

AN ABSTRACT OF THE THESIS OF

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Title NULL POINT POTENTIOMETRIC DETERMINATION OF
FLUORIDE WITH THE BISMUTH-BISMUTH³ FLUORIDE
ELECTRODE

Abstract approved 
(Major professor)

The bismuth-bismuth fluoride electrode was found to be thermodynamically reversible to fluoride ion. An estimate of the standard potential of the reaction $\text{BiF}_3 + 3e = \text{Bi} + 3\text{F}^-$ was determined to be -0.010 ± 0.001 volts. The electrode was used to determine fluoride in sodium fluoride solutions containing 50 to 1000 p.p.m. fluoride ion with an accuracy of about 1 percent by means of a null-point potentiometric method. Nitrate and sulfate ions interfered slightly and chloride, bromide, iodide, cyanide, phosphate and acetate ions caused a serious loss of accuracy.

NULL-POINT DETERMINATION OF FLUORIDE WITH
THE BISMUTH-BISMUTH FLUORIDE ELECTRODE

by

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NULL-POINT POTENTIOMETRIC DETERMINATION OF FLUORIDE WITH THE BISMUTH-BISMUTH FLUORIDE ELECTRODE

I. INTRODUCTION

In many of the gravimetric, titrimetric and colorimetric methods for determining fluoride it is generally necessary to separate this ion from other cations and anions (9, p. 238). The method most generally used to accomplish this separation was first proposed by Willard and Winter (21, p. 7) and essentially amounts to the distillation of fluoride as hexafluosilicic acid, H_2SiF_6 , from a perchloric or sulfuric acid solution in the presence of quartz, glass, or porous plate with steam vapor as the carrier gas. After the fluoride has been isolated it may be determined gravimetrically as lead chlorofluoride or calcium fluoride for 10 to 100 milligram amounts of fluoride. For 0.05 to 30 milligram amounts the method most widely used is the titration with thorium nitrate using Alizarin Red S as the indicator (9, p. 260). The separation is time consuming and the thorium nitrate titration requires an experienced operator for accurate results.

It was the aim of the present investigation to find a method for determining free fluoride ion which would: 1) not require the isolation of fluoride, 2) give accurate results down to 10^{-4} M fluoride concentration, and 3) be reasonably rapid. At the suggestion

of Dr. Harry Freund, a method called precision null-point potentiometry (17, p. 283) in conjunction with a bismuth-bismuth fluoride electrode was investigated, with the hope that this system would meet the requirements listed above.

The null-point method as described by Malmstadt and Winefordner was as follows: a reference solution of known chloride concentration having a large ionic strength due to 1 M H_2SO_4 was placed in an isolation compartment with an asbestos plug in the lower end acting as a salt bridge. Into the compartment was placed a silver-silver chloride electrode. The compartment was placed in a beaker provided with a stirrer and another silver-silver chloride electrode; the unknown solution was then placed in the beaker. In series with the two electrodes was a network which provided a maximum of 10 millivolts bucking potential and a Leeds and Northrup Speedomax recorder which indicated when zero potential difference existed between electrodes. Any initial difference in potential between two electrodes immersed in the same reference solution was bucked out by the network. A definite volume of the unknown chloride solution made up to the same ionic strength as the reference solution was poured into the beaker and a solution with or without chloride of the same ionic strength as the solution in the compartment was added by buret to the unknown. If the

unknown solution was more concentrated than the reference solution, 1M H_2SO_4 was added to the beaker and when the potential difference between electrodes was zero the chloride concentration in the compartment and the beaker was presumed equal and the concentration of unknown, C_u , could be calculated from (1)

$$C_u = \frac{V_o + V_a}{V_o} C_r$$

where: C_r = concentration of the reference solution

V_o = original volume of the unknown solution

V_a = volume of electrolyte added

When the concentration of the unknown was less than the reference then (2)

$$C_u = \frac{V_o - V_a}{V_o} C_r, \text{ when}$$

$C_a = 2C_r$, C_a being the chloride concentration of the reagent added.

The advantages of this technique are:

- 1) No dependence is placed on an absolute potential, since differences between electrodes are compensated.
- 2) No temperature compensation need be employed since the reference and unknown solutions will come to temperature equilibrium if the volumes are small.
- 3) Very low concentrations of chloride may be titrated, since chloride contributed by the electrodes themselves will be the same

in the unknown and reference solutions.

A limitation of the method may be illustrated by the following tables giving data for some theoretical titrations.

Table 1. The effect of relative concentrations on the error in the determination of $C_u : C_u < C_r$

C_u	C_r	$\frac{V_o - V_a}{V_o}$	V_o ml.	V_a ml.	Error of C_u $V_a \pm 0.1$ ml.
x	20x	0.05	20	19	10%
x	10x	0.10	20	18	5%
x	8x	0.125	20	17.5	4%
x	4x	0.25	20	15	2%
x	2x	0.50	20	10	1%

When $C_r = 10C_u$ an error of 0.1 ml. in V_a results in a 5 percent error in C_u compared to a 1 percent error when $C_r = 2C_u$. Probably the reference solution should not be more than 10 times as concentrated in chloride as the unknown; this was the limit suggested by Malmstadt and Winefordner (17, p. 290).

Table 2. The effect of relative concentrations on the error in the determination of $C_u : C_u > C_r$

C_u	C_r	$\frac{V_o + V_a}{V_o}$	V_o ml.	V_a ml.	Error of C_u for $V_a \pm 0.1$ ml.
20x	x	20	20	380	< 0.1%
10x	x	10	20	180	< 0.1%
8x	x	8	20	140	< 0.1%
4x	x	4	20	60	0.125%
2x	x	2	20	20	0.25%

It is apparent that the total volume, $V_o + V_a$, becomes comparatively large if C_u becomes about four times greater than C_r . As V_a increases, chloride in the electrolyte added may become a factor leading to errors; also refilling a buret would result in a loss of precision. Malmstadt and Winefordner (17, p. 290) established a limit of $C_u = 2C_r$ due to the size of their beaker.

The null-point method described was applied to the analysis of sodium fluoride solutions using bismuth-bismuth fluoride electrodes instead of silver-silver chloride electrodes.

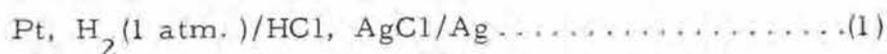
A paper entitled "Null-point Potentiometric Determination of Fluoride" has been published (18, p. 337). The method described in this paper involves two half cells connected by a salt bridge,

each containing a mixture of Ce(III) and Ce(IV) in 0.25M H_2SO_4 . To one half cell was added an unknown amount of fluoride and then a standard solution of sodium fluoride was added to the other half cell. A platinum electrode was placed in each half cell and the potential difference measured with a potentiometer. When the potential difference was zero, the end point had been reached. Data were presented showing an accuracy of 0.2 percent for 0.05 to 0.5M NaF solutions. It was claimed that sulfate and nitrate did not interfere and chloride interfered slightly.

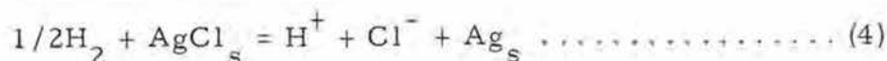
In conjunction with the investigation of the null-point potentiometric determination of fluoride with the bismuth-bismuth fluoride electrode, a study of the electrode system $BiF_3 + 3e = Bi + 3F^-$ was undertaken. Data presented by Johns and Kendall (12, p. 3) showed a 56 millivolt change in the potential of a bismuth-bismuth fluoride electrode versus a saturated calomel electrode for a ten fold change in fluoride concentration. However, no attempt was made to control the ionic strength and the temperature; the possibility of an appreciable junction potential at higher NaF concentrations was also overlooked. This investigation will show that the electrode is thermodynamically reversible to fluoride ion, i. e. the potential changes 59 millivolts for a ten fold change in fluoride concentration at 25 degrees centigrade. Also an estimate will be given for the

standard potential of the reaction $\text{BiF}_3 + 3e = \text{Bi} + 3\text{F}^-$.

The most accurate E° values are obtained with a concentration cell without liquid junction. The classical example of this type of cell is:



The half cell reactions are:



By convention P_{H_2} , Ag_s and $\text{AgCl}_s = 1$. Substituting reactions (2) and (3) into the Nernst equation

$$E = E^\circ_{2\text{H}^+, \text{H}_2} + \frac{RT}{nF} \ln a_{\text{H}^+} \dots \dots \dots (5)$$

$$E = E^\circ_{\text{AgCl, Ag, Cl}^-} + \frac{RT}{nF} \ln \frac{1}{a_{\text{Cl}^-}} \dots \dots \dots (6)$$

By convention

$$E^\circ_{2\text{H}^+, \text{H}_2} = 0 \dots \dots \dots (7)$$

The overall cell potential is

$$E = E_{\text{AgCl, Ag, Cl}^-} - E_{2\text{H}^+, \text{H}_2} \dots \dots \dots (8)$$

Substituting equations (5) and (6) in equation (8)

$$E = E^\circ_{\text{AgCl, Ag, Cl}^-} - \frac{RT}{nF} \ln a_{\text{Cl}^-} - \frac{RT}{nF} \ln a_{\text{H}^+} \dots \dots (9)$$

Then

$$E = E^{\circ}_{\text{AgCl, Ag, Cl}^-} - \frac{RT}{nF} \ln a_{\text{H}^+} a_{\text{Cl}^-} \dots \dots \dots (10)$$

Since $a_{\pm} = m\gamma$ and $n = 1$, upon substituting and rearranging terms

$$E + \frac{RT}{F} \ln m_{\text{H}^+} m_{\text{Cl}^-} = E^{\circ}_{\text{AgCl, Ag, Cl}^-} - \frac{RT}{F} \ln \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} \quad (11)$$

The values on the left side of equation (11) are usually plotted against $m^{1/2}$ and extrapolated to infinite dilution. Since at infinite dilution the activity coefficients equal unity the log term on the right of equation (9) becomes zero and the intercept at $m^{1/2} = 0$ is equal to E° . It must be pointed out, however, that in order to achieve good results by this method accurate measurements must be obtainable at low concentrations (ca. 10^{-3} M) which is often a difficult experimental procedure (14, p. 353). The electrode just discussed is one of the most reproducible electrodes and is frequently used as a reference and was quoted as having an E° of -0.2245 in 1930 (8, p. 827) and -0.2224 more recently (14, p. 342).

