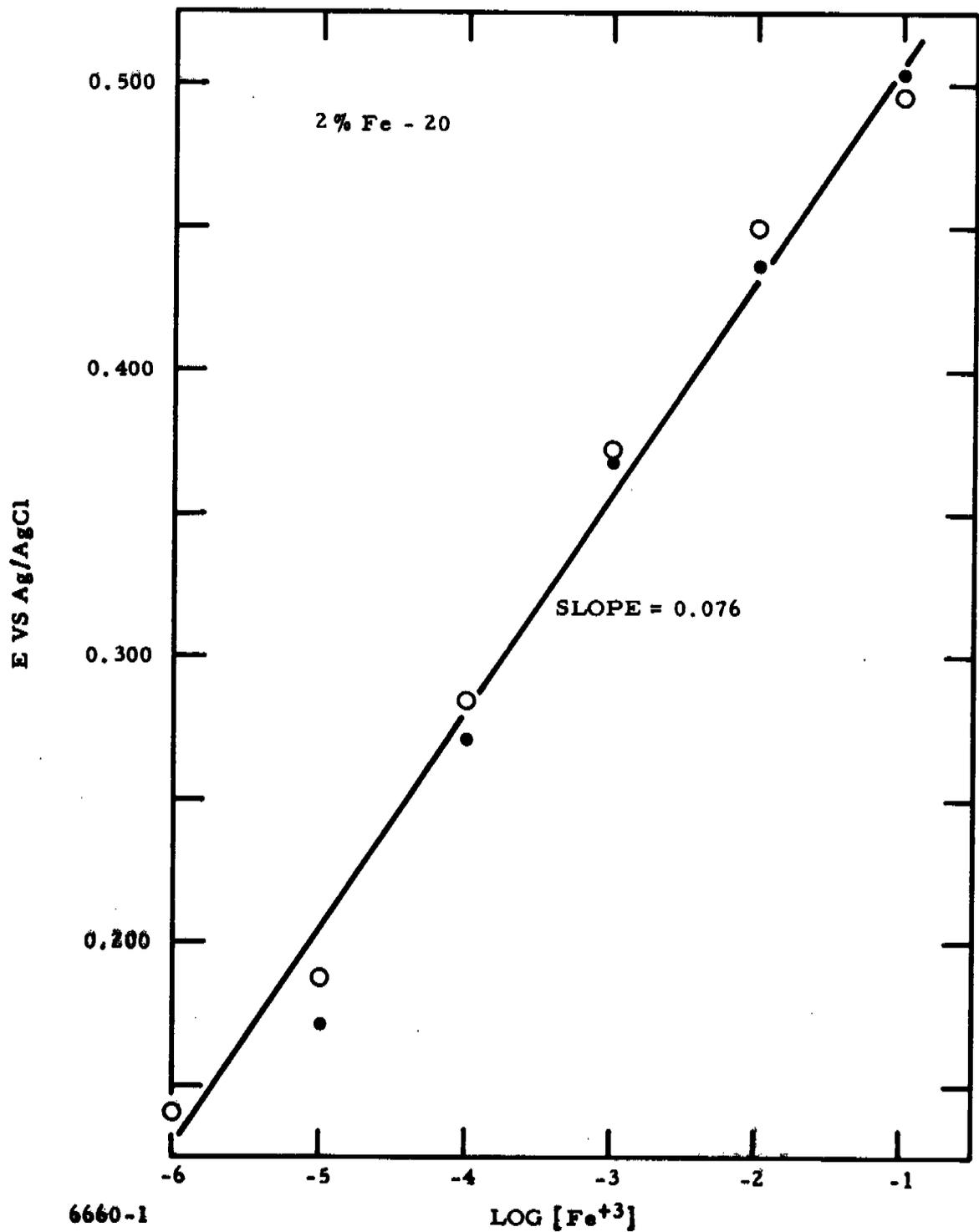
The Ge-sensor work was repeated, this time varying the equilibration time before taking the reading. In unstirred solution, after waiting five minutes for the electrode to equilibrate, a slope of 96 ± 4 mV/decade was obtained. The solution was then stirred moderately for five minutes and a new potential recorded. The slope of the response curve was found to be 63 ± 2 mV/decade, approaching the expected 59 mV/decade. These results are illustrated in Figure 3. The reproducibility of the results for the stirred solutions was independent of time after 30 seconds. This was not the case for the unstirred solutions.

The 2% Fe- $\text{Ge}_{15}\text{Se}_{85}$ sensors showed limited response to Fe^{+3} in the 10^{-1} to 10^{-3} M range. Two slices from the same sample yielded identical responses. A small effect on potential was observed when the solution was stirred; however, this did not change the slope of the curve, which was 45 mV/decade in the limited range.

Table III

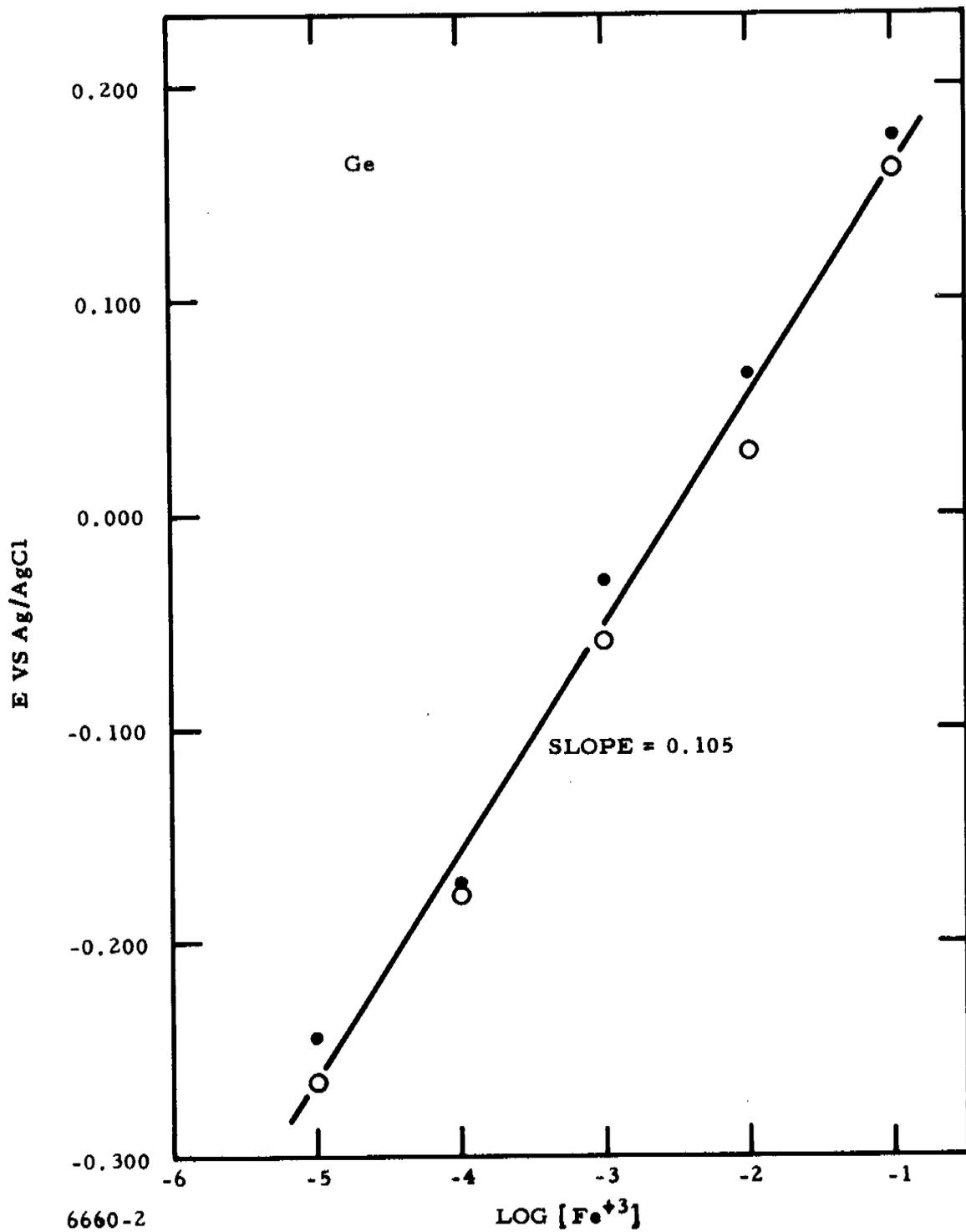
Resistance of Some Undoped Chalcogenide Glasses

<u>Sample</u>	<u>Resistance (Ω-cm)</u>
GeAs ₄ Te ₅	1.4×10^6
Si ₁₅ As ₂₅ Te ₆₀	5.1×10^6
GeAs ₂ Te ₇	2.7×10^5



6660-1

Figure 1 Potential Response of 2 Mole % Fe-20 Glass Electrode to Fe³⁺ Concentration at pH 1.7. (All solutions < 0.1 M in Fe³⁺ were 0.1 M KNO₃.)



6660-2

Figure 2 Potential Response of Ge Electrode to Fe³⁺ Concentration at pH 1.7. (All solutions < 0.1 M Fe³⁺ were 0.1 M KNO₃.)

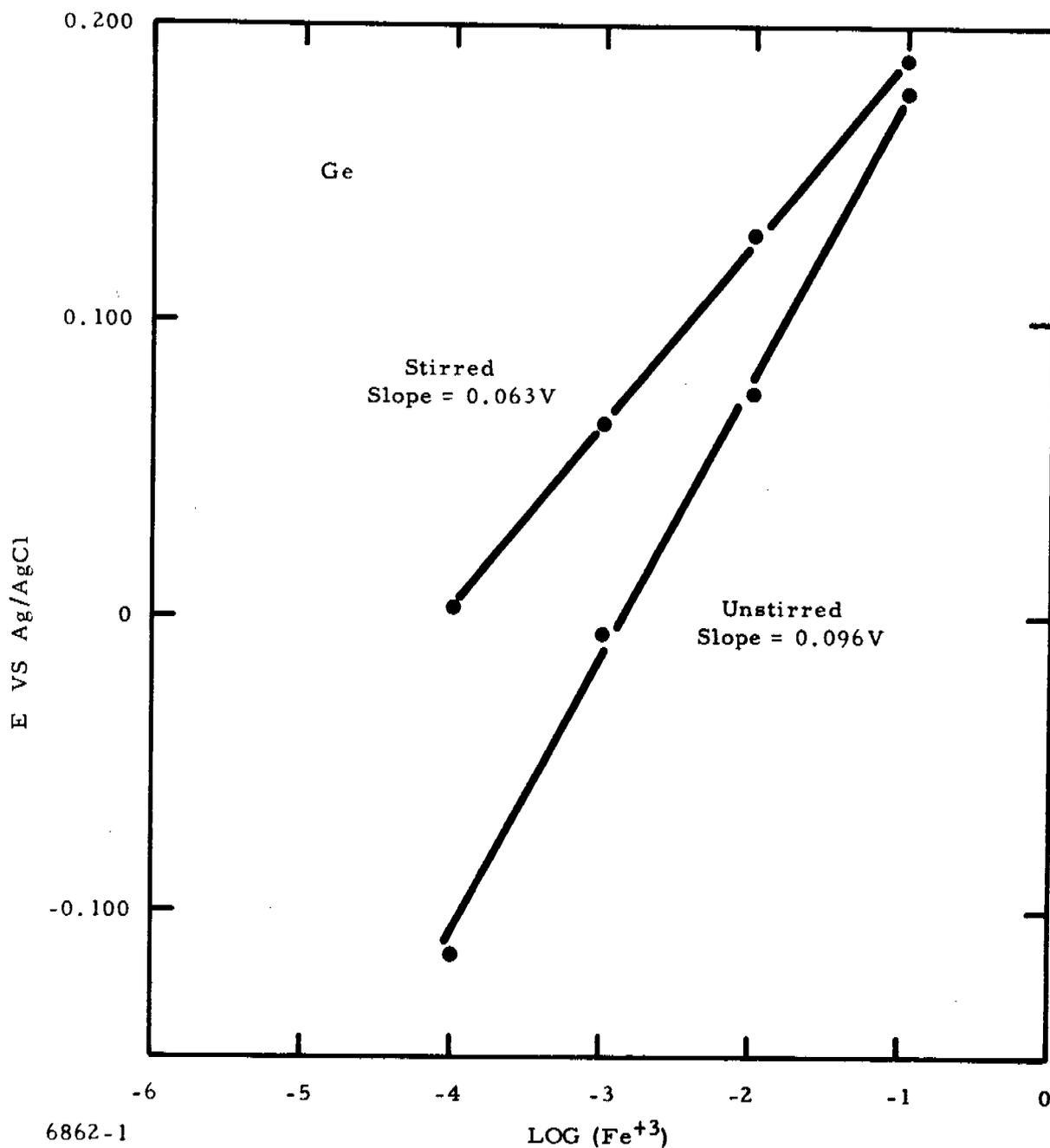


Figure 3 Potential Response of Ge Electrode to Fe³⁺ Concentration at pH 1.7 (All solutions < 0.1 M Fe³⁺ were 0.1 M KNO₃)

A 2% Fe-1173 and a 1.5% Ni-1173 (described in OSW report # 619) were reevaluated for response to pH and $[Fe^{+3}]$ in stirred and unstirred solutions. No effect of eight months storage was noted. There was no significant difference between stirred and unstirred solutions, as illustrated in Table IV.

Of the various undoped chalcogenide glasses and crystals tested, $GeAs_4Te_6$, $GeAs_2Te_7$, and $Si_{15}As_{25}Te_{60}$ exhibited the best response to changing $[Fe^{+3}]$. Response to pH and $[Fe^{+3}]$ were measured in stirred and unstirred solutions. The results of the latter test are presented in Table IV.

The data for Table IV were obtained by placing the sensor in a quiet solution, waiting approximately five minutes for equilibrium, recording the potential, then stirring the solution for about five minutes and recording the new equilibrium potential. The slopes are calculated using a least square computer program which also calculates the standard error of the slope. The range of concentration used to calculate the slope was always 10^{-1} to 10^{-4} or 10^{-5} M Fe^{+3} .

To test the hypothesis that some of the sensors were dissolving into the solutions, seven sensors were placed in 0.1 M $Fe(NO_3)_3$ (pH 1.7) and allowed to stand for 32 days. A blank of the 0.1 M $Fe(NO_3)_3$ solution was also allowed to stand. After this time interval, the solutions were analyzed by emission spectroscopy for trace amounts of the sensor materials. Eight solutions were analyzed.

- (1) $Fe(NO_3)_3$ blank. No sensor.
- (2) Ge
- (3) 4% Fe - #20 ($Ge_{33}As_{12}Se_{60}$)
- (4) 2% Fe - $As_{40}Se_{60}$
- (5) 2% Fe-1173 ($Ge_{28}Sb_{12}Se_{60}$)
- (6) $GeAs_2Te_7$
- (7) $Si_{15}As_{25}Te_{60}$
- (8) p-type Si

The method of analysis was as follows: A 0.05 ml portion of each solution was evaporated in a wet-proofed electrode, 18 to 20 mg of graphite was added, and the sample was dc arced. The emission spectrum of each sample was compared with the spectra of graphite standards from Spex Industries. Analyses were performed for the following elements with an estimate of the lower limit of detection in ppm.