Roughly half (14, p. 10) of all the values for standard potentials are derived from specific heat measurements utilizing the equations $\Delta F = \Delta H - T\Delta S$ and ΔF (cal.) = $-nE(23,060)$. Unfortunately, thermal data for calculating E° for $\text{BiF}_3 + 3e = \text{Bi} + 3\text{F}^-$ are not available.

II. A STUDY OF THE ELECTRODE SYSTEM $\text{BiF}_3 + 3e = \text{Bi} + 3\text{F}^-$

A. EXPERIMENTAL

1. Reagents

The bismuth-bismuth fluoride electrodes used in all of the experimental work were prepared from 99.98 percent pure bismuth granules. The lot analysis (#2373, J. T. Baker Chemical Co.) showed the following impurities:

Silver	0.003 percent
Lead	0.005 percent
Arsenic	0.0005 percent
Copper	0.002 percent
Iron	0.0003 percent
Zinc	<u>0.001</u> percent
	0.0178 percent total impurities

The sodium fluoride used was C. P. grade, 100.0 percent NaF.

The sodium fluoride solutions were made up as follows with triple distilled water:

<u>Grams of NaF/1000 gm. H₂O</u>	<u>molality</u>
5.565	1.325×10^{-1}
2.226	5.30×10^{-2}
1.113	2.65×10^{-2}
0.5565	1.325×10^{-2}

0.2226

 5.30×10^{-3}

0.1113

 2.65×10^{-3}

C. P. grade NaClO_4 , F. W. 122.45, was used to control the ionic strength.

2. Electrodes and Apparatus

In order to verify the composition of the electrode surface, a large bismuth electrode five centimeters long and one centimeter in diameter was cast using the same 99.98 percent pure bismuth metal referred to previously. Bismuth trifluoride was then prepared by anodically electrolyzing the metal in one molar sodium fluoride acidified to a pH of 3.5 with hydrofluoric acid using a current density of four milliamperes per square centimeter for a period of one half hour. The electrode was then washed with distilled water and the BiF_3 coating scraped from the electrode, taking care not to remove any bismuth metal. This process was repeated until enough BiF_3 was obtained for an X-ray diffraction analysis. The compound prepared in this manner was a grey-black powder.

The electrodes for the voltage measurements were prepared by tamping the powdered bismuth into Pyrex funnels and then melting the bismuth with a Tirrill burner. After the metal had cooled the glass stem was broken and the cylindrical electrodes of 0.317

cm. diameter were removed. The electrodes prepared in this manner had a bright, silvery appearance indicating there was no oxide coating on the metal. Where the metal did come in contact with oxygen a yellow oxide of Bi_2O_3 was formed. It was rarely possible to prepare electrodes longer than two inches in this manner due to the brittle nature of the cast bismuth. The electrodes were center drilled and a piece of number 20 copper wire was soldered into place. Then the electrodes were sealed into number six soft glass tubing with an epoxy bonding agent (Devcon) taking care that no water would come into contact with the solder or the copper wire. The average surface area of the electrodes was 1.4 cm.^2 . The coating of bismuth fluoride on the electrodes was prepared by first scouring the electrodes with steel wool and detergent and then immersing them in a 1M sodium fluoride solution which was acidified with hydrofluoric acid to a pH of 3.5. The bismuth electrode was electrolyzed at a current density of 4 milliamperes/ cm.^2 for approximately 15 minutes versus a platinum cathode while agitating the solution with a magnetic stirrer. This procedure gave a smooth grey-black coating of bismuth fluoride.

The analysis of the BiF_3 sample was run on a Philips Electronics X-ray diffraction unit with a General Electric powder diffraction camera. The Radiographic Laboratory of the Oregon State

University Department of Mechanical Engineering kindly allowed the use of the aforementioned instrument.

A constant temperature bath was employed, consisting of an electric heater actuated by a mercury controlled thyatron relay. The sensing element consisted of a large bulb of mercury which constricted to a capillary at the top. A slight expansion of the mercury in the bulb caused an adjustable contact to make or break with the mercury in the capillary at a pre-set temperature; this was a commercially available unit, the Sargent Mercurial Thermoregulator. Since only a few microamperes flowed at the capillary contact junction, the current was amplified by a thyatron which had a relay in its plate circuit and the relay contacts controlled the current to an electric heater immersed in the water bath. The water in the bath was constantly stirred by a G.K. Heller Co. thyatron controlled motor driven paddle wheel stirrer. The temperature of the water bath was thus kept at 25 ± 0.01 degrees centigrade.

A saturated calomel electrode was used as the reference electrode. This electrode was constructed using a Cenco 70069 electrode vessel and adding mercury, calomel (Hg_2Cl_2) and saturated potassium chloride according to the method of Bates (4, p. 180). A platinum wire made contact with the mercury. A one inch piece of Tygon tubing was fitted onto the sidearm of the calomel

cell. Into this tubing was inserted a one inch long, one quarter inch O. D. rod of leached but unfired Vycor glass (9, p. 473). Another five inch piece of Tygon tubing was fitted over this piece of Vycor and a similar rod of Vycor closed the distal end of the Tygon tube. The tube between the two pieces of Vycor was filled with 0.2 molal NaClO_4 . The object of this arrangement was to eliminate any possibility of chloride ion entering the test solutions and to obtain as nearly reproducible liquid junctions as possible. The test solutions were contained in 250 ml. Erlenmeyer flasks which were then immersed in the water bath and allowed to attain temperature equilibrium for two hours. The Vycor salt bridge and three bismuth-bismuth fluoride electrodes were inserted into the test solution along with a paddle wheel stirrer which was rotated at 600 R. P. M. E. m. f. measurements were obtained with a Leeds and Northrup potentiometer with an internal standard Weston cell. The accuracy of the unit was checked by taking voltage measurements of three calibrated Weston cells and the average error of the potentiometer was found to be minus 0.0001 volt which was negligible compared to other experimental inaccuracies.

A Beckman model B spectrophotometer was used in the experiment dealing with the effect of NaClO_4 on the solubility of BiF_3 in water. All reagents used in conjunction with this study were of

C. P. grade.

3. Procedure

X-ray diffraction analysis. A brief explanation of the powder method used in the analysis of BiF_3 follows: if a powder, which consists of many very small crystals, is placed in an X-ray beam a continuous cone of diffracted rays will be produced. The cone thus produced will intercept the circular film surrounding the sample. Since the film and the base of the cone are circular the lines produced on the film will be curved. The angle θ can be calculated from the radius of the film. If the wavelength of the X-rays is known, the spacing of the planes in the crystal may be determined by using the Bragg equation $n\lambda = 2d\sin \theta$. The diameter of the circular camera was 143.2 mm. Letting X be the distance in millimeters from the diffraction line to the center of the film then:

$$1) \theta = \frac{X}{2R} \text{ radians.}$$

$$2) \theta = \frac{X}{2R} (57.295) \text{ degrees. When } 2R = 143.2 \text{ mm., then}$$

$$3) \theta = \frac{X}{143.2} (57.295) = 0.4001X, \text{ and substituting this in the}$$

Bragg equation,

$$4) d = \frac{n\lambda}{2 \sin 0.4001 X}$$

A sample calculation for a measured value of $X = 34.0 \text{ mm.}$, using

a copper target (wavelength $\text{Cu K}_{\alpha 1} = 1.5374$ angstroms) and a nickel filter for removing the K_{β} lines of copper, is:

$$\begin{aligned} 5) \quad d &= \frac{(1) (1.5374 \text{ \AA})}{2 \text{ Sin } (0.4001 \times 34.0 \text{ mm.})} \\ &= \frac{1.5374}{(2) (0.2351)} \\ &= 3.269 \text{ \AA} \end{aligned}$$

The effect of NaClO_4 on the solubility of BiF_3 . A stock solution of 100 p. p. m. Bi(III) was prepared by dissolving 0.1000 gm. of C. P. grade bismuth granules in hot dilute sulfuric acid. Then 0, 1, 2, 3, 5, and 10 ml. of the stock solutions were added to 100 ml. volumetric flasks. To these flasks were added 15 ml. of 8N H_2SO_4 , 4ml. of 10 percent KI, 4 ml. of 1 percent Na_2SO_3 and 20 ml. of 1 percent ascorbic acid; all reagents except the sulfuric acid solution were freshly prepared each day. The absorbance was measured at 460 millimicrons with a Beckman Model B spectrophotometer. The procedure followed the method described in Sandell (20, p. 355). A large 5.5 cm. long, 1.0 cm. diameter rod was anodically coated with BiF_3 as previously described. This rod was then equilibrated in 500 ml. of triple distilled water at 25 ± 0.01 degrees centigrade for eight hours. The rod was continually rotated at approximately 200 r. p. m. Three 50.00 ml.

aliquots were then analyzed for Bi(III) by the aforementioned method against a reagent blank. The above procedure was repeated except the BiF_3 coated rod was equilibrated in 0.05m, 0.10m, and 0.20m NaClO_4 .

E. m. f. measurements of the bismuth-bismuth fluoride electrode versus a saturated calomel electrode. The ionic strength of each of six concentrations of NaF (1.325×10^{-1} m, 5.30×10^{-2} m, 2.65×10^{-2} m, 1.325×10^{-2} m, 5.30×10^{-3} m, and 2.65×10^{-3} m) was changed by adding successively 0.311, 0.311, 0.622, 1.244, 2.488, 2.488, 2.488, and 2.488 grams of NaClO_4 . The NaClO_4 was stored in a desiccator prior to use because of its deliquescence. Equilibrium at each ionic strength was usually attained within 20 to 30 minutes. The potential of each of three electrodes was obtained by successively clipping a lead from the potentiometer to each electrode. The electrodes were stored in 1 percent NaF while the solutions were replaced.

B. RESULTS AND DISCUSSION

X-ray Diffraction Analysis. A table (6, p. 11) which has solved the calculation on page 15 of this thesis for all possible values of X to the nearest 1/10 of a millimeter was used

for finding the d spacings of the compound under consideration. Table 3 will show the experimental values of X , the corresponding tabular values of d , the relative intensity of the lines, I/I_1 , and the literature d values of bismuth fluoride (1, 2-1235) and bismuth (1, 5-0519) with their relative intensities.

Table 3. Experimental and literature values of d for BiF_3 .

X, mm.	Sample		BiF_3		Bi	
	d	I/I_1	d	I/I_1	d	I/I_1
28.3	3.916	10	----		3.95	9
32.0	3.470	10	----		----	
33.0	3.366	70	3.38	70	----	
34.0	3.269	20	----		3.28	100
38.1	2.924	60	2.92	60	----	
49.6	2.264	20	----		2.27	41
54.8	2.060	100	2.07	100	----	
55.5	2.035	50	----		----	
56.4	2.004	60	----		----	
60.9	1.864	20	----		1.868	23
64.8	1.758	100	1.76	100	----	
68.1	1.680	50	1.68	70	----	
78.0	1.485	10	----		1.49	13
79.5	1.460	10	----		1.44	16
88.0	1.334	80	1.34	90	1.33	11
90.1	1.307	60	1.31	70	----	
100.6	1.190	50	1.20	90	----	
103.0	1.167	30	----		----	
108.5	1.119	40	1.13	90	----	

The coincidence of nine d spacings of the sample (plus or minus 0.01 angstrom unit) with those of bismuth fluoride was evidence for the identity of the two. It was also apparent that a very small amount of bismuth metal was removed with the BiF_3 in the process of scraping the BiF_3 from the surface of the bismuth metal. No lines corresponding to BiOF (I, 5-0531) were observed.

The effect of NaClO_4 on the solubility of BiF_3 . It was decided to analyze for Bi(III) rather than the fluoride ion due to the greater inaccuracies inherent in colorimetric methods for the latter, and the longer time required for the analysis. The method involving the iodobismuth complex ion, BiI_4^- (20, p. 335) was selected since one p. p. m. may easily be detected and the only interferences are antimony and arsenic. A method employing dithizone with greater sensitivity was rejected due to the much larger number of interfering heavy metal ions, lead and zinc being prominent among these; also the reagent is not stable over extended periods.

Table 4. Absorbance of known Bi(III) solutions.

P. P. M. Bi(III)	Absorbance		
	I	II	III
1	0.035	0.036	0.036
2	0.075	0.075	0.075
3	0.114	0.115	0.114
5	0.182	0.185	0.183
10	0.365	0.370	0.368

Figure 1 shows a plot of these data.

Table 5. Absorbance of BiF_3 in distilled water.

Samples	Absorbance	
	I	II
#1	0.036	0.036
#2	0.040	0.040
#3	0.038	0.038
	0.038 \pm 0.001 average deviation	

From the calibration curve this was 1.08 p. p. m. but since the solution was diluted 2:1 the Bi(III) concentration was 2.16 p. p. m.

Table 6. Absorbance of BiF_3 in NaClO_4 solutions.

BiF_3 in:	Absorbance	p. p. m. Bi(III)
0.05 m NaClO_4	0.018	0.5
0.10 m "	none	not detectable
0.20 m "	none	not detectable

To see if NaClO_4 had any effect on the absorbance of a BiI_4^- solution, 5.00 ml. of the stock bismuth solution was made up with the reagents listed above and diluted to 100 ml. with distilled water and 0.20 m NaClO_4 ; no difference in absorbance was noted. The conclusion was that NaClO_4 inhibited the hydrolysis of BiF_3 .

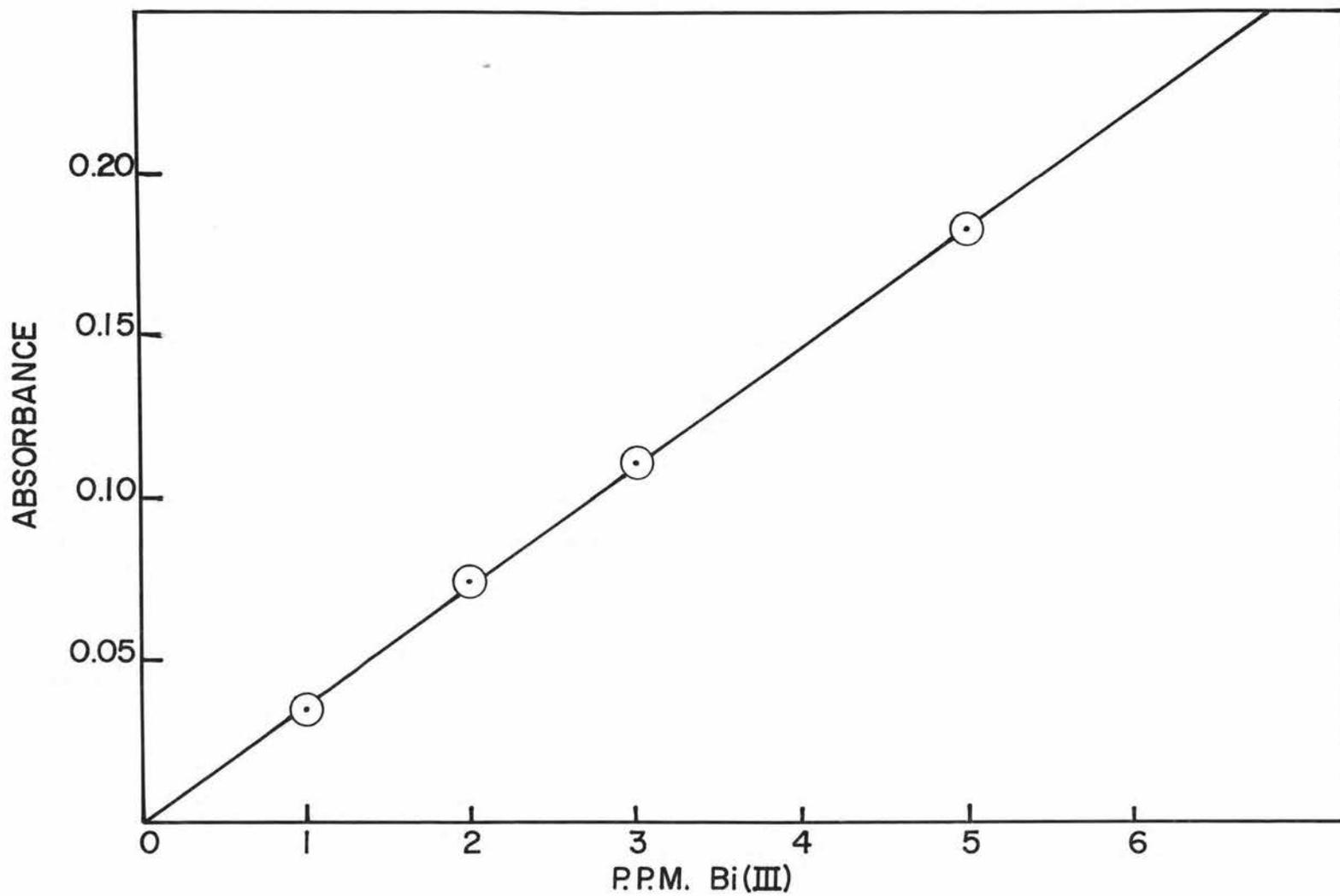


Figure 1. Calibration curve for standard Bi(III) solutions.

E. m. f. measurements of a bismuth-bismuth fluoride electrode versus a saturated calomel electrode.

Table 7. Experimental e. m. f., bismuth-bismuth fluoride electrode versus a saturated calomel electrode.

A. Fluoride conc. = 1.32×10^{-1} molal					
NaClO ₄ molality	ionic strength	(ionic strength) ^{1/2}	millivolts		
			a	b	c
0.00	0.132	0.363	190.2	191.1	192.4
0.025	0.157	0.396	190.7	191.8	192.0
0.10	0.232	0.482	190.4	192.9	193.3
0.20	0.332	0.576	191.0	192.1	193.4
0.40	0.532	0.729	191.3	192.2	192.8
0.60	0.732	0.856	188.5	190.9	191.2
0.80	0.932	0.965	185.1	187.6	189.4
1.00	1.132	1.063	184.3	185.2	186.1
B. Fluoride conc. = 5.30×10^{-2} molal					
0.00	0.0530	0.230	161.0	160.6	160.3
0.05	0.1030	0.321	162.3	162.0	161.8
0.10	0.1530	0.391	168.0	169.0	170.1
0.20	0.2530	0.503	167.1	168.8	170.5
0.40	0.4530	0.673	164.5	166.8	169.1
0.60	0.6530	0.808	163.7	164.4	165.2
0.80	0.8530	0.923	158.4	160.9	162.8
1.00	1.053	1.027	157.4	158.0	158.5

C. Fluoride conc. = 2.65×10^{-2} molal

NaClO ₄ molality	ionic strength	(ionic strength) ^{1/2}	millivolts		
			a	b	c
0.00	0.0265	0.163	128.2	128.3	128.2
0.025	0.515	0.227	136.5	136.0	136.0
0.050	0.0765	0.277	139.0	142.2	144.0
0.10	0.1265	0.355	145.0	146.2	146.8
0.20	0.2265	0.475	145.9	148.4	149.8
0.40	0.4265	0.653	147.9	149.6	150.5
0.60	0.6265	0.791	147.5	148.0	149.8
0.80	0.8265	0.909	143.0	145.7	147.9
1.00	1.0265	1.015	142.2	143.9	145.8

D. Fluoride conc. = 1.32×10^{-2} molal

0.00	0.0132	0.115	103.2	103.0	103.2
0.025	0.0382	0.195	116.8	118.0	119.1
0.050	0.0632	0.251	124.1	124.5	125.9
0.10	0.1132	0.336	128.6	129.8	131.7
0.20	0.2132	0.461	131.0	132.1	133.3
0.40	0.4132	0.643	130.0	131.4	132.5
0.60	0.6132	0.783	127.4	128.5	130.0
0.80	0.8132	0.902	126.3	127.4	129.0
1.00	1.0312	1.005	124.8	126.1	126.8