<u>Element</u>	<u>Limit (ppm weight)</u>
As	10
Ge	1
Sb	1
Se	50
Si	1
Te	10

Only two solutions showed any of the elements listed above. The solution in contact with the Ge electrode contained about 500 ppm Ge, and the solution in contact with the 4% Fe-#20 sensor contained about 4 ppm Ge. Visual observation

Table IV

Response of Various Sensors
to Changing $[\text{Fe}^{+3}]$ in Stirred and Unstirred Solutions*

<u>Electrode</u>	<u>Slope in Stirred Solution (mV/decade)</u>	<u>Slope in Unstirred Solution (mV/decade)</u>
Ge	63 ± 2	96 ± 4
4% Fe - #20	77 ± 4	85 ± 3
GeAs ₄ Te ₅	67 ± 3	72 ± 4
GeAs ₂ Te ₇	45 ± 3	60 ± 4
Si ₁₅ As ₂₅ Te ₆₀	36 ± 5	55 ± 6
2% Fe As ₄₀ Se ₆₀	54 ± 6	53 ± 5
1.5% Ni-1173	52 ± 2	49 ± 2
2% Fe-1173	50 ± 2	51 ± 2

* All solutions pH 1.7; solutions less than 0.1 M Fe^{+3} contained 0.1 M KNO_3 .

of the electrodes after the 32 day stand confirmed that the Ge electrode was indeed severely etched.

D. Mechanism of Chalcogenide Sensors

Doping a chalcogenide glass with Fe metal and then checking a sensor prepared from the resulting material for Fe ion activity is analogous to preparing a mercury amalgam concentration cell. This concept was discussed previously. The assumption that the measured electrochemical activity of the electrode in the presence of Fe^{+3} solutions is due to the Fe doping came under question after good electrochemical activity was found for Fe doped TI #20 glass (Ge-As-Se) electrodes. We realized that the function the iron served could be simple lowering of the resistivity of the glass to a point at which the electrochemical activity could be measured with conventional equipment. Resistivity thus emerges as a complicating factor in the measurement of electrochemical activity.

What, then, is the origin of the electrochemical potential of the electrode if iron serves only to reduce the resistivity? The answer may be electrochemical activity of constituent elements. Activity has been observed for glasses made from Ge-Se and As-Se. In addition, good response to iron activity was found for a Ge electrode as expected from electrochemical considerations, with the obvious implication that Ge was the active constituent element which produces the electrochemical response to Fe^{+3} in sensors made from TI 1173 and TI #20 glasses.

More definitive results were obtained when electrodes fabricated from chalcogenide glasses from the SiAsTe and GeAsTe systems were evaluated. Glasses based on Te have much higher electronic conductivity relative to Se based glasses due to the smaller forbidden gap of amorphous Te. A higher concentration of intrinsic carriers results at room temperature. These two glasses were selected because attempts could be made to measure the electrochemical activity of Ge and As in a glass matrix without the added complication of doping. Good activity was found, as reported in the previous evaluation section. The mechanism which produces the response to Fe^{+3} solutions then must involve the dissolution or reaction of constituent elements with a simultaneous reduction of $Fe^{+3} \rightarrow Fe^{+2}$ in the immediate area of the electrode surface, a process which must be complex and involve several steps as well as more than one constituent element. Clearly, such a process cannot be considered reversible in a thermodynamic sense because a constituent element leaving the glass in an aqueous medium assumes some sort of an oxide form. Because of the relative stability of oxide and chalcogenide bonds in glasses,⁴ the constituent element cannot return to its original nonoxide bond form in the glass, a necessary condition for complete thermodynamic reversibility of the electrode process.

Tables listing electrode reactions and standard potentials⁵ furnish very few clues regarding the complex reactions between the constituent elements and the Fe^{+3} solutions. However, they do indicate another interesting fact reported in earlier work under this contract. Electrodes formed from chalcogenide glasses should be affected by pH. Table V lists reactions involving the constituent elements, along with their potentials for both basic and acidic solutions. The sign of the standard potential given in mV has the conventional meaning: negative indicates proceeds as written to the right, while positive indicates the reaction is not favored. Table VI lists the potentials measured for the different types

Table V

Standard Electrode Reactions and Potentials
Pertinent to Chalcogenide Glass Electrodes

ACID REACTIONS

Ge + 2H ₂ O	=	GeO ₂ + 4H ⁺ + 4e	-150
Si + 2H ₂ O	=	SiO ₂ + 4H ⁺ + 4e	-851
2Sb + 3H ₂ O	=	Sb ₂ O ₃ + 6H ⁺ + 6e	+152
As + 2H ₂ O	=	HAsO ₂ (aq) + 3H ⁺ + 3e	+248
Se(gray) + 3H ₂ O	=	H ₂ SeO ₂ (aq) + 4H ⁺	+740
Te + 2H ₂ O	=	TeO ₂ + 4H ⁺ + 4e	+529

BASIC REACTIONS

Ge + 5 (OH) ⁻	=	HGeO ₃ + 2H ₂ O + 4e	-1030
Si + 6 (OH) ⁻	=	SiO ₃ ⁼ + 3H ₂ O + 4e	-1618
As + 4 (OH) ⁻	=	AsO ₂ ⁻ + 2H ₂ O + 3e	-675
Se + 6 (OH) ⁻	=	SeO ₃ ⁼ + 3H ₂ O + 4e	-366
Te + 6 (OH) ⁻	=	TeO ₃ ⁼ + 3H ₂ O + 4e	-570

Table VI

Potential Generated by Various Electrodes
Over the pH Range from 2 to 11

Electrode Material	Measured Potential (mV) at pH 2 (Acid)	Measured Potential (mV) at pH 11 (Base)	Difference Measured	Difference from Standard Tables (Normalized for Composition)	Ratio Meas./Stand.
Tl 1173 Ge ₂₈ Sb ₁₂ Se ₆₀	+180 (+411)	-475 (-500)	655	911	0.72
Tl # 20 Ge ₃₃ As ₁₂ Se ₅₅	+150 (+388)	+35 (-615)	115	1000	0.11
Ge ₁₅ Se ₈₅	+430 (+607)	+400 (-465)	30	1072	0.03
As ₄₀ Se ₆₀	+325 (+554)	-150 (-492)	475	1046	0.45
Ge ₁₀ As ₄₀ Te ₅₀	-100 (+403)	-525 (-34)	425	437	0.97
Si ₁₅ As ₂₅ Te ₆₀	+230	-190	420	327	1.3
Ge	+165 (-150)	-225 (-1000)	390	850	0.46
Si	+120 (-850)	-641 (-1500)	761	750	1.0

of glass electrodes as well as Si and Ge measured at pH 2 and pH 11. In Table VI all potentials are referred to the Ag/AgCl reference electrode. The values shown in parentheses immediately below are the values calculated using the expressions given in Table V, but normalized for composition. The measured differences over the pH range from 2 to 11 are compared to those calculated from the table by a ratio in the last column. Agreement is good in a qualitative sense for all but TI #20 and $\text{Ge}_{15}\text{Se}_{85}$, for as yet unexplained reasons. No attempts have been made to unravel the complexities of the electrode reactions. This is certainly true in basic solutions.

Additional experimental evidence to support the dissolution of the various sensor constituents has been presented. If the sensor shows a pronounced effect of stirring, it is probably the result of dissolution of at least one constituent of the sensor. Furthermore, one should be able to find this constituent in the solution. Both the Ge and the 4% Fe- #20 sensor showed these effects. Clearly, these two sensors operate by a mechanism that involves sensor dissolution. The GeAs_2Te_7 electrode exhibited an effect of stirring, but no actual dissolution of the sensor was detected. The Si-containing materials show an effect of stirring, but no dissolution, probably because SiO_2 is very insoluble. The 2% Fe- $\text{As}_{40}\text{Se}_{60}$ and the doped 1173 sensors show neither a stirring effect nor any sensor dissolution.

It is apparent that there must be at least two different mechanisms by which chalcogenide-based sensors respond to Fe^{+3} . One involves dissolution of the sensor, probably because of electrochemical activity, and indicates limited sensor lifetime. The other mechanism is still not clearly defined, but must have to do with a redox mechanism of some kind involving the sensor itself; however, the species is not lost and somehow is conserved or regenerated, as evidenced by the long life (greater than six months in solution^{1,2}) of the doped 1173 sensors. One explanation for this observed behavior is that the bounding may be different in the various glasses and that oxide formation on contact with the solution may affect either the dissolution or the passivation of the active centers in the sensors.

The realization that oxide formation can prevent reversible electrode reactions led to the decision to evaluate another type of glass material, oxy-chalcogenide glasses. Oxy-chalcogenide glasses³ are made by adding small atomic percentages (10 to 20) of oxide into nonoxide systems such as As_2S_3 or As_2Se_3 . Conceptually, then, the glass could exhibit ionic conduction by the movement of the metal oxide through the nonoxide glassy matrix. Reversible metal - metal oxide ionic reactions should be able to occur at the electrode solution interface. Conceivably, the ionic specificity would be guaranteed by the oxide used in the preparation.

Although the mechanism of the Fe doped sensor is still somewhat in doubt, several statements can still be made, particularly for the Fe doped 1173 ($\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$) glass sensor. The sensor functions as the basis of a redox mechanism. The oxidized half of the couple is in solution. The reduced half of the couple is on or in the sensor. The reduced and/or oxidized species in the sensor do not dissolve in solution. Since the sensor is fairly stable to dissolution, it has shown and should continue to show extended life. There are

some problems with reproducible sensor material). However, a sensor that does not deactivate in a week will continue to function for a long time (greater than six months). In summary, the Fe doped 1173 sensors function because of unique electrochemical activity.

III. Cu^{+2} SENSORS

Investigations of Cu^{+2} sensors were undertaken as a result of the work on the Fe^{+3} sensor. In OSW Reports #496 and #619 the response of varying Fe^{+3} sensors to Cu^{+2} was described. However, in the presence of Fe^{+3} the sensors did not respond to Cu^{+2} . The mechanistic studies of Fe^{+3} also suggested that use of oxy-chalcogenide glass could result in a family of sensors for different ions. The first attempt to apply this concept was the formation of an $\text{As}_2\text{S}_3\text{-CuO}$ glass. The material exhibited a low resistivity and was sensitive to Cu^{+2} in a variety of electrolytes. The work on this type of sensor material was then directed to preparation, evaluation, and extension to other ionic systems. Attempts to make sensors for ions other than Cu^{+2} with oxy-chalcogenide systems are discussed in this section.

A. Material Preparation

The first oxy-chalcogenide glass sensor material was prepared from a mixture of 20% CuO and 80% As_2S_3 . The As_2S_3 was obtained from the British Drug House and was described as native orpiment. Much of the original work was accomplished with this material. Detailed analysis revealed that the material contains significant amounts of impurities, particularly Fe and Sb . A second source of As_2S_3 was obtained from Ventron Alfa Inorganics. This material contained excessive amounts of H_2O , and satisfactory material could not be prepared. Finally, to avoid the impurities, As_2S_3 was prepared from 6-9's pure elements. There were slight differences in the preparation required using the British Drug House As_2S_3 and the pure As_2S_3 prepared from the elements. In this report all material containing As_2S_3 will be the British Drug House material, unless otherwise specifically stated.

A large number of varying compositions of oxy-chalcogenide glasses were prepared by essentially the same procedure. The mixture of metal oxide and As_2S_3 is placed in a quartz ampule heated to 600°C for four to 64 hours and then air-quenched to room temperature. The glass compositions prepared during this report period are listed in Table VII.

Several comments are in order about some of the preparations.

The CaO glass (23-119) was not well formed. It crumbled and exhibited some water solubility.

The CuO glasses were the easiest to prepare. The major difficulty was the nonuniformity of the sample in terms of resistivity from top to bottom. However, this inhomogeneity was reduced in sample 23-136 by carefully premixing the CuO and As_2S_3 prior to sealing the ampule, reacting for a longer time, and allowing the rocking furnace to be stopped in the upright position and waiting 10 to 15 minutes before quenching the sample.

The several samples of $\text{PbO}\cdot\text{As}_2\text{S}_3$ glasses were prepared to try to overcome problems of nonuniformity and high resistivity.

Table VII
Oxy-Chalcogenide Glasses of $(MO)_x(As_2S_3)_{1-x}$

<u>Sample No.</u>	<u>MO</u>	<u>%</u>	<u>Reaction Time at 600°C (hours)</u>
23-118	CuO	20	4
23-119	CaO	10	5
23-121	CuO	10	5
23-122	CuO	5	4
23-123	PbO	10	4
23-124	CuO	10	4
23-125	PbO	10	4
23-126	CuO	15	6
23-127	PbO	15	7.2
23-128	CuO	25	7.5
23-129	PbO	25	18.0
23-131	Fe ₂ O ₃	15	13.4
23-132	CuO	15	17.0
23-134	FeO	10	20.0
23-136	CuO	15	21.0
23-137	FeO	20	64
23-138	FeO	10	17 (at 800°C)
23-139	MnO	15	23
23-140	Cu	10	3
23-141	MnO	15	20
23-142	Cu	10	20 (at 700°C)
23-147	Ag	10	25.7 (at 700°C)
70-4 ^(a)	Cu	10	17 (at 700°C)
70-6 ^(b)	Cu	10	16.2
70-7	CuO	15	16.9
70-8	CuO	25	19

(a) As₂S₃ glass made by reacting 6-9's As and 6-9's S in a sealed ampule. Temperature raised to 300°C then slowly raised to 490°C in six hours. Temperature finally raised to 700°C and maintained there for 18.3 hours.

(b) Improved As₂S₃ glass preparation involved mixing 6-9's As and S in proper ratio, placing in quartz ampule, evacuating, sealing, and then allowing to react for 92 hours at 525°C.

Usable $\text{FeO}\cdot\text{As}_2\text{S}_3$ material could not be produced at 600°C , and the last preparation was accomplished at 800°C . The final preparation was also slow-cooled from 800°C to 600°C before air-quenching.

Several of the preparations, notably the MnO , were repeated because of poor resistivity of the resulting material.

A new source of As_2S_3 was obtained when it was discovered that the British Drug House material contained significant amounts of impurities. The most significant contaminants in the As_2S_3 were Fe and Sb. Both elements were present at about the 0.1% level. Other impurities in the As_2S_3 were well below 0.01%.

A second supply of As_2S_3 was obtained from Ventron Alfa Inorganics. This material was immediately analyzed for impurities and found to contain only small amounts of Si and Na in the 0.01% or less level. Fe was less than 0.001%, and Sb was not detected. However, this material was very wet and considerable effort was made to dry it. Several attempts were made to prepare oxy-chalcogenide glasses with this material. Both Cu and CuO glasses were prepared. None of the four attempts was successful. In each case, pressure built up in the quartz ampule and the distinct odor of SO_2 was discernible when the ampule was opened. Attempts to use this material in material preparations were finally abandoned when an ampule exploded as it was being removed from the furnace.

An attempt to obtain pure As_2S_3 was made by compounding the glass from the elements. The availability of 6-9's As and 6-9's S facilitated this preparation. The proper mixture of As and S was weighed, mixed, and placed in a quartz ampule. The ampule was evacuated and sealed, then placed in a rocking furnace. The temperature was raised to about 400°C , where it was maintained for several hours before continued heating to 525°C . The mixture was maintained at 525°C for about 90 hours. The sample was air quenched from 525°C , and the resulting glass was a deep red and, in 50 mil slices, was transparent. This material was then broken into small pieces, mixed with the desired metal or metal oxide, and the oxy-chalcogenide glass prepared as previously described.

Results of this new material are not complete at this writing; however, preliminary indications are that it requires more metal and metal oxide to achieve the same resistivity as the material prepared from the impure (British Drug House) As_2S_3 .

Attempts to characterize the oxy-chalcogenide glasses were made by infrared transmission spectroscopy and microprobe analysis. The infrared transmission spectrum of As_2S_3 is well known, and except for the impurities, this spectrum was obtained. The pure As_2S_3 was transparent between 2 and 12 to 14 micrometers. The oxy-chalcogenide glasses, even in very thin slices, were opaque in this region.

Semiquantitative microprobe composition analyses were made on the As_2S_3 (British Drug House) and 15% $\text{CuO}\text{-As}_2\text{S}_3$ samples. As expected, the As_2S_3 showed As and S with trace quantities of Fe and Sb. However, only one phase was present. The $\text{CuO}\text{-As}_2\text{S}_3$ samples revealed massive second phase particles with very evident dendritic morphology. Theoretically, the dendrites had precipitated homogeneously

from supersaturated solid solutions. Element distribution micrographs showed that the dendrites were Cu-rich. Distance-concentration profiles taken across a precipitate indicated that its As content was below that of the adjacent matrix phase, but that its S content was about equivalent to that of its matrix phase. To determine the second phase composition more accurately, point counts for As, Cu, and O were taken with a low voltage, high current beam, finely focused on each of two precipitates and on the matrix phase far from any precipitates. The results of this analysis indicate that the original CuO had dissolved in the As_2S_3 glass. During cooling, dendrite nucleation and growth apparently occur by reaction of the copper with S and As, forming a Cu-S-As compound, the dendrites. The oxygen and some copper remain in the matrix.

The interesting feature to be pointed out here is that the dendrites contain very little oxygen. In addition, the oxygen in the matrix appears to be low on the basis of the added CuO. It is possible that the quartz reactor is acting as a getter for oxygen.

Additional work will have to be accomplished on characterization of this material. Better understanding will lead to more reproducible material and better sensors.

B. Resistivity Measurements

Resistivity measurements on material for Cu^{+2} sensors prepared during this report period were made according to the procedure outlined in Office of Saline Water Research and Development Progress Report No. 496. In addition, some measurements were made with a General Radio 1650A ac bridge. The results are summarized in Table VIII.

The last number in the sample code refers to the slice. The slices are numbered from top to bottom of the sample. Thus, sample number 23-122-2 refers to slice number 2 near the top, and 23-122-12 refers to slice number 12 at the bottom as the sensor material cooled.

A few generalizations may be made about the resistivity data. For the $CuO \cdot As_2S_3$ material the resistivity decreases with increasing CuO content. The last 15% CuO samples (numbers 23-136-2 and -8) indicate that this preparation procedure tends to yield more homogeneous material. The 25% CuO material is probably not homogeneous, but the resistivity is low and is therefore not a good measure of sample homogeneity.

The 15% PbO is definitely lower in resistance than the 10%, and it appears to be fairly uniform.

The last 10% FeO prepared at 800°C is certainly more uniform than the other FeO material prepared.

The good resistivity of the 23-140 $(Cu)_{0.10}(As_2S_3)_{0.90}$ material indicates that the oxide may not be required, but attempts to duplicate this preparation in 23-142 resulted in high resistivity material.

Table VIII

Specific Resistivities of Sensor Material at 20 V dc and
Ambient Temperature

<u>Sample Number</u>	<u>Composition</u>	<u>Resistivity (Ω-cm)</u>
23-122-2	(CuO) _{0.05} (As ₂ S ₃) _{0.95}	3.4×10^8
23-122-12	(CuO) _{0.05} (As ₂ S ₃) _{0.95}	5.5×10^{10}
23-121-2	(CuO) _{0.10} (As ₂ S ₃) _{0.90}	3.4×10^8
23-121-9	(CuO) _{0.10} (As ₂ S ₃) _{0.90}	3.1×10^6
23-124-1	(CuO) _{0.10} (As ₂ S ₃) _{0.90}	7.7×10^1 (ac bridge)
23-124-6	(CuO) _{0.10} (As ₂ S ₃) _{0.90}	1.56×10^2 (ac bridge)
23-126-4	(CuO) _{0.15} (As ₂ S ₃) _{0.85}	2.1×10^6
23-126-9	(CuO) _{0.15} (As ₂ S ₃) _{0.85}	2.5×10^3
23-132-1	(CuO) _{0.15} (As ₂ S ₃) _{0.85}	6.7×10^4
23-132-8	(CuO) _{0.15} (As ₂ S ₃) _{0.85}	5.8×10^6
23-136-2	(CuO) _{0.15} (As ₂ S ₃) _{0.85}	4.0×10^3
23-136-8	(CuO) _{0.15} (As ₂ S ₃) _{0.85}	4.5×10^3
23-128-3	(CuO) _{0.25} (As ₂ S ₃) _{0.75}	4.1×10^1
23-128-7	(CuO) _{0.25} (As ₂ S ₃) _{0.75}	4.5×10^1
23-125-1	(PbO) _{0.10} (As ₂ S ₃) _{0.90}	4.6×10^9
23-125-12	(PbO) _{0.10} (As ₂ S ₃) _{0.90}	1.5×10^9
23-127-1	(PbO) _{0.15} (As ₂ S ₃) _{0.85}	5.2×10^7
23-127-8	(PbO) _{0.15} (As ₂ S ₃) _{0.85}	2.1×10^8
23-129-1	(PbO) _{0.15} (As ₂ S ₃) _{0.85}	1.0×10^8
23-129-9	(PbO) _{0.15} (As ₂ S ₃) _{0.85}	1.2×10^8
23-134-2	(FeO) _{0.10} (As ₂ S ₃) _{0.90}	4.4×10^7
23-134-5	(FeO) _{0.10} (As ₂ S ₃) _{0.90}	2.20×10^2 (ac bridge)

Table VIII
(Continued)

<u>Sample Number</u>	<u>Composition</u>	<u>Resistivity (Ω-cm)</u>
23-134-7	(FeO) _{0.10} (As ₂ S ₃) _{0.90}	3.9 (ac bridge)
23-138-1	(FeO) _{0.10} (As ₂ S ₃) _{0.90}	1.2×10^6
23-138-7	(FeO) _{0.10} (As ₂ S ₃) _{0.90}	1.6×10^6
23-140-2	(Cu) _{0.10} (As ₂ S ₃) _{0.90}	2.4×10^4
23-140-5	(Cu) _{0.10} (As ₂ S ₃) _{0.90}	3.1×10^3
23-142-2	(Cu) _{0.10} (As ₂ S ₃) _{0.90}	5.4×10^7
23-142-9	(Cu) _{0.10} (As ₂ S ₃) _{0.90}	1.9×10^8
23-141-2	(MnO) _{0.15} (As ₂ S ₃) _{0.85}	1.6×10^8
23-141-4	(MnO) _{0.15} (As ₂ S ₃) _{0.85}	3.7×10^8
23-147-3	(Ag) _{0.10} (As ₂ S ₃) _{0.85}	3.1×10^8

The high resistivity of sample 23-147 $(Ag)_{0.10}(As_2S_3)_{0.90}$ was surprising but has not been investigated further to date.

There is still some problem of resistivity variation throughout the sample. Several new techniques in preparation will be attempted to minimize this effect. In general, if the specific resistivity is above $10^3 \Omega\text{-cm}$, slice to slice variation can be used as a rough check of homogeneity.

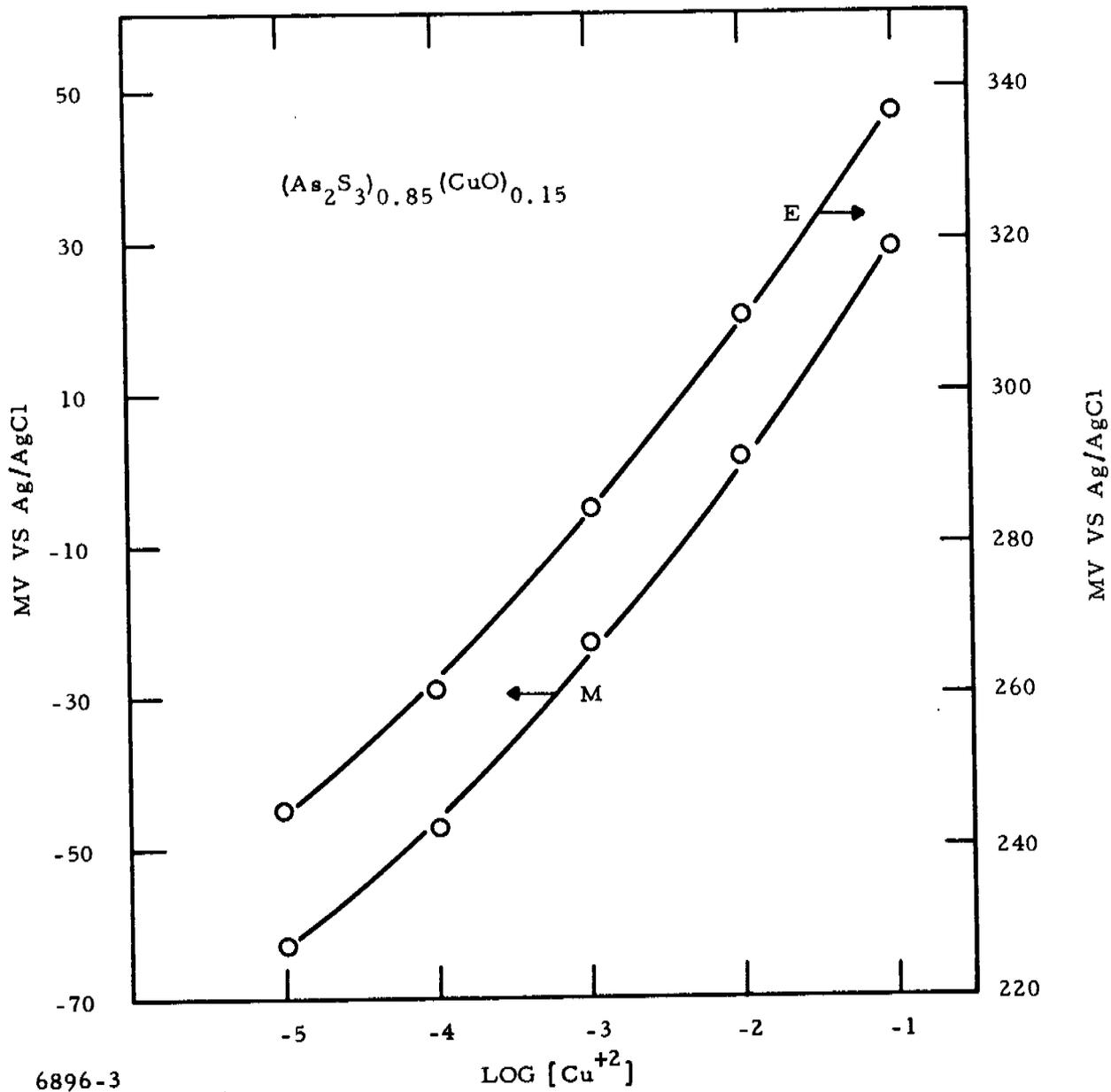
C. Sensor Evaluation

Sensors were prepared for material consisting mainly of As_2S_3 with varying amounts of CuO , Cu , PbO , MnO , Fe_2O_3 , and FeO added. Sensors in both membrane and electrode configurations were fabricated and tested for response to Cu^{+2} , Pb^{+2} , Mn^{+2} , Fe^{+2} , and Fe^{+3} . Several interference tests were also performed. Only the CuO and $Cu-As_2S_3$ sensors responded with any significance or reproducibility. At best, other materials made only very poor sensors because of high resistivity. Since the CuO sensor responded well, it was evaluated rather extensively.

Considerable progress has been made in obtaining good, reproducible, selective sensors using oxy-chalcogenide material, particularly the $CuO \cdot As_2S_3$ compositions. The $(CuO)_{0.20}(As_2S_3)_{0.80}$ sensor responded well, but over a period of several weeks it tended to lose its activity. Activity could be easily restored by physically removing a few micro-inches from the surface. Other compositions of $CuO \cdot As_2S_3$ were prepared and tested. The 5% CuO sample exhibited high resistivities and was unstable in Cu^{+2} solutions. The first 10% preparation showed lower resistivity than the 5%, but the resistivity was still rather high and the sample showed poor, nonreproducible responses. A second 10% CuO sample was good. Compositions of 15% and 25% CuO were also studied. The 25% CuO has good conductivity, low resistance, and good responses; but like the 20% samples, these samples exhibited a tendency to deactivate.

The following discussion will emphasize results with the $(CuO)_{0.15}(As_2S_3)_{0.85}$ sensors; however, some data will be presented for the other compositions. It should be pointed out that all compositions do respond, but for various reasons (such as lifetime reproducibility) the 15% membrane configuration sensor appears to be preferred.

Sensors in the membrane and electrode configurations were prepared from material 23-126. Response of these sensors to 0.1 M KNO_3 containing $Cu(NO_3)_2$ are presented in Figure 4. Least-square best fit of the data to a straight line indicates slopes of 23.3 ± 1.2 mV/decade for the electrode sensor and 23.2 ± 1.2 mV/decade for the membrane configuration. Additional data are presented in Figure 5 for this same membrane electrode. The sensors were several days older and had been conditioned by exposure to a variety of solutions. The effects of stirring and of different supporting electrolytes were determined. These experiments indicate that there is a definite effect of electrolyte. The slopes are not the same in chloride and nitrate media. The effect of stirring in nitrate is negligible, and this has been verified with other electrodes of the same and different compositions. The effect of stirring may be real in the case of 0.1 M $NaCl$ solution. The calculated best straight line for this sensor



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Figure 4 Response of Sensor 23-126 to Varying Concentrations of Cu^{+2} in $0.1 \text{ M } KNO_3$.