E. Fluoride conc. = 5.30×10^{-3} molal

NaClO ₄ molality	ionic strength	(ionic strength) ^{1/2}	millivolts		
			a	b	c
0.00	0.00530	0.0728	76.4	76.0	74.4
0.025	0.03030	0.174	92.5	93.1	94.6
0.050	0.05530	0.235	99.3	101.2	103.4
0.10	0.1053	0.324	105.5	107.3	108.2
0.20	0.2053	0.453	107.2	109.5	111.2
0.40	0.4053	0.636	110.0	109.6	110.0
0.60	0.6053	0.778	104.2	106.8	109.3
0.80	0.8053	0.897	103.1	105.2	107.5
1.00	1.0053	1.003	102.0	104.1	106.2

F. Fluoride conc. = 2.65×10^{-3} molal

0.00	0.00265	0.0514	38.4	41.2	45.2
0.025	0.02765	0.166	75.7	78.9	81.0
0.050	0.05265	0.229	83.2	86.1	88.8
0.10	0.10265	0.321	89.8	92.8	94.6
0.20	0.20265	0.450	90.2	93.0	95.3
0.40	0.40265	0.635	88.5	91.6	93.6
0.60	0.60265	0.776	86.0	89.0	91.1
0.80	0.80265	0.896	83.8	86.8	88.7
1.00	1.00265	1.002	82.0	85.0	87.1

These data are graphically illustrated in figures 2 to 4.

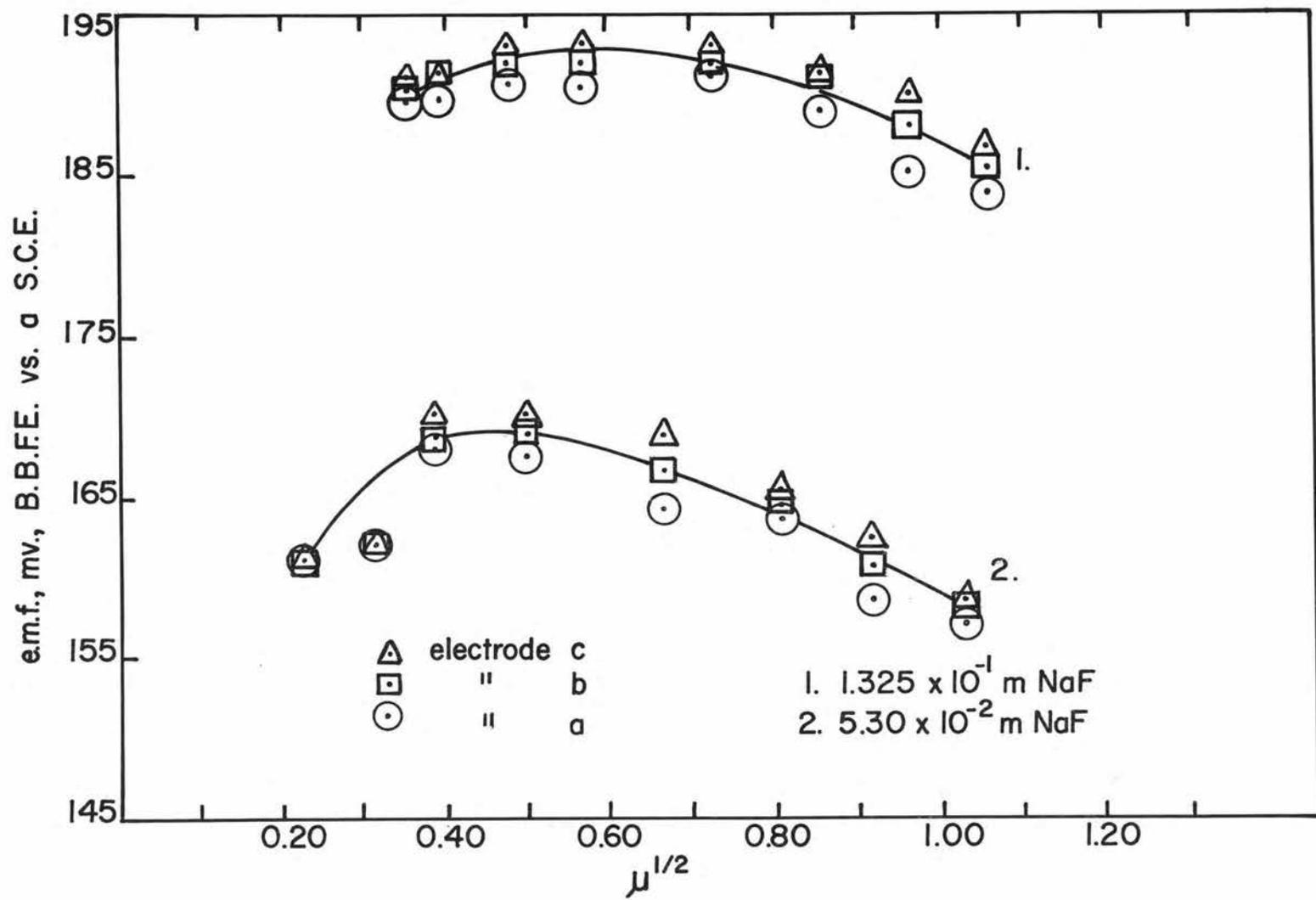


Figure 2. Variation of potential of the B. B. F. E. with increasing NaClO_4 concentration.

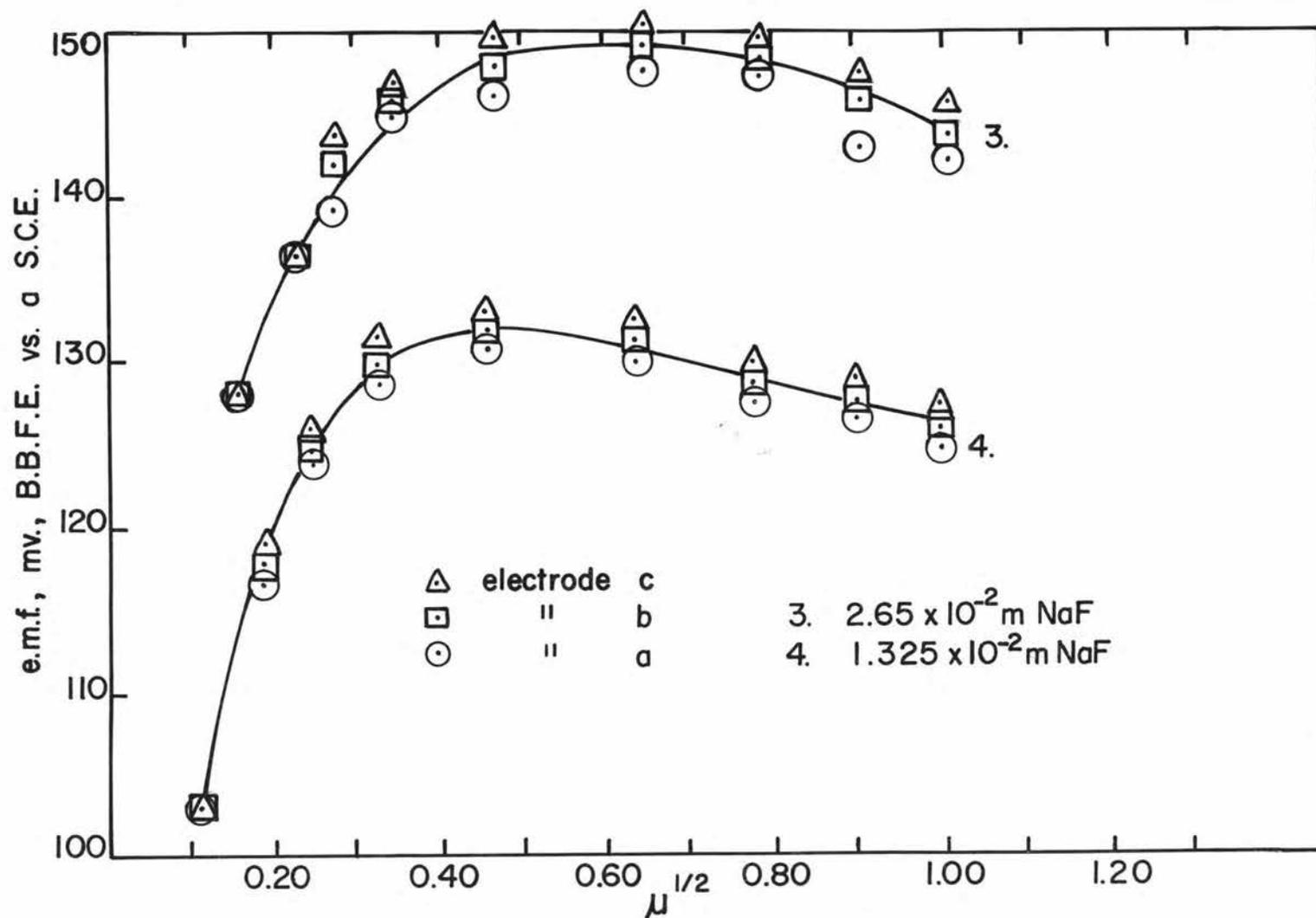


Figure 3. Variation of potential of the B. B. F. E. with increasing NaClO_4 concentration.