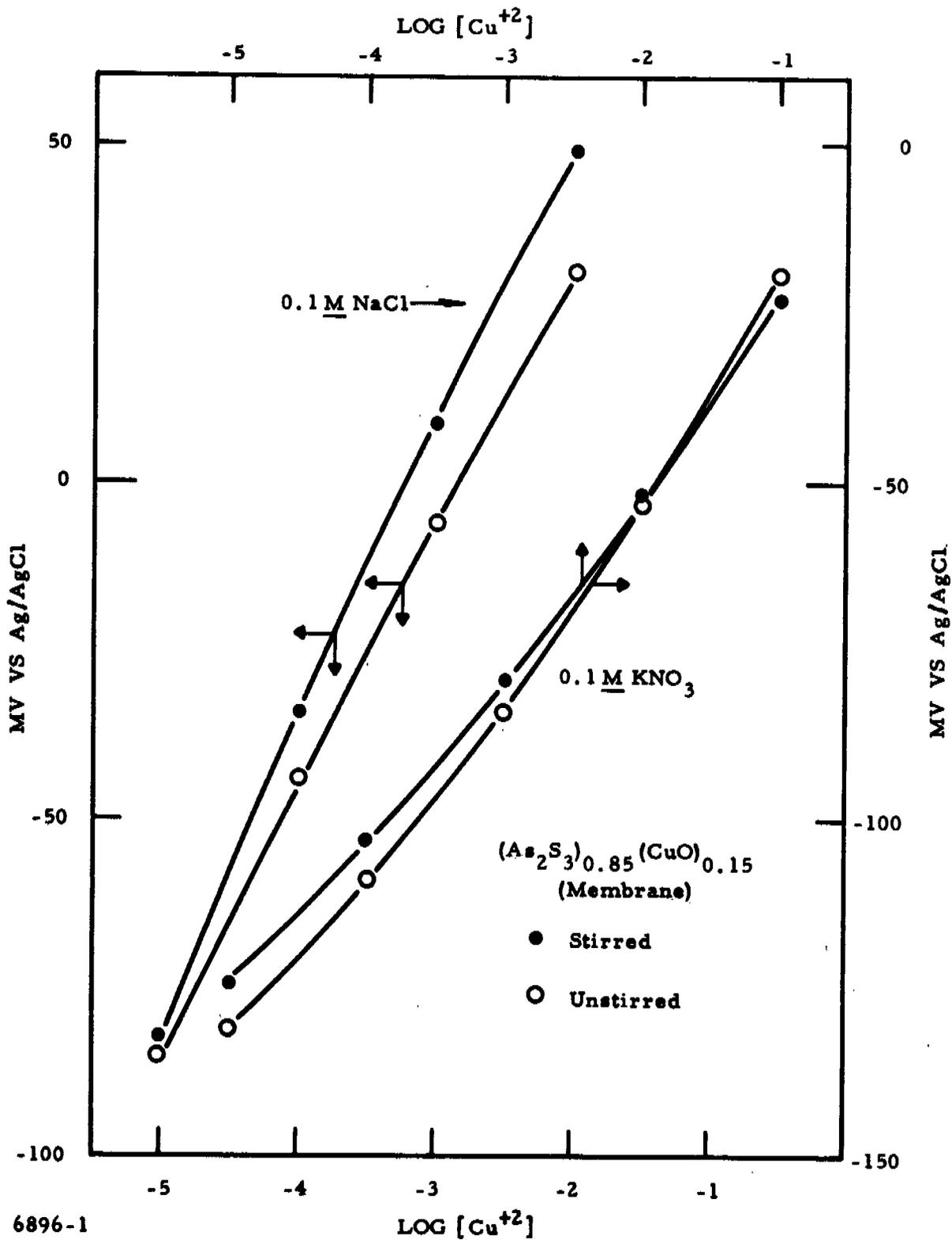


Figure 5 Response of Membrane Sensor 23-126 to Varying Cu²⁺ Concentrations in 0.1 M KNO₃ and 0.1 M NaCl in Both Stirred and Unstirred Solutions

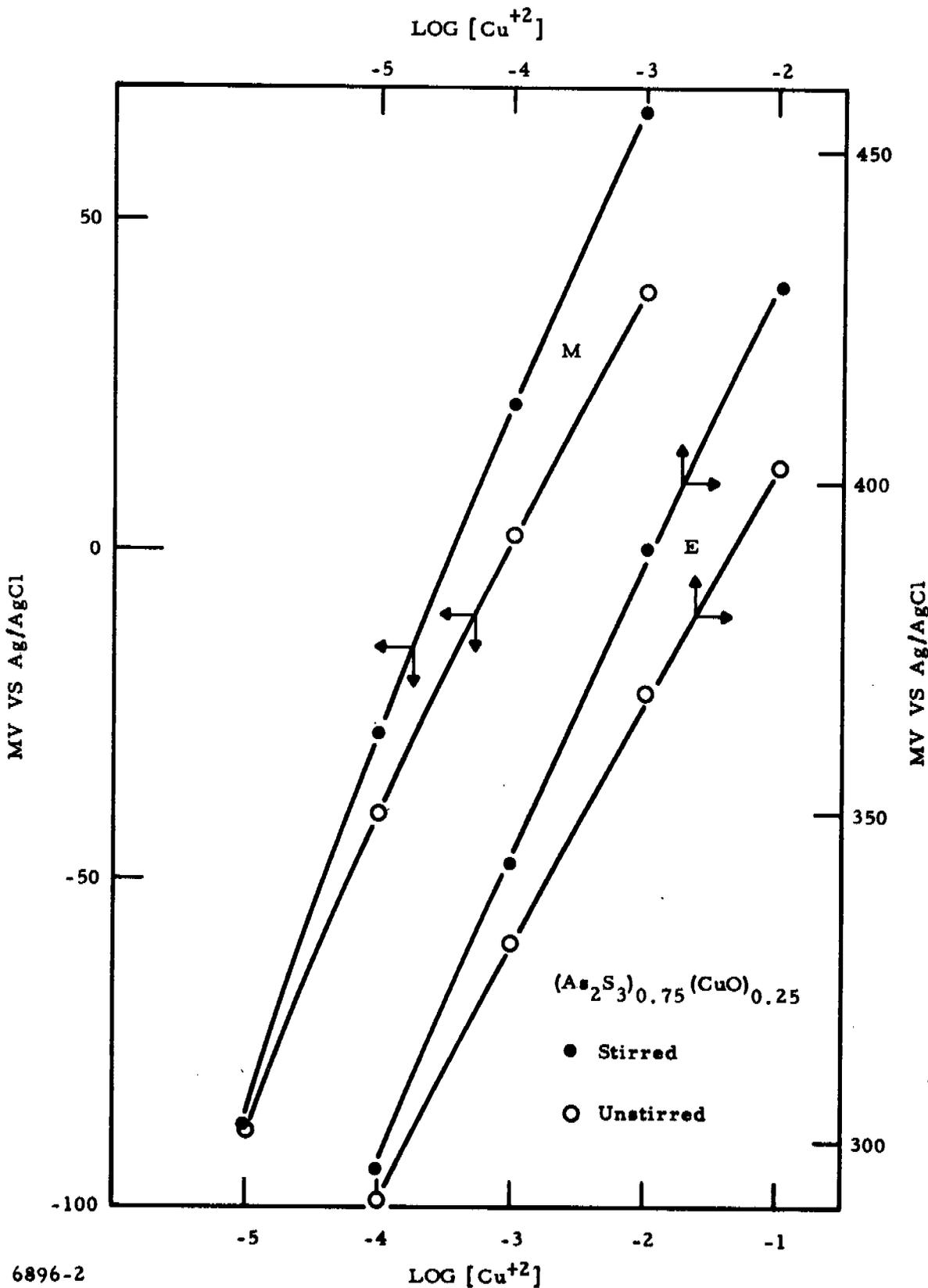
was found to increase with stirring. Data for sample 23-128, a $(\text{CuO})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$, are presented in Figure 6. These data were taken with varying CuCl_2 concentrations in 0.1 M NaCl . Two sensor configurations (electrode and membrane) were tested in both stirred and unstirred solutions. It appears that in the 0.1 M Cl^- solution there is an effect of stirring, but not due to electrode dissolution. The slopes change in the opposite direction. In 3 M KCl the effect of stirring no longer exists, as illustrated by the data in Table IX. These data are obtained by a computer program of least-square fitting. The slope of the best straight line through the points is calculated along with the standard error. The error, in effect, indicates that if the experiment were repeated, the slope would be within the given range about two-thirds of the time.

The actual data on the three salt solutions for $(\text{CuO})_{0.15}(\text{As}_2\text{S}_3)_{0.85}$ sensor 23-126-4 are presented in Figure 7. Additional work has shown that the 3 M KCl solution can be extended to the 10^{-6} (0.06 ppm) M Cu^{+2} range. The best slopes for these curves are given in Table IX.

The data in Figure 8 illustrate the effect of sensor composition on response. The $(\text{CuO})_{0.10}(\text{As}_2\text{S}_3)_{0.90}$ sensor was fabricated from material 23-124, the $(\text{CuO})_{0.15}(\text{As}_2\text{S}_3)_{0.85}$ from material 23-126, and the $(\text{CuO})_{0.20}(\text{As}_2\text{S}_3)_{0.80}$ from material 23-118. Although it does appear that increasing the CuO content results in increased slope, the difference between the 10 and 15% and the 15 and 20% compositions appears to be within the limits of the standard error. A few tentative comments may be in order. There certainly is an effect of stirring. The KNO_3 experiment points to either a redox or an ion exchange mechanism. The 0.1 M NaCl results are confusing, but suggest a combination of ion exchange and redox. Stirring these solutions seems to bring more Cl^- to the electrodes and tends to make redox more predominant. The increased slope with 3 M KCl and the fact that the effect of stirring is decreased also support this idea. The effect of composition in Cl^- media suggests that fewer sites are available for exchange of Cu^{+2} as the copper content of the sample is increased and that more redox reactions occur. A slope of 59 mV/decade would be expected in a Cl^- medium if the mechanism were solely one of redox.

Several experiments were run to check the effect of interference. Univalent ions -- Na^+ , K^+ and H^+ -- do not interfere. Cu^{+2} has been determined and monitored successfully down to 10^{-6} M (0.06 ppm) Cu^{+2} in 3 M KCl , 0.1 M NaCl , and 0.1 M KNO_3 . The effect of pH on sensor response is clearly demonstrated in Figure 9. In the absence of Cu^{+2} the sensor is pH-sensitive, probably due to some adsorption or reaction of the surface with OH^- . However, in the presence of Cu^{+2} the potential response is independent of pH until Cu^{+2} begins to precipitate. The change in potential value at pH 2 is due to the changing Cu^{+2} concentration. Even as the Cu^{+2} begins to precipitate, the potential still follows the remaining Cu^{+2} concentration until it gets below 10^{-5} M Cu^{+2} . These data clearly indicate that the sensor is not pH-dependent as long as Cu^{+2} remains in solution.

The response to other ions is shown in Figure 10. A 10^{-3} Cu^{+2} in 0.1 M KNO_3 is used as the standard solution. Varying amounts of Ca^{+2} , Ni^{+2} , and Fe^{+2} were added separately. The results indicate no interference due to either Ni^{+2} or Cu^{+2} . The effect of Fe^{+2} indicates a titration curve effect, suggesting that

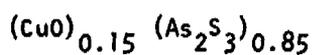


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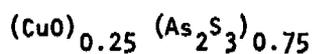
Figure 6 Response of (CuO)_{0.25}(As₂S₃)_{0.75} Sensors to Varying Concentrations of Cu²⁺ in 0.1 M NaCl

Table IX

Calculated Least-Square Slopes in Millivolts/Decade



<u>Electrolyte</u>	<u>Membrane Sensor (unstirred)</u>	<u>Membrane Sensor (stirred)</u>	<u>Electrode Sensor (unstirred)</u>	<u>Electrode Sensor (stirred)</u>
0.1 <u>M</u> KNO_3	28.0 ± 1.5	25.3 ± 0.9	25.7 ± 1.3	23.8 ± 1.2
0.1 <u>M</u> NaCl	36.5 ± 1.8	43.6 ± 1.3	38.6 ± 0.1	43.1 ± 0.8
3 <u>M</u> KCl	51.1 ± 2.1	54.5 ± 2.0	48.0 ± 3.0	51.2 ± 2.1



0.1 <u>M</u> KNO_3	24.7 ± 1.4	23.7 ± 1.4	26.8 ± 1.1	25.8 ± 1.3
0.1 <u>M</u> NaCl	42.6 ± 1.9	51.2 ± 2.5	37.1 ± 0.8	45.0 ± 1.2
3 <u>M</u> KCl	53.1 ± 4.8	54.4 ± 4.4	-	-

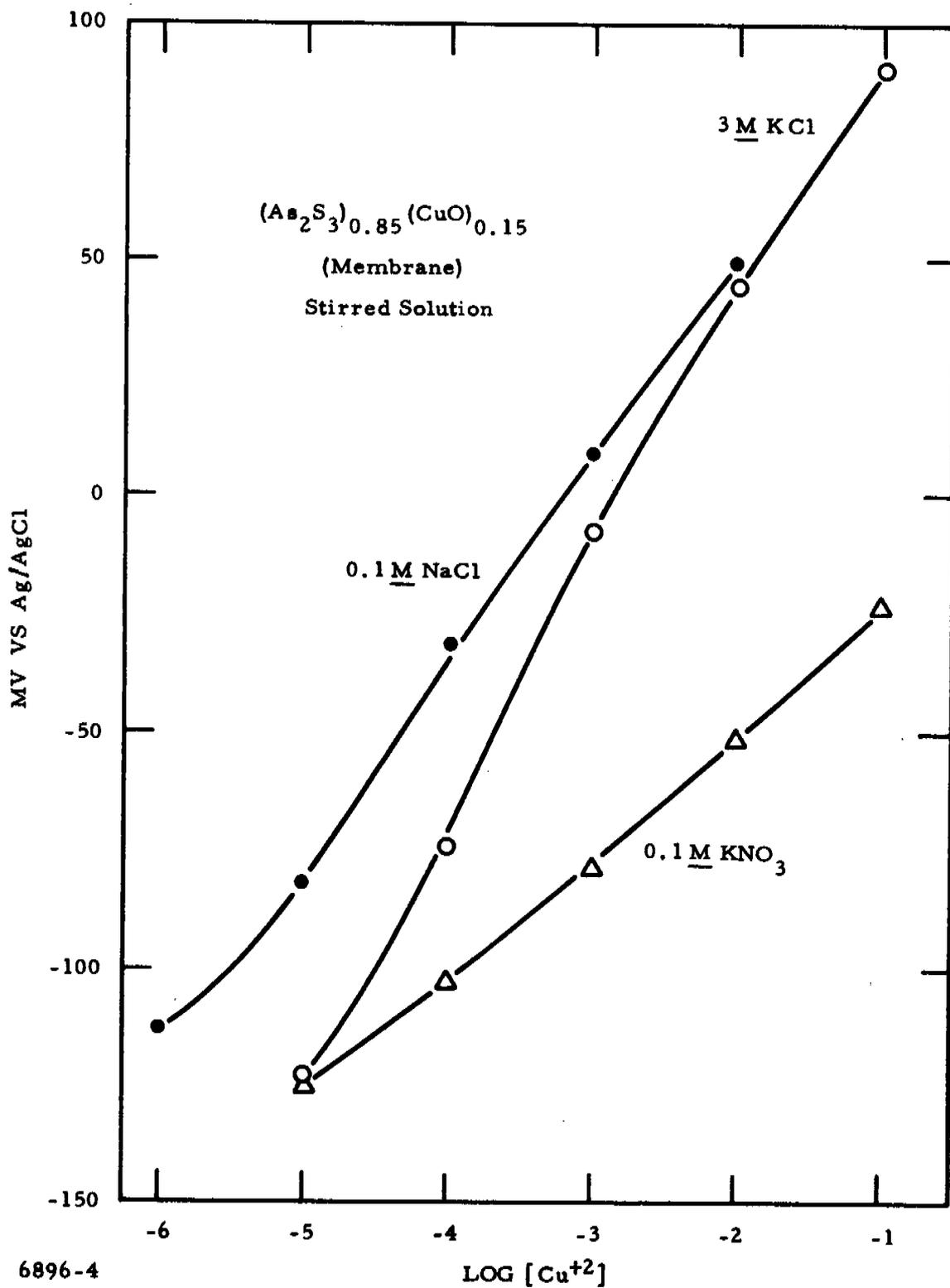


Figure 7 Response of CuO · As₂S₃ Membrane Sensor to Copper Ions in Various Electrolyte Solutions

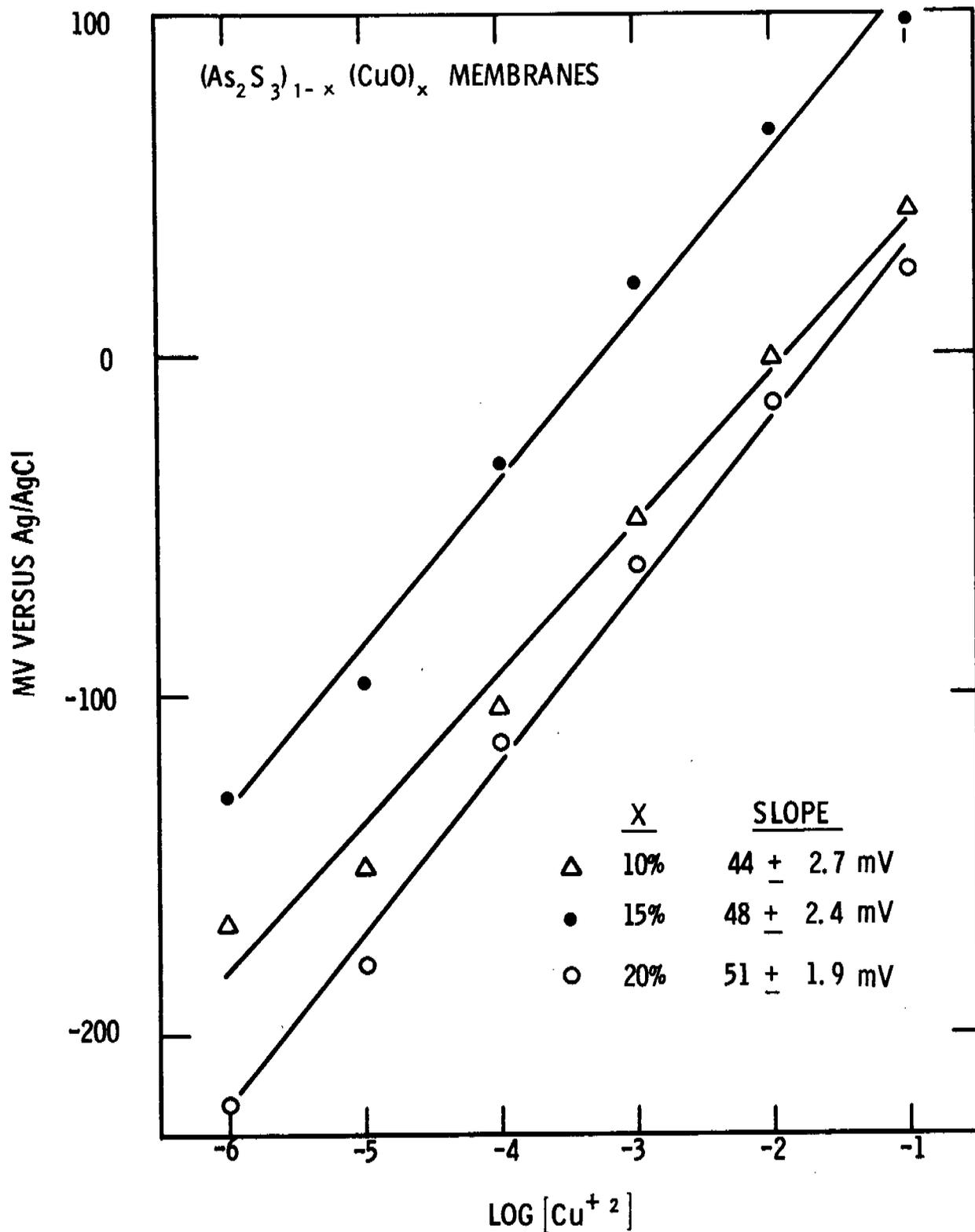
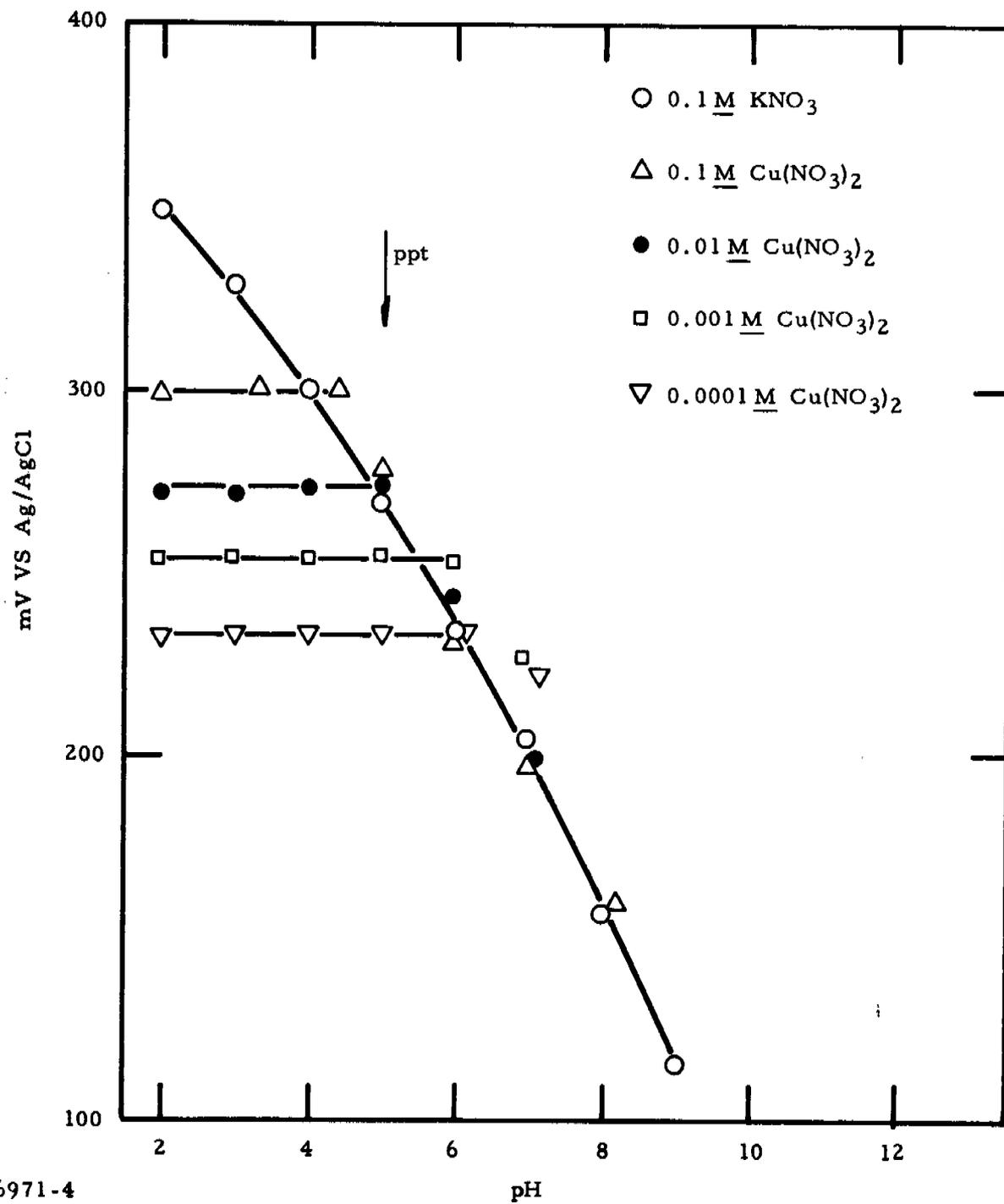
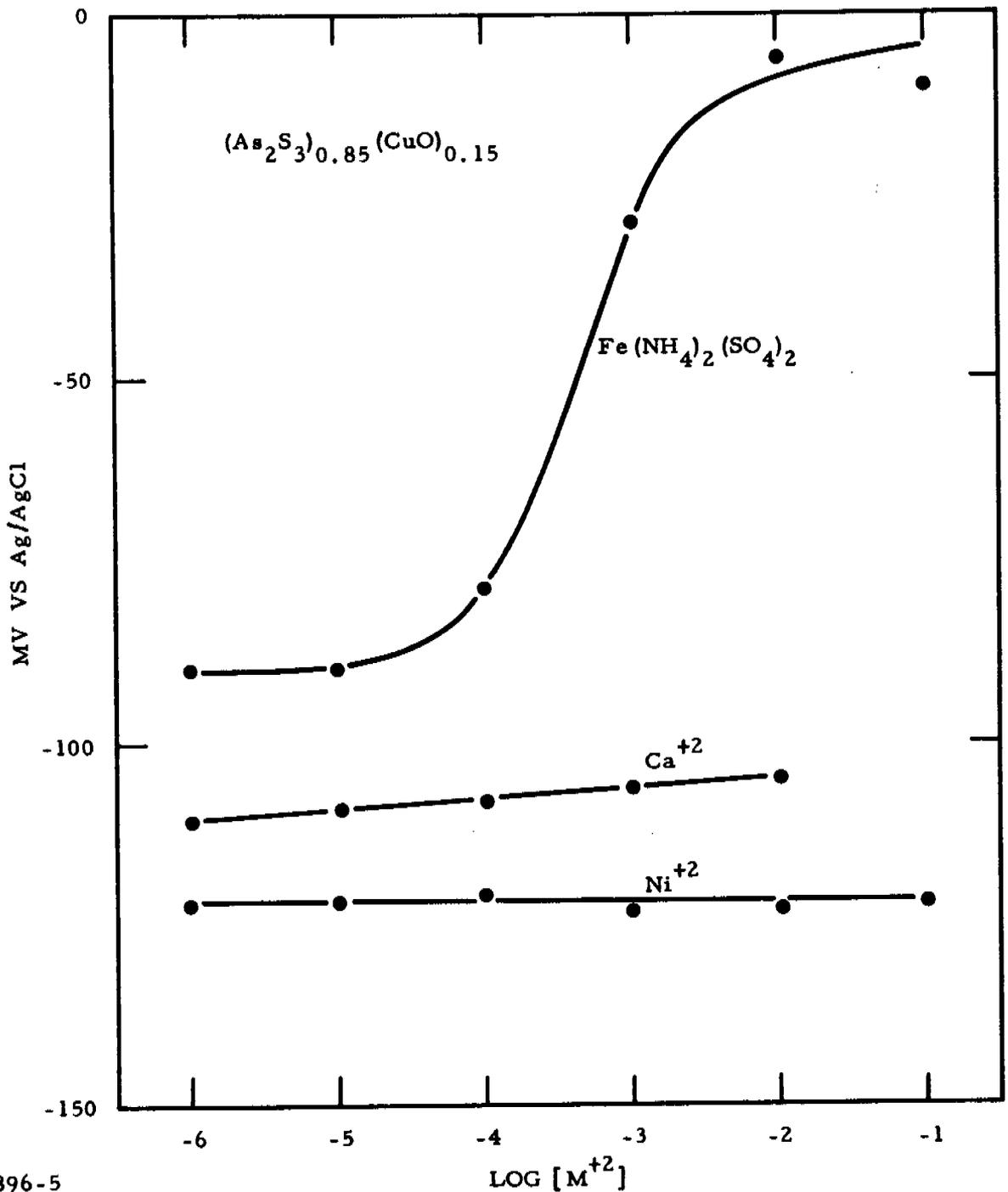


Figure 8 Responses of $(CuO)_x (As_2S_3)_{1-x}$ Sensors to Cu^{+2} in 3 M KCl pH 3.1. Slopes obtained by least-square fitting of data.



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Figure 9 Response of a $(\text{CuO})_{0.15}(\text{As}_2\text{S}_3)_{0.85}$ Membrane Sensor to Varying $[\text{Cu}^{+2}]$ and pH. All solutions 0.1 M KNO₃.



6896-5

Figure 10 Response of Membrane Sensor 23-126 to Varying Concentrations of Indicated Ions in $10^{-3} Cu(NO_3)_2$

Cu^{+2} is reduced and Fe^{+2} is oxidized to Fe^{+3} . Additional experiments have shown a response to Fe^{+3} in the absence of Cu^{+2} . However, when Cu^{+2} is present, there is a selectivity for Cu^{+2} over Fe^{+3} . In addition, there is no interference from either Pb^{+2} or Mn^{+2} .

Response of a second sample of the 15% CuO (23-132) is shown in Figure 11. The two 0.1 M KNO_3 slopes are for slice No. 1 and No. 8 from the same sample. The 3 M KCl data are for slice 1. These data support previous results from other sensor material samples. The Cu^{+2} of concentration was verified by using atomic absorption as a check on the total Cu^{+2} concentration in the solutions. These results are very encouraging.

By way of an application to an existing monitoring problem, a sample of sea water was obtained from the Gulf of Mexico at the beach in Galveston, Texas. Cu^{+2} was added to this water in varying amounts. The total copper concentration was determined independently by atomic absorption. The responses of two sensors of different compositions are presented in Figure 12. The pH of the solution was 6.8, indicating that some of the Cu may have precipitated, particularly at the higher concentrations. This could account for the nonlinearity of the potential total Cu plots. Sensor 23-124-1 is a $(\text{CuO})_{0.10}(\text{As}_2\text{S}_3)_{0.90}$ sensor, and 23-126-10 is a 15% CuO sensor.

Some interference does result when excessive amounts of Fe^{+3} are present. This effect is illustrated in Figure 13. Each plot represents a constant Fe^{+3} concentration with varying Cu^{+2} concentrations. These curves indicate that the Fe^{+3} must be at least 10 times greater than the Cu^{+2} concentration before significant interference is observed. Tests with other sensors of the same composition indicate that the Fe^{+3} must be at least 100 greater than the Cu^{+2} concentration.