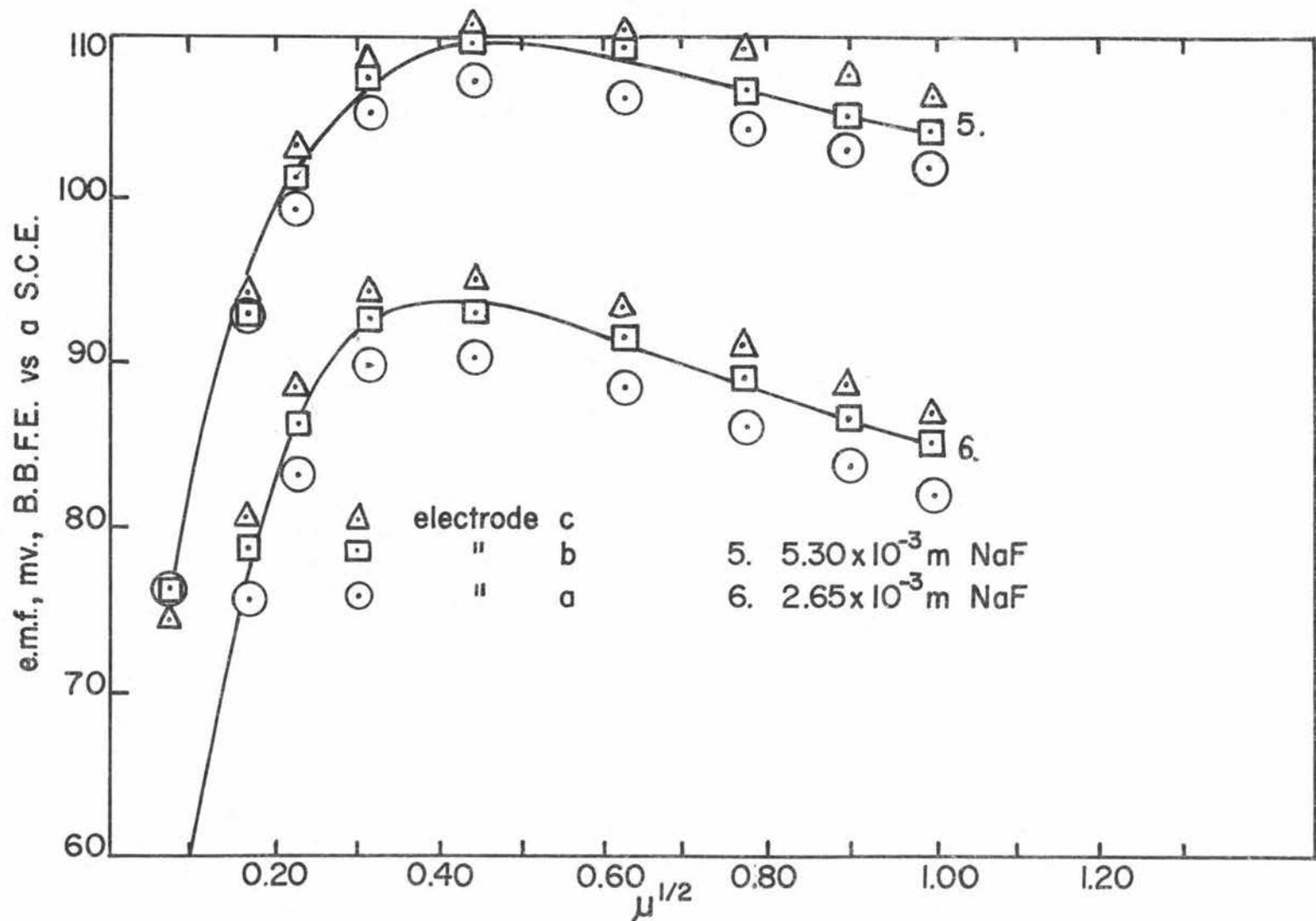


Figure 4. Variation in potential of the B. B. F. E. with increasing NaClO_4 concentration.

Calculations and discussion. It was found that the bismuth-bismuth fluoride electrode (B. B. F. E.) behaved reversibly towards fluoride ion only if the total ionic strength of the solution was greater than 0.1 either in NaF alone, or a combination of NaF and NaClO₄. Concentrations of NaF higher than 0.13m were not used for two reasons: increasingly divergent values of the mean activity coefficient of NaF have been reported in the literature for concentrations of NaF greater than 0.1 m and the greater alkalinity of higher NaF concentrations also increases the possibility of the hydrolytic reaction of BiF₃.

Activity coefficients. It was fortunate that the activity coefficients of NaF and NaClO₄ were nearly identical so that calculations may be made using an average value of γ according to the principle stated by Lewis and Randall (15, p. 380) "in dilute solution the activity coefficient of any ion depends solely upon the total ionic strength of the solution". Table 8 presents activity coefficients reported in the literature at 25°C. for NaClO₄ (21, p. 805) and for NaF (19, p. 628), (11, p. 2824).

Table 8. Reported activity coefficients of NaF and NaClO₄

molality	NaF			NaClO ₄
	e. m. f.	f. p.	v. p.	f. p.
0.01	0.903	0.90		0.90
0.02	0.872	0.87		0.87
0.05	0.814	0.81		0.82
0.1	0.782	0.75	0.764	0.77
0.2	0.725	0.69	0.708	0.72
0.3	0.697		0.675	
0.5	0.666	0.62	0.631	0.64
0.7	0.639		0.602	
0.9	0.621			
0.98	0.617		0.572	
1.0				0.58

These data are plotted in Figure 5 using an average of the e. m. f., f. p., and v. p. values for NaF and the f. p. values for NaClO₄.

Activity coefficients from the modified Debye-Huckel equation.

Kielland (4, p. 52) has estimated the value of a_i , the ion size parameter, in the equation

$$(10) \quad \log \gamma_i = - \frac{A Z_i^2 u^{1/2}}{1 + B a_i u^{1/2}}$$

for ClO₄⁻ and F⁻ to be 3.5 Å from data for ionic mobilities, radii in the crystalline solid, deformability and hydration numbers. For the sodium ion he gives $a_i = 4.5 \text{ \AA}$. Thus a mean value of a_i for either

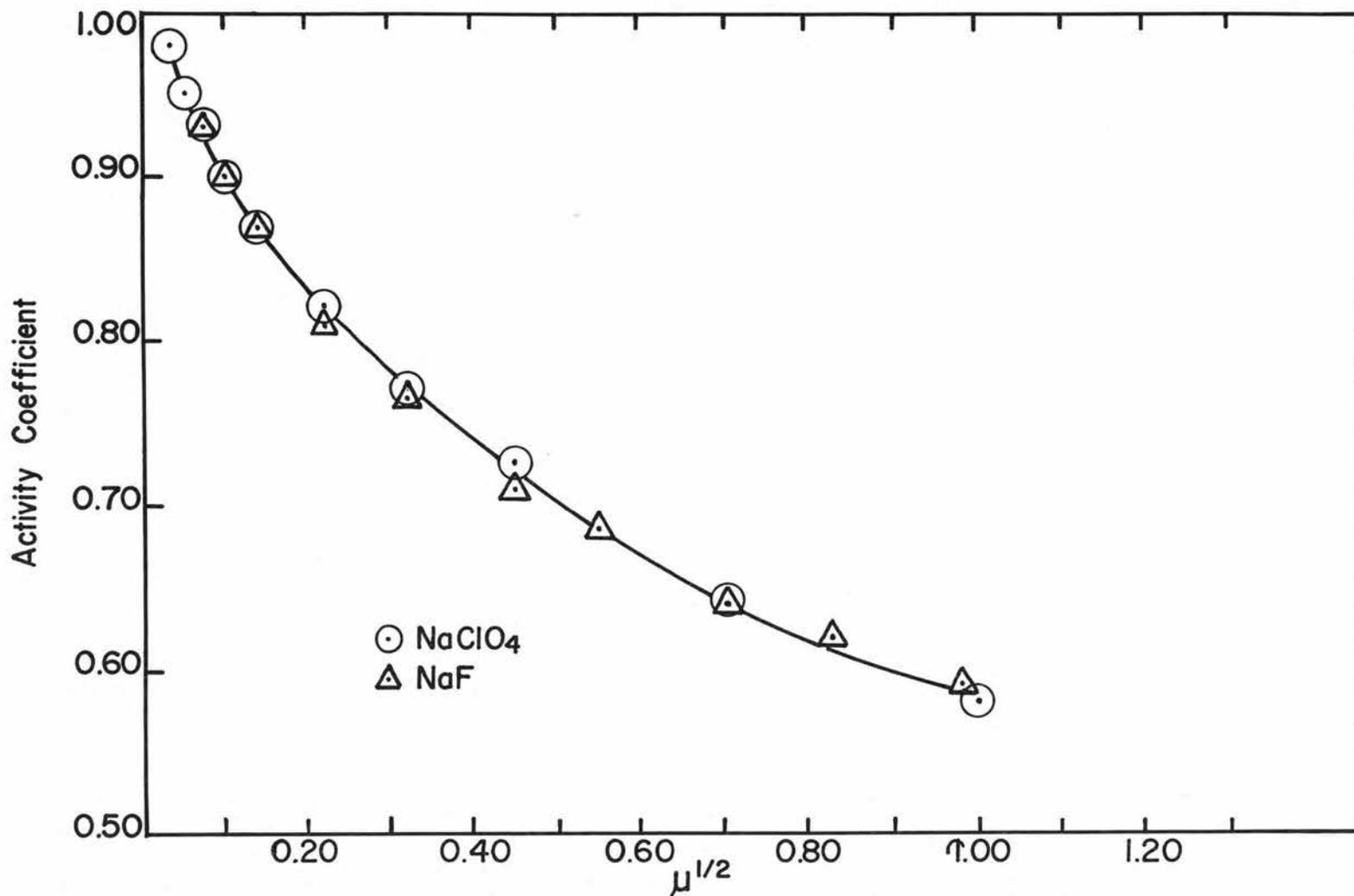


Figure 5. Average of reported activity coefficients for NaClO₄ and NaF.

NaF or NaClO₄ would be 4.0 Å. Calculating an individual ion activity coefficient for F⁻ or ClO₄⁻ using a_i = 3.5 or a mean ion activity coefficient for NaF or NaClO₄ using a_i = 4.0 results in a difference in activity coefficients from equation (10) of less than one percent.