The previous work³ on Fe-1173 sensors demonstrated that these sensors will respond to Fe^{+3} in the presence of Cu^{+2} . The more recent work described above indicates that the $(\text{CuO})_{0.15}(\text{As}_2\text{S}_3)_{0.85}$ sensors will respond selectively to Cu^{+2} in the presence of Fe^{+3} . In addition, both sensors have the capability of responding in the 0.1 to 1 ppm range, or possibly lower. The response appears to be unaffected by concentrated Na or KCl solutions and many of the more common divalent ions (Ca^{+2} , Mg^{+2}) found in brackish and saline water. The prospects of obtaining a system for detection and monitoring of Fe^{+3} and Cu^{+2} (from various corrosion processes) in natural and process waters, including hot brines, appear excellent.

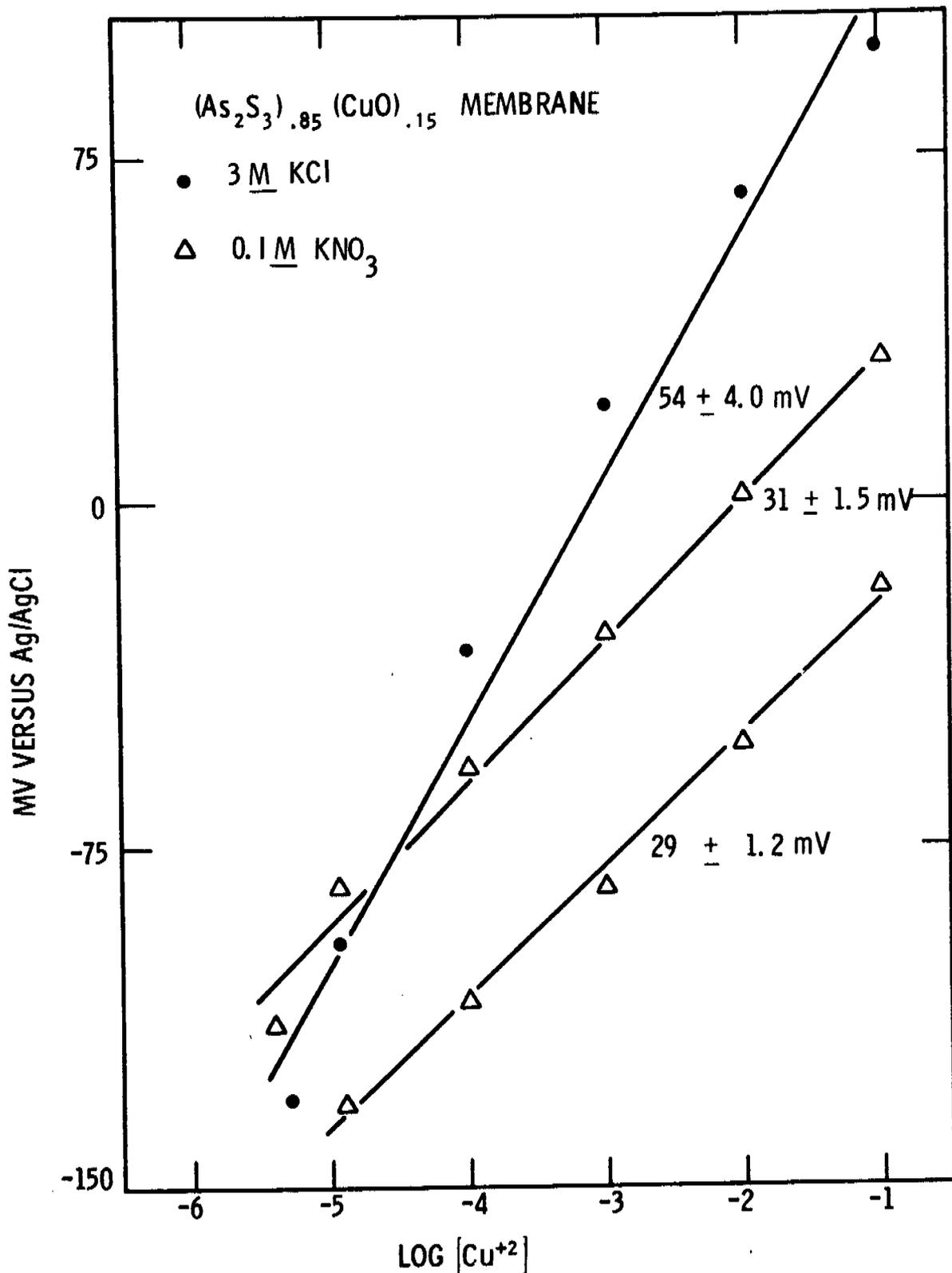


Figure 11 Response of Different Sensors of Same Composition to Cu²⁺ in the Presence of Various Electrolytes. Slopes obtained by least-square fitting of data.

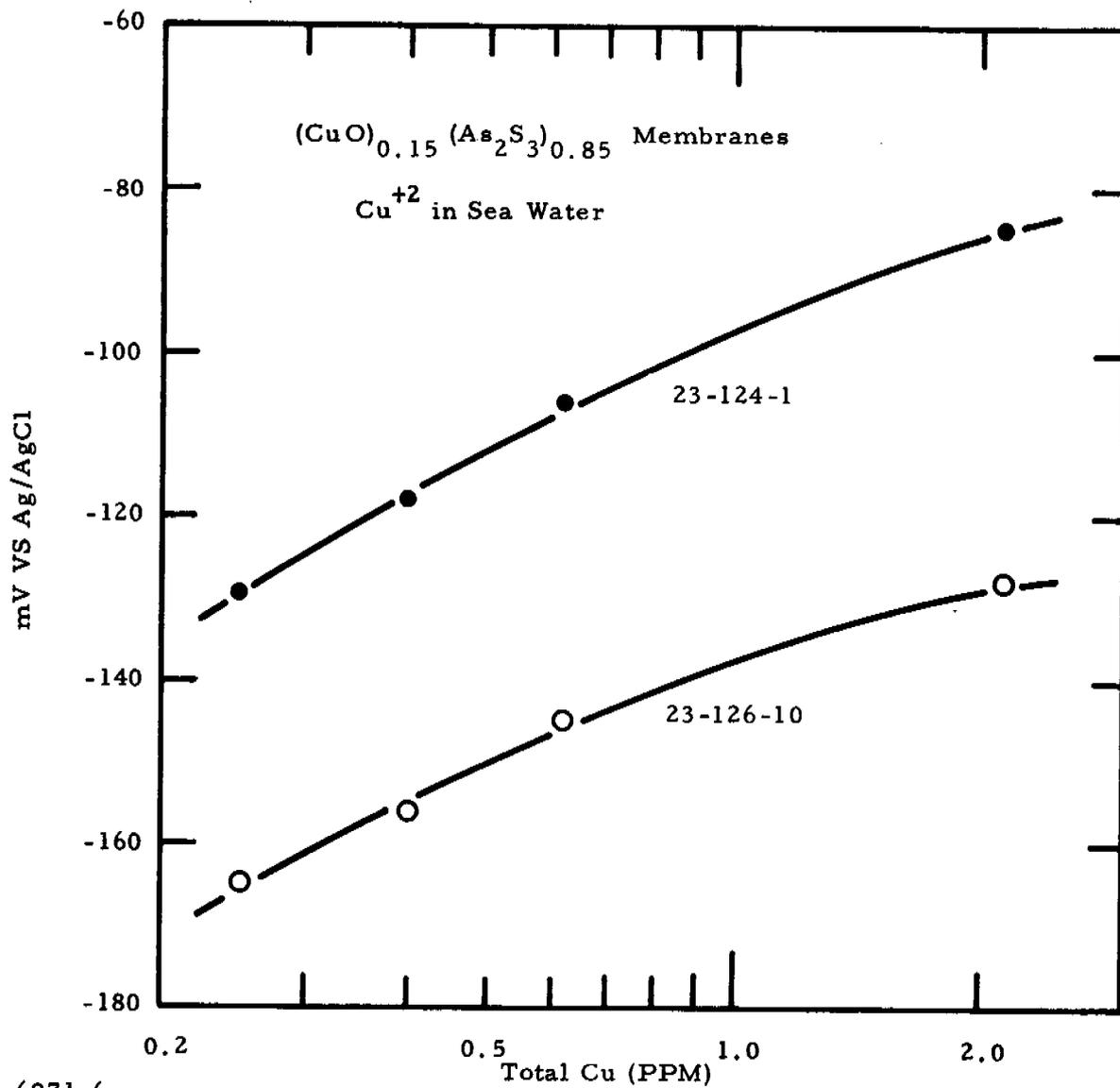
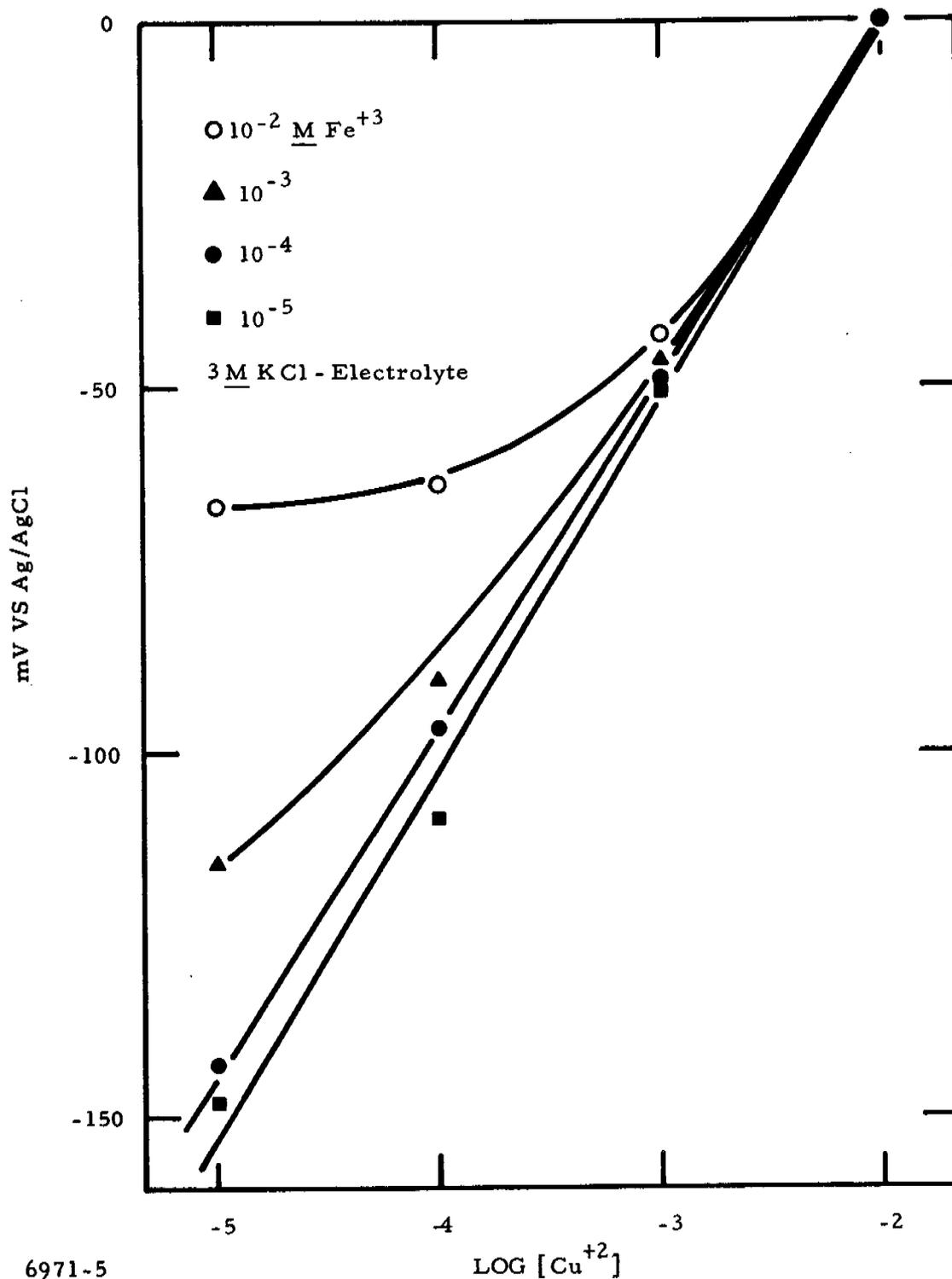


Figure 12 Response of Two Membrane Sensors to Cu⁺² in Sea Water. Total Cu determined by atomic absorption.



6971-5

Figure 13 Response of $(\text{CuO})_{0.15}(\text{As}_2\text{S}_3)_{0.85}$ Membrane Sensors to $[\text{Cu}^{+2}]$ in the Presence of Varying $[\text{Fe}^{+3}]$ Concentrations

IV. Ca⁺² AND Mg⁺² SENSORS

Two materials approaches have been taken for the development of solid state sensors for Ca⁺² and Mg⁺²: (1) doping of semiconductors and (2) doping of alkaline earth single crystal salts with either univalent or trivalent ions. All the materials prepared during this report period are described in Table X.

A. Materials Preparation

The calcium-doped polycrystalline silicon (Ca-poly Si) was prepared by heating calcium with polycrystalline silicon in graphite crucibles in a helium atmosphere at 1440°C for two hours. The 1% and 3% samples were usable, but the 5% and 10% samples crumbled. Similar preparations using quartz crucibles in air were unsuccessful. The 3% magnesium-doped polycrystalline silicon preparation did not form a homogeneous mass.

Samples of magnesium in p-type silicon were successfully prepared by diffusion in the sandwich type configuration. Magnesium was evaporated onto both sides of a slice of p-type Si, and additional slices of p-type Si were placed on both sides of the evaporated slice. The sandwich was then heated for 18 hours at 1390°C in a He atmosphere. The magnesium diffused into both sides of the center slice, and this slice was used as a membrane electrode. The single-side diffusion of the outside slices permitted them to be made in the electrode configuration.

The ionic activity of an electrode material should be an indication of a bulk material property. For an activity to represent bulk properties, the ion in question must occupy some substitutional or interstitial position in the crystalline lattice. Examination of diffusion data for different ions in silicon and germanium shows that considerably fewer ions diffuse readily in silicon than in germanium, probably because germanium has a larger lattice. For example, silicon can be doped with Be or Mg, but not with Ca or Ba. This may explain the poor results obtained in our earlier attempts to dope silicon. In contrast to silicon, germanium can be doped with the larger ions such as Ca, Sr, and Ba.

Samples of Ca- and Mg-doped germanium slices were prepared by making a paste of CaCO₃ or MgCO₃ with H₂O and applying this paste drop by drop to warm (60°C) slices of germanium. The slices were then placed in a tube furnace and heated to 800°C for one hour in a He atmosphere. The furnace was allowed to cool to room temperature before the slices were removed.

Several attempts were made to prepare 10% YF₃-90% CaF₂ from reagent grade polycrystalline CaF₂. The most successful condition required heating to 1550°C for one hour in He atmosphere to protect the graphite crucibles used. A similar preparation was made using single crystal CaF₂ in a platinum crucible. Here again, the sample was heated at 1550°C for one hour.

Large crystals of alkaline earth tungstates and molybdates are readily obtained following a procedure described by Van Uitert, et al.,⁷⁻⁹ which involves pulling the crystals from a melt. Since these materials tend to lose oxygen at the melting temperature, they can be grown in air or even in an oxygen-rich ambient. The apparatus used to prepare barium tungstate, for example, is shown

Table XMaterial Prepared for Solid State Sensors
for Ca⁺² and Mg⁺²

<u>Sample</u>	<u>Dopant</u>	<u>Mole %</u>	<u>Comments</u>
Ca-poly Si	Ca	1 3	1440°C, 2 hours, He atmosphere. Material appeared homogeneous.
Mg - p-type Si	Mg	-	Sandwich diffused slice, 1390°C, 18 hours; He atmosphere.
Germanium	Ca	-	60°C, 1 hour; 800°C, 1 hour; He atmosphere.
Germanium	Mg	-	60°C, 1 hour; 800°C, 1 hour; He atmosphere.
YF ₃ -CaF ₂	YF ₃	10	1550°C, 1 hour, He atmosphere. Two samples: CaF ₂ powder and CaF ₂ single crystal.
BaWO ₄	Sm ₂ O ₃	1	Pulled at 1540°C. Crystal brown and opaque.
BaMoO ₄	Sm ₂ O ₃	1	Pulled at 1500°C. Sm content only 0.14%.
PbMoO ₄	Sm ₂ O ₃	1	Pulled at 1070°C.
CaWO ₄	Nd ₂ O ₃	-	Vacuum heat treated slices at 1025°C for two hours.

in Figure 14. The melt is contained in a rhodium crucible approximately 40 mm tall by 40 mm I.D. with a wall thickness of 1.5 mm. The 75 mm diameter, six-turn induction coil and the rhodium susceptor are surrounded by 100 mesh alumina powder to thermally insulate the melt and reduce oxidation of the rhodium. A platinum wire connects the susceptor to ground. Both the seed holder and the thermocouple tubing are made from alumina. A length of split alumina tubing rests on the wall of the susceptor and serves as a heat shield to prevent rapid cooling of the crystal as it is being pulled. Temperature control at the melting point (1540°C) is obtained with an L & N type G controller. A platinum wire with a small loop in the end serves as an effective seed. Approximately 2.5 cm/hour is a typical withdrawal rate at a rotation rate of 10 rpm.

In the case of BaWO₄, approximately 125 g of the reagent grade material was melted in the rhodium crucible together with a weighed amount of 99.9% Sm₂O₃ calculated to achieve 1 mole % samarium in the resulting crystal. Since BaWO₄ crystallizes in the tetragonal scheelite structure, most crystals show a tendency toward fourfold symmetry. Extreme care must be taken in slow-cooling the crystals to prevent excessive cracking. In the absence of a dopant, the crystals are generally colorless and transparent. Addition of 1 mole % samarium results in a crystal which is largely opaque and brown in color.

The same apparatus and technique can also be used to prepare crystals of the alkaline earth molybdates.

Initial attempts to grow Sm₂O₃ doped BaWO₄ were unsuccessful because of fumes given off by the material when it was heated to 1540°C. A new supply of reagent grade BaWO₄ which did not fume was obtained from Matheson, Coleman, and Bell. Two crystals approximately 3 inches long were successfully grown. Figure 15 is a photograph of one of these crystals, 10 cm long and 1 cm in diameter. Although precautions were taken to prevent rapid cooldown, the crystals still fractured when sliced. However, large pieces were obtained and sensors fabricated.

Crystal grade barium molybdate powder was received from Matheson, Coleman, and Bell Co. As in the case of barium tungstate, described above, the barium molybdate powder was melted in a rhodium crucible under ordinary atmospheric ambient. Seeding was attempted, as before, with a 2 mm diameter loop on the end of twisted platinum wire. Barium molybdate melts congruently at about 1500°C, and no difficulty was encountered in nucleating the crystal on the platinum wire. Samarium oxide, 99.999% pure, was added to the barium molybdate as a dopant. Melts were composed of 1 mole % samarium. Emission spectrographic analysis on the first-to-freeze portion of the resulting crystals showed a samarium content of about 0.14 mole%, suggesting an effective segregation coefficient of about 0.14 for samarium in barium molybdate. While the crystals were maintained at temperatures of 600°C and higher, they appeared clear and translucent, with no visible cracks. Unfortunately, in every case so far, severe cracking and fracture resulted when the crystals were brought to room temperature. Attempts to reduce the strain by reducing the diameter of the crystals were unsuccessful. Crystals as small as 4 mm in diameter were also observed to fracture when brought to room temperature. Fracturing is not believed to be caused by the high concentration of samarium dopant in the crystal, since it was also observed in undoped

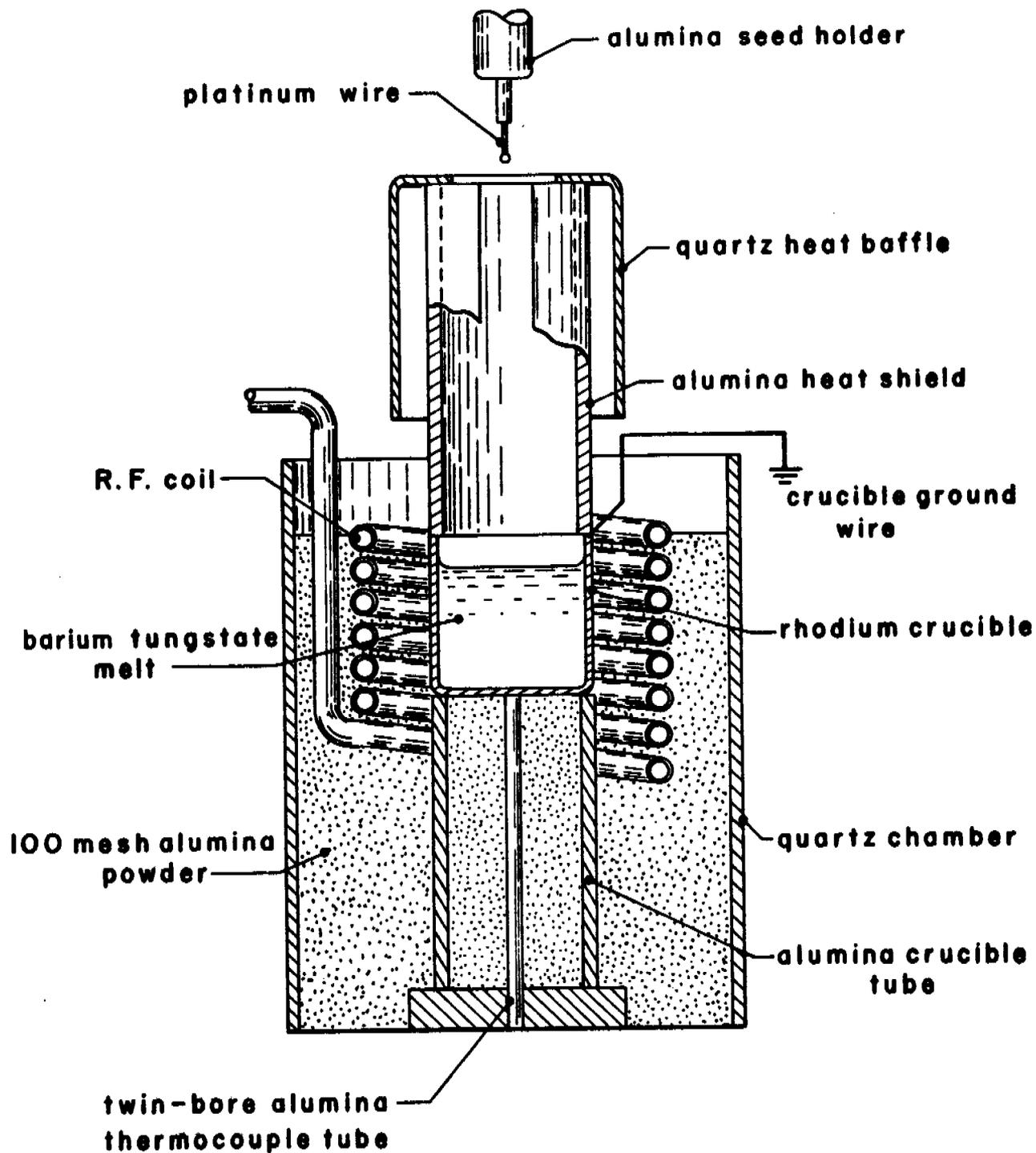


Figure 14 Apparatus for Growth of $BaWO_4$

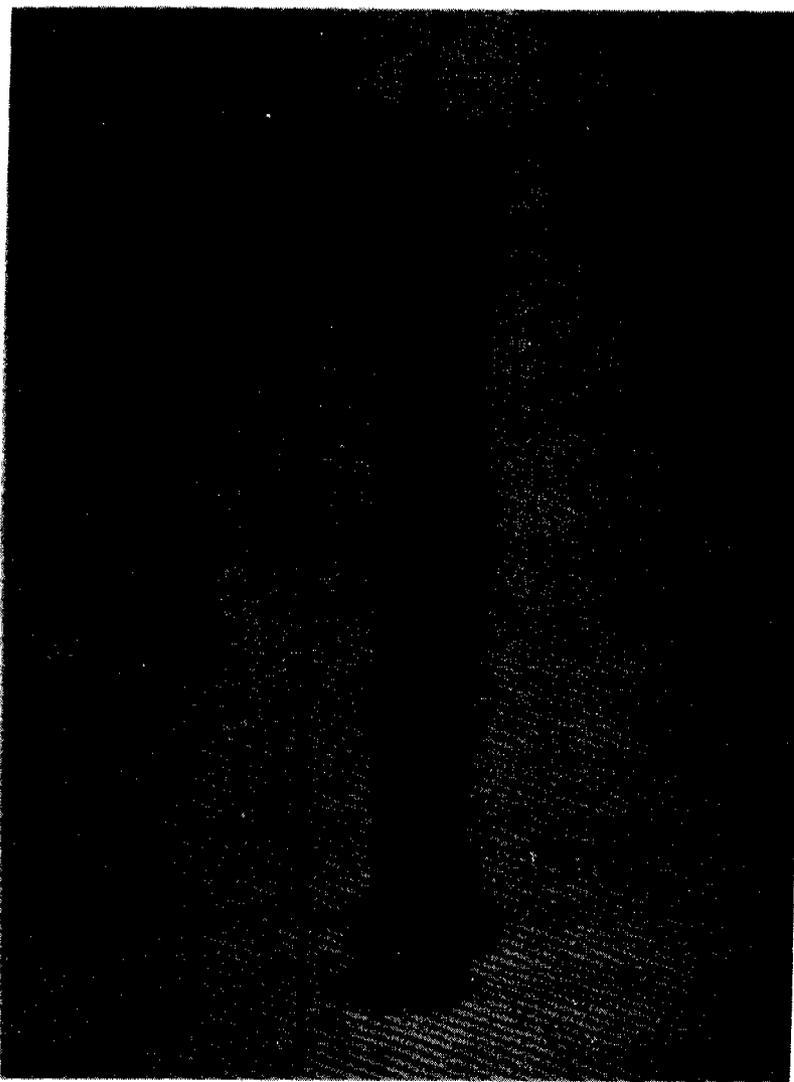


Figure 15 Crystal Containing 0.14 Mole % Sm_2O_3 in BaWO_4

crystals. To alleviate this problem, an annealing furnace with a programmable temperature controller was constructed.

Lead molybdate single crystals were pulled successfully from a rhodium crucible in a crystal pulling apparatus similar to that described above. The starting material, in powder form, was obtained from Electronic Space Products Company. The melting point is approximately 1070°C. As long as the melting point is not exceeded, little or no vaporization of the material occurs. As the temperature is increased beyond the melting temperature, vaporization rapidly becomes excessive. Seeding was again carried out on a small loop in a platinum wire. The first crystals pulled were about 1 cm in diameter and 2 cm long. In every case the crystals fractured badly after cooling to room temperature, and small vertical pipes were clearly visible on the cross sections of the crystals. Attempts to improve crystal quality by growing smaller diameter (4 mm) crystals and slow-cooling the material in the crystal puller after growth were unsuccessful.

An annealing furnace with a programmable temperature controller was constructed adjacent to the crystal puller. Whereas the crystals grown previously were in more or less cylindrical shapes, the crystal grown next was relatively wide in diameter (2.5 cm), but very thin (5 mm). The melt contained 1 mole % samarium added as Sm_2O_3 . Growth was carried out by dipping the platinum loop in the melt with normal rotation (10 rpm), but no seed withdrawal. As the melt temperature was gradually lowered, the material solidified slowly outward from the seed across the surface of the melt. The crystal was then withdrawn from the crystal puller and placed in a quartz boat inside an annealing furnace at 850°C for about 16 hours. At the end of 16 hours it was slow-cooled (1°/min) to room temperature. Samples cut from this crystal were free of holes and microcracks.

Several samples were cut from a crystal of calcium tungstate doped at about 1 mole % with neodymium in the form of Nd_2O_3 . The crystal had been grown previously at Texas Instruments in the same crystal pulling apparatus used for growing barium tungstate, barium molybdate, and lead molybdate. Although calcium tungstate crystals also have a tendency to crack and fracture upon cooling, the problem does not appear to be as severe as it is with the molybdates. Sound crystals of calcium tungstate are readily obtained by slow cooling after growth.

Because the resistivity of these samples as-grown was too high, they were heat-treated under vacuum to lower the resistance. The heat treatment was performed in an evaporator by placing the samples in the heating coils and slowly increasing the power. This treatment was carried out for about six hours. The pressure in the evaporator was of the order of 10^{-6} atmosphere. The coil temperature reached a maximum of 1125°C, but the alumina slab supporting the Nd-doped CaWO_4 crystals did not exceed 1025°C. The maximum temperatures were maintained for about two hours.

B. Resistivity

Resistivity measurements on materials prepared for Ca^{+2} and Mg^{+2} sensors during this report period were made according to the procedure outlined in the first

intermediate report.¹ These measurements are summarized in Table XI. No measurements were made on the Mg - p-type Si samples, since the resistivity of the initial p-type Si ($\rho = 0.006$ to $0.009 \Omega\text{-cm}$) was very low.

C. Sensor Evaluation

The 1% and 3% Ca-doped polycrystalline silicon materials were evaluated in the membrane configuration. The 1% sample did not respond well, but the 3% sample showed a good response to Ca^{+2} . With a 1 M Ca^{+2} internal solution, a linear response slope of 0.031 ± 0.001 volt/decade was observed in the range 10^{-1} M to $10^{-6} \text{ M Ca}^{+2}$. In the presence of 10^{-3} M K^+ , the slope was reduced to 0.022 ± 0.001 volt/decade, and the linear range was 10^{-1} M to $10^{-4} \text{ M Ca}^{+2}$. In addition, the 3% Ca - poly Si sensor showed no response to SO_4 .