If equation (10) is substituted in the equation

$$(11) E = E^{O'} - \frac{0.05915 \log m_{F^-}^3 \gamma_{F^-}^3}{3} \quad A Z_i^2 u^{1/2}$$

$$\text{then } (12) E = E^{O'} - 0.05915 \log m_{F^-} + 0.05915 \frac{A Z_i^2 u^{1/2}}{1 + B a_{NaF} u^{1/2}}$$

where A = 0.509 and B = 0.328 (4, p. 315). Good agreement is obtained when E^{O'} is calculated using experimental activity coefficients and equation (12). Both values are listed in the subsequent calculations.

Junction potentials. The experimental junction potential for 0.1F NaCl/3.5F KCl is -0.2 millivolt (4, p. 41) and -1.9 millivolt for 1F NaCl/3.5F KCl, about a tenfold increase in E_j for a tenfold increase in the concentration of NaCl. Since the equivalent conductances at infinite dilution of Cl⁻ and ClO₄⁻ are 76.34 and 68.0 ohms⁻¹ cm.² the mobility of these two ions are roughly equal, the ClO₄⁻ ion being somewhat slower; in any case, however, the majority of the current is carried by the KCl. Taking the foregoing factors into consideration, an estimate of E_j for 0.2m NaClO₄/4.2F KCl is -0.5 mv.

The junction potential of 0.2m NaClO₄/0.05m NaClO₄ to 1m NaClO₄ did not appear to be large in magnitude since values calculated for E^{0'} at u^{1/2} = 0.50 were for the junction 0.2m NaClO₄/0.2m NaClO₄ when the junction potential should be zero and E^{0'} did not differ significantly when the junction was 0.2m NaClO₄/0.3m, 0.5m, and 0.8m NaClO₄.

The type 2 liquid junction potential 0.2m NaClO₄/1.32 x 10⁻¹m to 2.65 x 10⁻³m NaF was estimated from the Lewis-Sargent equation: $E_j = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2}$ where Λ_1 and Λ_2 are the equivalent conductances of each salt at the actual concentration. From data in the International Critical Tables (10, p. 231) Λ is about 77 ohms⁻¹cm.² for 0.2m NaClO₄ and 0.05m NaF has the same value of Λ ; thus an E^{0'} value calculated for 0.05m NaF should theoretically incorporate a junction potential of zero volts for 0.2m NaClO₄/0.05 NaF. The maximum junction potential should be for 0.2m NaClO₄/2.65 x 10⁻³m NaF, since Λ for NaF at that concentration is 86.3 ohms⁻¹cm.² and E_j from the Lewis-Sargent equation is approximately 3 millivolts. Experimental values of E^{0'} calculated at this concentration are from 1 to 2 millivolts more negative than at higher NaF concentrations; however, E^{0'} values calculated for NaF solutions 5.65 x 10⁻³m to 2.65 x 10⁻²m agree quite well with the E^{0'} value calculated when NaF = 0.053m, which should have the negligible junction potential. In

summary, the junction potential for 0.2m NaClO₄/exp. conc. NaClO₄, NaF was shown to be small enough to neglect within the precision of the experiment. The estimate of 0.5 mv for 4.2F KCl/0.2m NaClO₄ was incorporated in the calculated E^{0'} value; i. e., E_j was in series with the S. C. E. thus making the effective potential approximately 0.2415 volts + 0.0005 volts = 0.242 volts.

In the e. m. f. measurements the S. C. E. was the positive electrode and the B. B. F. E. was negative. For example, if the measured e. m. f. were 0.170 volts then E in the equation (13) $E = E^{0'} - 0.05915 \log m_{F^-} \gamma_{F^-}$ was 0.072 volts (0.242 - 0.170), where E^{0'} was the estimate of the standard reduction potential. Solving equation (13) with six concentrations of NaF each at ionic strengths of 0.122, 0.250, 0.490 and 0.81 using the average activity coefficients of NaClO₄ and NaF from Figure 5 gave E^{0'}.

Table 9. Solution of equations (11) and (12).

I. $u^{1/2} = 0.35$ $\gamma = 0.76$ NaF conc., molal	E	E ^{0'}	E ^{0'} (equation 12)
1.325×10^{-1}	0.051	-0.008	-0.0086
5.30×10^{-2}	0.075	-0.0075	-0.0080
2.65×10^{-2}	0.096	-0.0040 ^a	-0.005 ^a
1.325×10^{-2}	0.111	-0.0070	-0.0084
5.30×10^{-3}	0.134	-0.0075	-0.0077
2.65×10^{-3}	0.149	-0.0105	-0.0113
		<u>-0.0088</u>	<u>-0.0088</u>

^aomitted from average

II. $u^{1/2} = 0.50$ $\gamma = 0.70$

NaF conc., molal	E	$E^{O'}$	$E^{O'}$ (equation 12)
1.325×10^{-1}	0.050	-0.011	-0.0117
5.30×10^{-2}	0.074	-0.0104	-0.0111
2.65×10^{-2}	0.094	-0.0090	-0.0088
1.325×10^{-2}	0.110	-0.0100	-0.0115
5.30×10^{-3}	0.133	-0.0100	-0.0108
2.65×10^{-3}	0.149	<u>-0.012</u> -0.0104	<u>-0.0134</u> -0.0112

III. $u^{1/2} = 0.70$ $\gamma = 0.64$

1.325×10^{-1}	0.052	-0.0115	-0.0117
5.30×10^{-2}	0.076	-0.0107	-0.0111
2.65×10^{-2}	0.0935	-0.0110	-0.0113
1.325×10^{-2}	0.111	-0.0110	-0.0125
5.30×10^{-3}	0.135	-0.0107	-0.0108
2.65×10^{-3}	0.152	<u>-0.0120</u> -0.0111	<u>-0.0124</u> -0.0116

IV. $u^{1/2} = 0.90$ $\gamma = 0.59$

1.325×10^{-1}	0.053	-0.0125	-0.0124
5.30×10^{-2}	0.079	-0.012	-0.0118
2.65×10^{-2}	0.0965	-0.011	-0.0100
1.325×10^{-2}	0.1145	-0.0105	-0.0107
5.30×10^{-3}	0.137	-0.012	-0.0105
2.65×10^{-3}	0.155	<u>-0.011</u> -0.0115	<u>-0.0111</u> -0.0111

The average of 23 E° values calculated using experimental activity coefficients is -0.010 ± 0.001 volts; using activity coefficients from the modified Debye-Huckel equation the average is ± 0.011 volts.

Experimentally, for ionic strengths less than 0.12 the E° values become more positive. For example, when $\mu = 0.09$, E° has an average value of -0.005 , and when no NaClO_4 has been added E° is -0.008 , 0.000 , 0.017 , 0.014 , 0.030 , and 0.047 for the six NaF concentrations from 1.325×10^{-1} to 2.65×10^{-3} m, respectively. Thus the E° values become more positive at lower fluoride ion concentrations even when corrections are made for the activity of the fluoride ion. This probably indicates the hydrolytic reaction $\text{BiF}_3 + \text{HOH} = \text{BiO}^+ + 2\text{H}^+ + 3\text{F}^-$ is increasing with decreasing fluoride ion concentration.

C. SUMMARY

The coating of the bismuth-bismuth fluoride electrode was determined to be BiF_3 by X-ray diffraction. It was found that NaClO_4 decreased the hydrolysis of BiF_3 , and that the electrode was reversible to fluoride ion provided the total ionic strength of $\text{NaClO}_4 + \text{NaF}$ was greater than about 0.12 and NaF was at least 2×10^{-3} m. An estimate of the standard potential for the reaction $\text{BiF}_3 + 3e = \text{Bi} + 3\text{F}^-$ was found to be -0.010 ± 0.001 volts.

III. NULL-POINT POTENTIOMETRIC DETERMINATION OF FLUORIDE WITH THE BISMUTH-BISMUTH FLUORIDE ELECTRODE

A. EXPERIMENTAL

1. Reagents

A stock solution of NaF was made up by dissolving 11.0520 grams of 100.0 percent C. P. grade NaF and 61.23 grams of dry NaClO_4 with distilled water to the mark of a one liter volumetric flask, to give 500 p. p. m. of fluoride ion and 0.50F NaClO_4 . This solution was diluted to 2500, 1000, 500, 250, 50, 25, and 10 p. p. m. of fluoride ion and each solution made 0.50F in NaClO_4 . The NaClO_4 was used to maintain constant ionic strength for the reference and unknown solutions. All other reagents used were C. P. grade.

2. Electrodes and Apparatus

The electrodes were prepared as previously described. The apparatus used may be seen in Figure 6. The simple network was used to buck out the small voltage difference between the two electrodes when they were both immersed in the same fluoride solution; the magnitude of this voltage was determined from a ten turn counting dial which was calibrated to read from one to one thousand. For example, if R_2 was adjusted so that a 50 mv. drop was measured

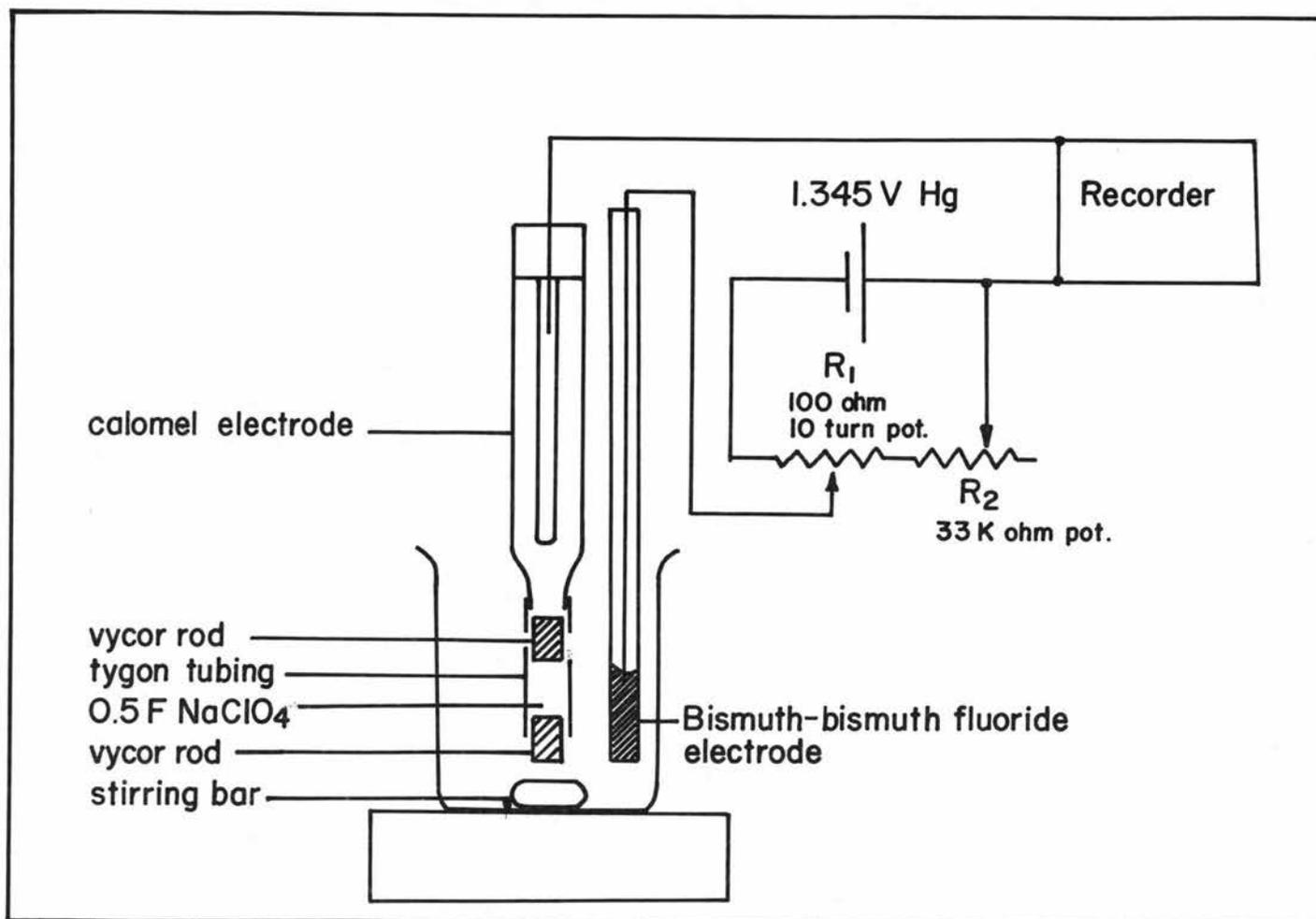


Figure 6. Diagram of apparatus for null-point potentiometry.

across R_1 with a Leeds and Northrup potentiometer, and if the turns counting dial read 180, then the absolute value of the voltage nulled was $50 \text{ mv.} \times 0.180 = 9.0 \text{ mv.}$ Originally the reference electrode was a rotating B. B. F. E. in a compartment containing a reference fluoride solution. The compartment containing the reference solution consisted of a 15 cm. long 18 mm. diameter glass cylinder tapered at one end. A one inch leached but unfired 1/4 inch diameter Vycor rod was connected to the tapered end with Tygon tubing, forming a low resistance (335 ohms) salt bridge. A later modification of this arrangement, shown in Figure 6, was the substitution of a modified Beckman calomel electrode as the reference electrode for the rotating bismuth-bismuth fluoride electrode. The bottom portion of a commercial Beckman electrode was removed and a tapered piece of glass was attached so that a Vycor rod would function as the salt bridge instead of the asbestos fiber in the commercial electrode. Using a Heathkit impedance bridge at 1000 C. P. S. it was found that the asbestos fiber electrode had a resistance of 4990 ohms and when the fiber was replaced by a Vycor salt bridge the resistance was 335 ohms. The lower impedance more closely matched that of the Brown recorder and no "dead zone" was observed in contrast to a considerable "dead zone" of ± 10 percent for the asbestos fiber electrode. Another Tygon-Vycor rod assembly which was filled with $0.5F \text{ NaClO}_4$

was attached to the calomel cell salt bridge in order to keep chloride ion out of the test solutions.

A Beckman model H-2 pH meter was used to make the pH measurements.

3. Procedure

A calibration curve consisting of a plot of the potential of the modified S.C.E. versus a B.B.F.E. was drawn using the particular electrode to be used in the analysis; see Figure 7 for a typical curve. When an unknown solution of NaF was to be analyzed, the approximate composition was determined by immersing the modified S.C.E. and the B.B.F.E. into the solution and nulling the recording potentiometer and noting the voltage from the turns counting dial. After determining the approximate composition a reference solution was selected which was $> 0.5 < 10$ times the concentration of unknown solution. Then the modified S.C.E. and B.B.F.E. were placed in the appropriate reference solution for at least 10 minutes and the potential difference was nulled- this required from 50 to 170 millivolts of bucking potential depending on the concentration of reference solution. The reference solution was removed, the electrodes rinsed with distilled water and the electrodes placed in unknown solution. If the potential increased, the unknown was more concentrated than the reference and

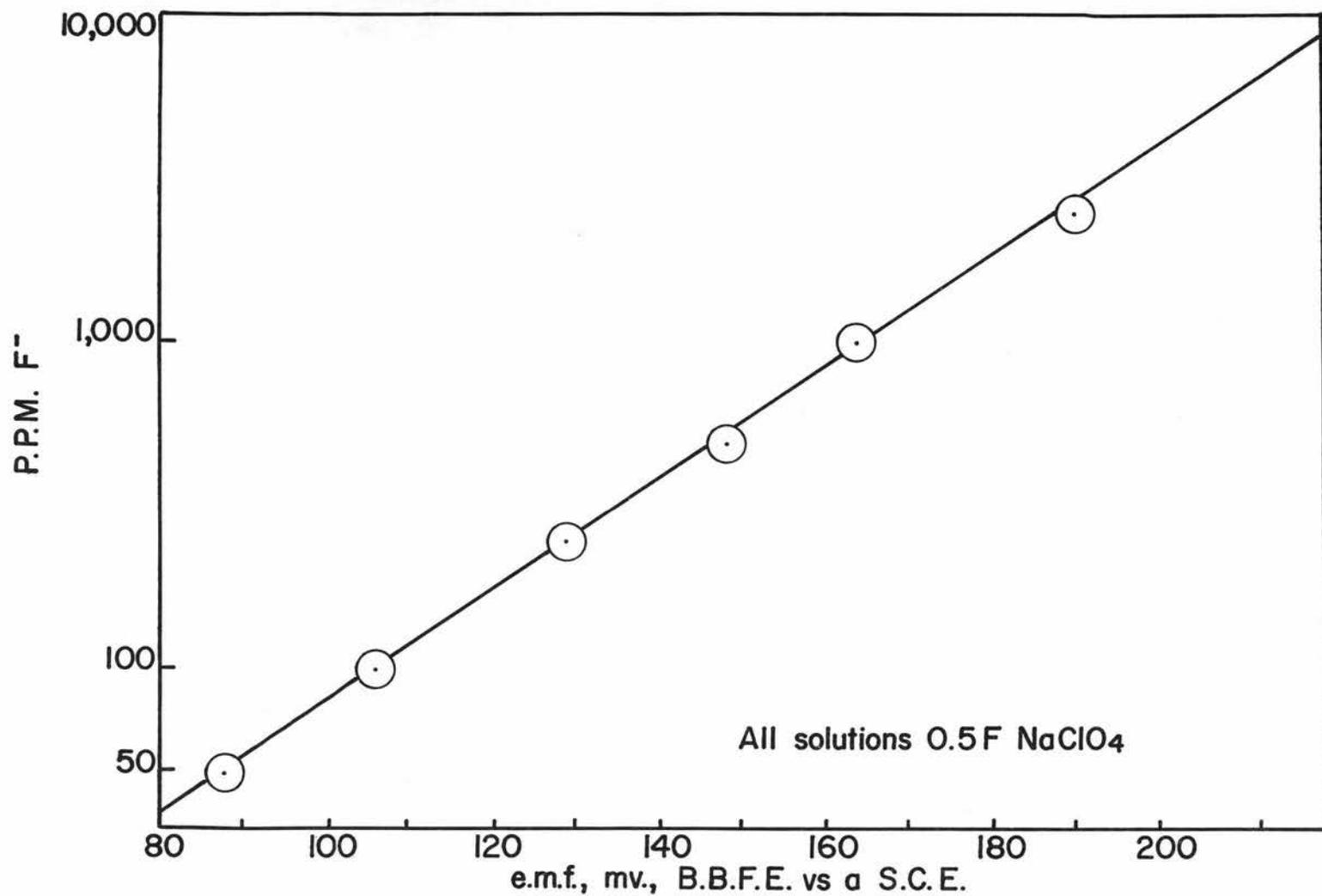


Figure 7. Calibration curve used to estimate the fluoride in an unknown sample.

if it decreased, the unknown was more dilute than the reference. For a more dilute solution than the reference, a solution which was twice the concentration of the reference and 0.5F in NaClO_4 was added. If the unknown was more concentrated than the reference, 0.5F NaClO_4 was added until the original null potential as indicated by the recorder was reached. Reagent was added slowly since the B. B. F. E. did not reach equilibrium immediately. A typical determination required 10 to 15 minutes.

pH study. The pH was lowered by the addition of HClO_4 and increased by addition of NaOH ; it was measured with a Beckman model H-2 pH meter. The potential difference of the B. B. F. E. versus the modified S. C. E. was measured with a Gray potentiometer.

Interference study. 25 mg. of each compound studied were added to 50.0 ml. of 100 p. p. m. fluoride which was also 0.5F in NaClO_4 and the solution analyzed by the null-point method.