The diffused Mg - p-type Si was evaluated in both the membrane and the electrode configuration. The slices of silicon which had Mg diffused on both sides were used as membranes. Slices with Mg diffused on only one side were used in the electrode configuration. An interesting effect was noticed on the double-diffused material. The diffusions were not symmetrical, and this caused a displacement from zero potential when the same solution was used on both sides of the membrane. The response of these materials as sensors was similar to the Ca-doped silicon samples. The sensor does not distinguish between Ca and Mg. The response to other divalent ions is somewhat reduced. In the presence of 10^{-3} M univalent cations the response to Ca or Mg is reduced somewhat, but a measurement can be made at concentrations as low as 10^{-4} M .

The 10% $\text{YF}_3\text{-CaF}_2$ sensors responded to both Ca^{+2} and Mg^{+2} with slopes near 30 mV/decade.

A number of sensors have been prepared which do respond well to Ca^{+2} and Mg^{+2} in the absence of univalent ions. These sensors have been evaluated for their selectivity to each of the ions in the presence of the other. In general, these membrane sensors of 10% $\text{YF}_3\text{-CaF}_2$, 10% NaF-CaF_2 , Mg - p-type Si, and 3% Ca - poly Si do not distinguish between Ca^{+2} and Mg^{+2} and exhibit only slightly lower responses to the other divalent ions. Typical data for the response of one of these sensors to mixtures of Ca^{+2} and Mg^{+2} are presented in Table XII.

The data in Table XII support a junction potential mechanism. However, it should be pointed out that this mechanism seems to apply only to divalent ions. Therefore, these sensors can be used to monitor brackish waters where the divalent ions are at least 10% of the monovalent ions.

Continuous monitoring of some Webster, South Dakota, water was attempted using the 10% $\text{YF}_3\text{-CaF}_2$ sensors and commercial K^+ and Na^+ sensors. Changes in concentration were allowed to take place by evaporation and then addition of deionized water. The 10% $\text{YF}_3\text{-CaF}_2$ tracked the concentration changes very well and was steady. The two commercial electrodes varied considerably from day to day and required calibration. It appears that improvements are still required in commercial electrodes if they are to be used for monitoring purposes.

Table XI

Specific Resistivities of Sensor Materials
at 20 V dc and Ambient Temperature

<u>Sample</u>	<u>Resistivity (Ω-cm)</u>
1% Ca-poly Si	4.1
3% Ca-poly Si	4.7
10% YF ₃ - 90% CaF ₃ (powder)	2.5×10^8
10% YF ₃ - 90% CaF ₃ (crystals)	2.3×10^8

Table XII

Response of 10% $\text{YF}_3\text{-CaF}_2$ to Ca^{+2} and Mg^{+2}

(Internal solution 0.1 M Ca^{+2})

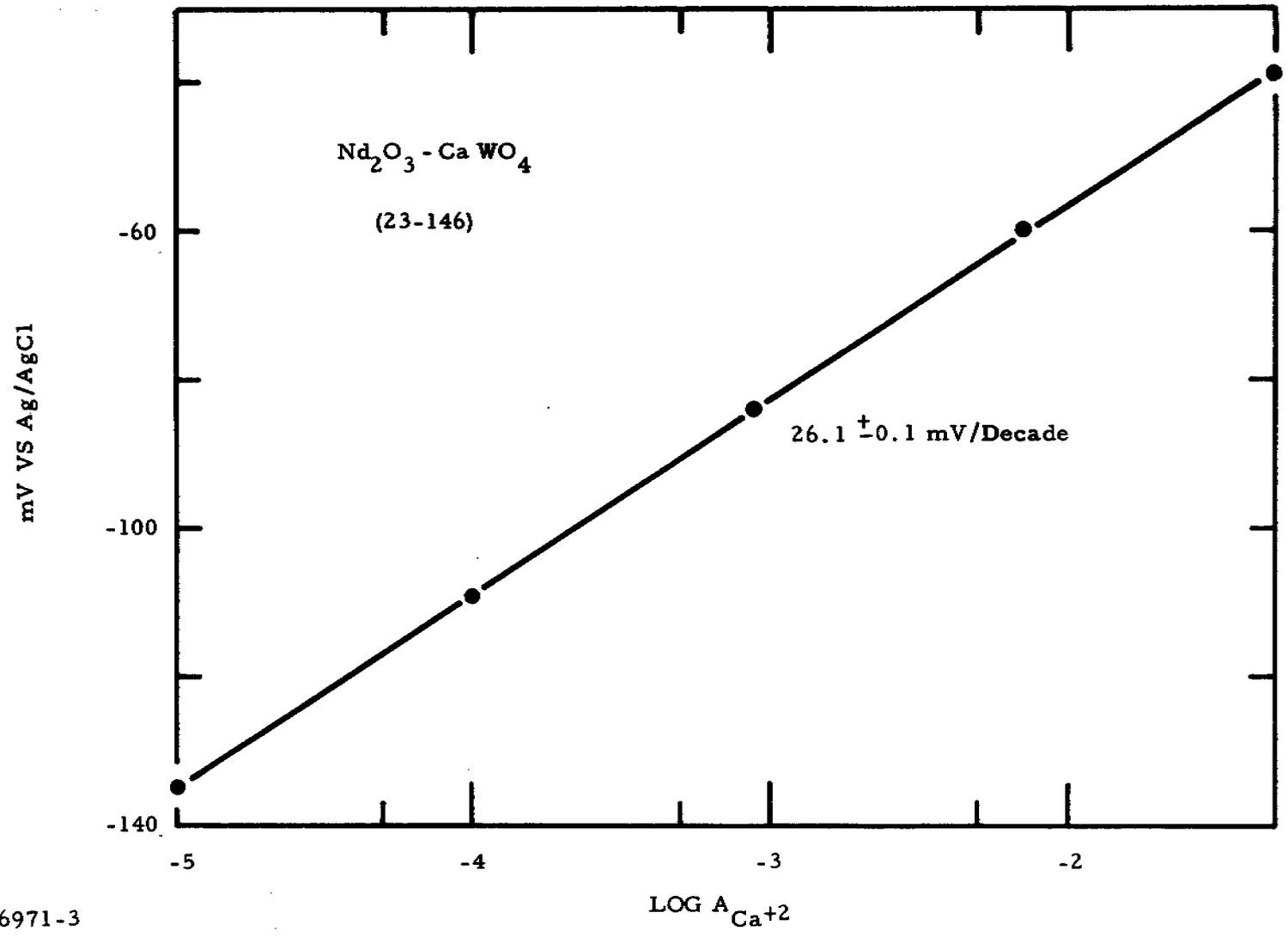
<u>Potential</u> <u>(volts)</u>	<u>$[\text{Ca}^{+2}]$</u> <u>(moles/liter)</u>	<u>$[\text{Mg}^{+2}]$</u> <u>(moles/liter)</u>
0.027	0.01	0.0001
0.055	0.001	0.001
0.027	0.0001	0.01
0.059	0.001	0.0001
0.060	0.0001	0.001

The 1% Sm_2O_3 - BaWO_4 sensors were evaluated for response to Ca^{+2} and Mg^{+2} and showed about the same response as previously reported CaWO_4 electrodes.²

The doped Ba and Pb molybdates did not respond to Ca^{+2} or Mg^{+2} . The problem appeared to be one of very high sensor resistance.

The Nd doped CaWO_4 sensor material which was vacuum heat-treated was fabricated into a membrane sensor. Its response to changes in Ca^{+2} activity is shown in Figure 16. However, like previous sensors of this type, univalent ions interfered. The interference appears effectively as a short between the two solutions. Conceivably, the univalent ions could transport through the membrane, although they would be hindered. This may be helped by a certain degree of microcracking.

The prospects of obtaining good solid state sensors for divalent ions with these systems are still good. Crystal preparation (crack-free) and increased conductivity could provide the improvements required for usable sensors.



6971-3

Figure 16 Response of Vacuum Heat-Treated Nd-CaWO₄ to Changes in Ca⁺² Activity

V. $\text{SO}_4^{=}$ SENSORS

Several attempts were made to prepare sensors for $\text{SO}_4^{=}$. One attempt employed small single crystals of BaSO_4 in an inert matrix. In a second attempt, barium salts of slightly greater solubility than the $\text{SO}_4^{=}$ were used, and the third method was an indirect method which utilized an Fe-1173 sensor and added $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to the solution containing $\text{SO}_4^{=}$.

Some small single crystals of BaSO_4 were grown from a melt of BaCl_2 and Na_2SO_4 . The two salts were mixed in equal mole % quantities, placed in a platinum crucible, and heated to 1000°C for 75 hours. The sample was then slow-cooled to 880°C in 8-1/2 hours and allowed to cool by turning the furnace off. Small crystals of BaSO_4 were recovered. This process was repeated several times, adding the BaSO_4 crystals from the previous run to the salt charge. After several runs, the BaSO_4 crystals were then fused in a matrix of CV-97 (an Owens-Illinois solder glass approximately 65% PbO , 10% ZnO , 25% B_2O_3). The glass containing single crystals of BaSO_4 was sintered at 450°C for 1.2 hours in a He atmosphere. The nonoxidizing atmosphere allows the glass to devitrify in a semi-conducting phase. Two samples of 5% and 15% BaSO_4 in CV-97 were prepared. The 15% sample crumbled. The measured resistivity of the 5% BaSO_4 -CV-97 was $5.3 \times 10^7 \Omega\text{-cm}$. This material was prepared as a membrane sensor and tested for its specific response to $\text{SO}_4^{=}$. The test results indicated that the membrane acts as a liquid junction and exhibits a response based on concentration, but is not specific to $\text{SO}_4^{=}$.

The 1 mole % Sm_2O_3 - BaWO_4 material was fabricated into membrane configuration sensors. Samples from both crystals were used. Tests with solutions of Na_2SO_4 and KNO_3 indicated a small response to $\text{SO}_4^{=}$. However, this response again is more an effect of ionic strength differences than a specific response to $\text{SO}_4^{=}$. Doped BaWO_4 responded similarly.

Several indirect methods were used to obtain a response to $\text{SO}_4^{=}$. It was previously reported^{1,2} that 2% Fe-1173 material did in fact respond well to persulfate ($\text{S}_2\text{O}_8^{=}$). A reduction product of $\text{S}_2\text{O}_8^{=}$ is $\text{SO}_4^{=}$. Solutions containing a fixed amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and varying amounts of $(\text{NH}_4)_2\text{SO}_4$ or Na_2SO_4 were tested with Fe-1173 sensors. An initial response was observed, but it was not reproducible after several days' exposure to solutions containing $\text{SO}_4^{=}$ and $\text{S}_2\text{O}_8^{=}$. The response diminished with time, and inspection of the electrode following the evaluation indicated considerable etching. As has been previously demonstrated,³ Fe-1173 responds only to the higher oxidation state of a redox couple (i.e., to Fe^{+3} , but not to Fe^{+2}); therefore, it is not surprising that the sensor did not respond to $\text{SO}_4^{=}$.

VI. SUMMARY

In an investigation related to this work it has been demonstrated, at least in the laboratory, that the Fe-1173 sensors can effectively monitor changes in Fe^{+3} concentration in preserved acid mine drainage water. At the same time, it was shown that a Ca^{+2} electrode, 10% YF_3 -90% CaF_2 , could accurately monitor the treatment process where limestone (CaCO_3) is added to neutralize the acid and precipitates the Fe^{+3} . Although these were only laboratory demonstrations, the data support the contention that further development and engineering (ruggedizing) of these sensors could result in practical, useful monitoring systems.

Although work on $\text{SO}_4^{=}$ has not resulted in a useful sensor, it has served to indicate the direction of future work. At this time it appears that the only hope for a partially selective $\text{SO}_4^{=}$ sensor must be based on some exchange reaction at the sensor surface or an indirect sensor. This will require either a renewable sensor surface or an exchange reaction that has a very favorable equilibrium which can be made surface-dependent, or some complex with a measurable ion.

The development of good solid state sensors for Ca^{+2} and Mg^{+2} appears within reach. Some modifications to the crystal growing process are necessary to insure the proper conductivity and to provide microcrack-free material. The area of surface treatment for enhanced response has not been investigated. A few preliminary experiments with doped CaF_2 indicate that considerable progress toward obtaining good sensors could be achieved by proper surface conditioning. There is a problem of selectivity between Ca^{+2} and Mg^{+2} ; however, the initial difficulty to be overcome is obtaining a high selectivity for the divalent ions in the presence of monovalent ions. Investigations currently under way indicate that progress is being made in achieving these goals.

Better understanding of the Fe-1173 sensor and the chalcogenide sensors in general is important to achieving reliability and low cost in these sensors. Control of material preparation is a very important factor. Knowledge of how the sensors function provides significant information on the parameters that must be controlled and on methods of quickly evaluating the material after it has been produced. These mechanistic studies guide the selection of other material systems which can lead to new and improved sensors, or possibly a series of sensors. While a complete understanding of the mechanism of these chalcogenide sensors has not yet been achieved, significant progress has been made. The investigation of the oxy-chalcogenide glasses is a direct result of this progress.

Sensors produced from $\text{CuO-As}_2\text{S}_3$ material have shown very selective response to Cu^{+2} in a variety of electrolytic media. There is essentially no interference from other monovalent (Na^+ , K^+ , H^+) ions or from many of the divalent (Ca^{+2} , Mg^{+2} , Ni^{+2} , Fe^{+2} , Pb^{+2} , Mn^{+2}) ions. There is an effect of anions, notably a considerable change in response between NO_3^- and Cl^- media. This, of course, is the result of complex formation and stabilization of the Cu^{+1} oxidation state in Cl^- . However, these sensors have demonstrated that they can monitor Cu^{+2} in a complicated electrolyte such as sea water.

The fact that $\text{CuO-As}_2\text{S}_3$ sensors have exhibited good selectivity for Cu^{+2} over Fe^{+3} is of considerable importance. Selectivity values at Cu^{+2} levels of 10^{-3} M over Fe^{+3} have been observed to be as high as 1000. Investigation to develop a monitoring system employing these sensors and the previously described¹⁻³ Fe-1173 which has a high selectivity for Fe^{+3} over Cu^{+2} should have some very practical applications. This system could be applied to monitoring a number of processes where corrosion rates may vary because of operating conditions. The multflash desalination process, or for that matter any process that uses hot brine solutions, could be monitored with such a system. The sensors in the laboratory have shown excellent response, even in concentrated (3 M KCl) brines.

Ion selective electrochemical sensors have considerable usefulness as a monitoring tool. Many practical applications can be conceived. These sensors can provide a wealth of information, particularly in process control (desalination by distillation, electrodialysis, reverse osmosis, etc.) if used with the proper precautions. The applications of these sensors to practical engineering problems is limited only by the imagination and ingenuity of the users. Continued research and development will serve to expand their usefulness.

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