B. RESULTS AND THEIR DISCUSSION

Electrode stability. The reference compartment containing a B. B. F. E. and a 250 ml. beaker were filled with the same NaF solution in order to test the stability of the system. It was found that a small potential difference existed between different electrodes,

ordinarily one or two millivolts in 100 p. p. m. or greater fluoride concentration, and two to five millivolts between 50 and 25 p. p. m. fluoride. This voltage was bucked out, but the magnitude of the potential difference between two electrodes usually changed over a period of time. The solution in the beaker was stirred by means of a magnetic stirrer and this halted the drift somewhat, but it still continued at a rate of one to five millivolts per hour, depending on the concentration of fluoride in the reference compartment and in the beaker. An arrangement in which the B. B. F. E. in the reference compartment was rotated with a Sargent synchronous motor at 600 r. p. m. did not reduce the drift significantly probably because of the different stirring action in the compartment and the beaker. The idea of employing a B. B. F. E. in a reference compartment was abandoned, since compensation for solubility of BiF_3 in 50 p. p. m. or greater fluoride concentration was of lesser importance than controlling electrode drift. It was thought that if there were only one B. B. F. E. to contend with the system could be better controlled.

A modified commercial Beckman calomel electrode was tried as a reference electrode. The potential of this electrode versus a B. B. F. E. in reference solution was bucked out and it was found that this combination gave a drift of approximately one millivolt per hour in 50 p. p. m. fluoride and less in higher fluoride concentrations which

was slow enough for a null-point analysis. This method was also more rapid and convenient since only one B. B. F. E. had to be equilibrated when the reference solution was changed.

Further efforts were made to reduce the drift so that 10 to 25 p. p. m. fluoride could be determined. Nitrogen was bubbled into the fluoride solutions in an effort to ameliorate the drift at lower fluoride concentrations, but oxygen in the solutions did not appear to be a factor causing the drift. Lead-bismuth alloys of 1.5 percent Pb--98.5 percent Bi, 5 percent Pb--95 percent Bi, and 10 percent Pb--90 percent Bi were tried as an electrode material, but electrode drift increased with increasing lead content of the electrode probably due to the higher solubility of PbF_2 . It became clear that one of the initial objectives of this investigation would not be attained-- that of determining fluoride in 10^{-4} M (1.9 p. p. m.) concentrations. The lower practical limit of determining fluoride with the B. B. F. E. using the null-point method was in the vicinity of 50 p. p. m. fluoride.

The following table lists some experimental results using a modified S. C. E. reference electrode, a B. B. F. E. as indicator electrode, and synthetic unknowns of sodium fluoride.

Table 10. Null-point titrations of NaF.

A. reference = 100 p. p. m. F^- , 0.5F $NaClO_4$ unknown = 50 p. p. m. F^- , 0.5F $NaClO_4$		
Found, p. p. m.	deviation	$V_o = 25.0$ ml.
1)	50.4	0.2
2)	50.7	0.5
3)	50.0	0.2
4)	49.0	1.2
5)	49.6	0.6
6)	51.5	1.3
7)	50.8	0.6
8)	48.8	1.4
9)	49.6	0.6
10)	<u>51.2</u>	<u>1.0</u>
	50.2	0.76 average
		1.5 percent average deviation
B. reference = 100 p. p. m. F^- , 0.5F $NaClO_4$ unknown = 200 p. p. m. F^- , 0.5F $NaClO_4$		
Found, p. p. m.	deviation	$V_o = 25.0$ ml.
1)	203	3.4
2)	198	1.6
3)	197	2.6
4)	199	0.6
5)	202	2.4
6)	201	1.4
7)	199	0.6
8)	201	1.4
9)	198	1.6
10)	<u>198</u>	<u>1.6</u>
	199.6	1.7 average
		0.86 percent average deviation

C. reference = 500 p. p. m. F^- , 0.5F $NaClO_4$
 unknown = 250 p. p. m. F^- , 0.5F $NaClO_4$

Found, p. p. m.	deviation	$V_o = 25.0$ ml.
1) 248	2	
2) 249	1	
3) 255	5	
4) 250	0	
5) 252	2	
6) 246	4	
7) 247	3	
8) 252	2	
9) 253	3	
10) $\frac{251}{250}$	$\frac{1}{2.3}$	0.92 percent average deviation

D. reference = 500 p. p. m. F^- , 0.5F $NaClO_4$
 unknown = 1000 p. p. m. F^- , 0.5F $NaClO_4$

Found, p. p. m.	deviation	$V_o = 25.0$ ml.
1) 995	6	
2) 994	7	
3) 997	4	
4) 1010	9	
5) 1003	2	
6) 1000	1	
7) 996	5	
8) 1008	7	
9) 998	3	
10) $\frac{1012}{1001}$	$\frac{11}{5.5}$	0.55 percent average deviation

The effect of pH on the B. B. F. E. was studied in detail and generally the results obtained agreed with those of Johns and Kendall (12, p. 10) i. e., the electrode potential versus a S. C. E. is essentially unchanged between pH 7 and 9. The electrode is affected to a greater extent by slightly acid solutions rather than by solutions of moderate alkalinity.

Table 11. Effect of change in pH on e. m. f. of a B. B. F. E. versus a S. C. E.

pH	change in millivolts, B. B. F. E. vs. S. C. E.
7.60	*
8.00	0
8.30	0
8.50	0
8.60	0
8.80	0
8.90	0
9.00	0
9.22	+0.5
<u>9.60</u>	<u>+4.0</u>
7.60	*
7.52	0
7.20	-0.5
6.70	-1.0
6.40	-2.5
6.26	-4.0
5.80	-6.0

* initial pH; 100 p. p. m. F^- 0.5F $NaClO_4$

Interferences. The potential of the B. B. F. E. versus a reference electrode is effected by numerous ions. This fact has also been mentioned by Horton (9, p. 266) who states: "almost every ion effects its (the B. B. F. E.) performance. . . ". Table 11 lists the extent of interference of different compounds in the determination of 100 p. p. m. fluoride by the null-point method.

Table 12. Interference of various compounds with the null-point determination of fluoride.

Compound (0.5 mg./ml.)	Error in determination of 100 p. p. m. F ⁻		
	>1% < 5%	>5% <10%	> 10%
NaCl		x	
KNO ₃	x		
NaNO ₃	x		
KCl		x	
K ₃ PO ₄			x
K ₂ SO ₄	x		
K ₂ CO ₃			x
AgNO ₃			x
ZnNO ₃		x	
Hg(NO ₃) ₂			x
NaC ₂ H ₃ O ₂		x	
KCN			x
NaBr			x
NaI		x	
Na ₂ SO ₄	x		

C. SUMMARY

A bismuth-bismuth fluoride indicator electrode and a saturated reference electrode with a NaClO_4 salt bridge were used to titrate 50 to 1000 p. p. m. fluoride ion using a method referred to as null-point potentiometry. The accuracy of a single determination was of the order of 1 percent. Nitrate and sulfate interfered slightly and other ions caused serious interference in the determination of fluoride. A typical titration required ten to fifteen minutes since the indicator electrode did not immediately reach equilibrium.

BIBLIOGRAPHY

1. American Society for Testing Materials. Card files of x-ray diffraction data and alphabetical and grouped numerical index of x-ray diffraction data. Philadelphia, 1950. (Special technical publication N. 48-B)
2. Baker, Bertsil B. and J.D. Morrison. Determination of microgram quantities of fluoride and cyanide by measurement of current from spontaneous electrolysis. *Analytical Chemistry* 27:1306-1307. 1955.
3. Baker, Bertsil B. Rapid estimation of hydrofluoric acid in red fuming nitric acid. *Ibid.* 30: 1085-1086. 1958.
4. Bates, Roger G. *Electrometric pH determinations*. New York, John Wiley and Sons, 1954. 415 p.
5. Carson, W.N., *et al.* Salt bridges of porous glass and ion exchange membranes. *Analytical Chemistry* 27:472-473. 1955.
6. General Electric X-ray Corp. Tables of interplanar spacings for angle 2θ . Milwaukee, Wis. n.d. 43 p.
7. Glasstone, Samuel. *Textbook of physical chemistry*. 2d ed. Princeton, N. J., D. Van Nostrand, 1946. 1320 p.
8. Harned, Herbert S. The electrochemistry of solutions. In: *A treatise on physical chemistry*. Hugh S. Taylor (ed.). New York, D. Van Nostrand, 1930. p. 731-852.
9. Horton, Charles A. Fluorine. In: *Treatise on analytical chemistry*. In, Kolthoff and Philip J. Elving (eds.). New York, Interscience Publishers, 1961. p. 207-334.
10. *International critical tables*, vol. 6. New York, McGraw Hill, 1929. 471 p.
11. Ivett, R.W. and Thomas De Vries. The lead amalgam-lead fluoride electrode and thermodynamic properties of aqueous sodium fluoride solutions. *Journal of the American Chemical Society* 63:2821-2825. 1941.

12. Johns, Theron and Kenneth K. Kendall. Direct potentiometric method for the determination of free fluoride ions. Paper presented at the Pittsburgh Conference on Analytical Chemistry. Pittsburgh, Feb. 27, 1956. 11 numb. leaves.
13. Kolthoff, I. M., E. J. Meehan and C. J. Sambucetti. Amperometric titration of fluoride with aluminum. *Analytica Chimica Acta* 22:351-363. 1960.
14. Latimer, Wendell M. The oxidation states of the elements and their potentials in aqueous solutions. Englewood Cliffs, N. J., Prentice Hall, 1952. 392 p.
15. Lewis, Gilbert Newton and Merle Randall. Thermodynamics and the free energy of chemical substances. New York, McGraw Hill, 1923. 653 p.
16. Lingane, James J. Electroanalytical chemistry. New York, Interscience Publishers, 1958. 652 p.
17. Malmstadt, H. V. and J. D. Winefordner. Precision null-point potentiometry - a simple, rapid and accurate method for low concentration chloride determinations. *Analytica Chimica Acta* 20: 283-291. 1959.
18. O'Donnell, T. A. and D. F. Stewart. Null-point potentiometric determination of fluoride. *Analytical Chemistry* 33:337-341. 1961.
19. Robinson, R. A. The activity coefficients of sodium and potassium fluorides at 25 degrees centigrade from isopiestic vapor pressure measurements. *Journal of the American Chemical Society* 63:628-629. 1941.
20. Sandell, E. B. Colorimetric analysis of traces of metals. 3d ed. New York, Interscience Publishers, 1959. 1032 p.