

EFFECTS OF INTERFERENCE IONS -Br^- AND I^- IN THE POTENTIOMETRIC
DETERMINATION OF CHLORIDE CONTENT OF WATER SAMPLES

A Thesis

Presented to

the Division of Physical Science

Kansas State Teachers College of Emporia

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

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December 1970

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ACKNOWLEDGMENTS

Since man's role in a society is to serve people, I strongly feel that Dr. A. T. Ericson's efforts to aid in bringing me up an educated man is one of the greatest contributions in international development, relations and goodwill. I am, therefore, highly indebted to him for his guidance throughout my research project and college career, so that I shall be able to help not only myself, but also millions of people whom I shall serve in Nigeria.

Furthermore, I am grateful to the entire faculty, students and secretaries of the Physical Science Division of Kansas State Teachers College of Emporia, for their help and moral support during my academic training at the above mentioned institution.

Finally, I give my thanks to Shirley Holdeman for her patience and hard work in typing my thesis.

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CHAPTER I

PROBLEM, PURPOSE, AND DEFINITION OF TERMS USED IN THE STUDY

This Investigation was initiated to find what effect other ions forming silver salts (which are less soluble than silver chloride) have on the accuracy of the volumetric method of chloride determination for water samples from the Cottonwood River. The interference ions studied were bromide (Br^-) and iodide (I^-). Sulfide, cyanide and a few other ions forming slightly soluble salts might also interfere. The solubilities of silver bromide, iodide, sulfide and cyanide in grams per 100 ml of water are 8.4×10^{-6} , 2.8×10^{-7} , 1.4×10^{-5} , and 2.3×10^{-5} respectively.¹ The effect of sulfide and cyanide was ignored because in acid solution they exist as HS^- and HCN respectively and so did not affect the precipitation of chloride as the analysis was conducted in acid solution.

Further aims of the study were to: 1) Investigate the chloride content of water samples from the Cottonwood River; 2) Repeat chloride analyses of preserved stream water samples which were collected and analyzed by W. Bolton in his research project; 3) Analyze more samples from the river and a few wells near it in order to provide preliminary data concerning ground water quality in the Cottonwood River Basin.

Definition of Terms

Experimental Equivalent Point

The volume of titrating reagent at which maximum rate of change of a measurable property occurs. Some properties that may undergo change

and thereby serve as a basis for the detection of equivalent end point are: 1) color of solution, that is, disappearance or appearance of one or more colored indicators. Dichlorofluorescein was used as an absorption indicator in some chloride determinations. 2) appearance of a slightly soluble product which can be observed. 3) change in some electrical property of the solution such as conductivity which could be measured.²

Average

A measure of central tendency.

Confidence Limit

A range in terms of arithmetic mean, standard deviation or other desired probability that the true value does lie within that range.

Salt Bridge

A tube containing an electrolyte and connecting two half cells.

Parts per Million (ppm)

A unit for expressing the concentration of chemical constituents per million grams of solution. For convenience in laboratory work, the results are expressed in weights of solutes in a given volume of water. Since the density of water is approximately one gram per milliliter, volume is often used interchangeably with mass.

Solute

Any substance derived from the atmosphere, vegetation, soil or rocks and dissolved in water.

Specific Resistance

A measure of the ability of a substance to resist the flow of an electric current. Because resistance is directly related to the number and specific chemical types of ions in solution, it can be used for approximating the salinity of water.

pH

A value for expressing acidity or alkalinity based on the hydrogen ion concentration. It is expressed mathematically as $-\log C_{H^+}$. Whereas 7.0 is a neutral point, values less than 7.0, indicate an acid solution.

Station Numbers

An added means of identification for each stream location where regular measurements of stream flow and determination of water quality have been made.

Well Numbers

The locations of wells in accordance with the Bureau of Land Management's system of land subdivision.

Activity

The apparent or effective concentration resulting by multiplying the concentration of each substance by a correction factor, called an activity coefficient.

CHAPTER II

REVIEW OF LITERATURE

The first chemical analysis to determine the quality of the Cottonwood River was conducted at Emporia, Kansas, on October 3, 1901, by the Atchison, Topeka, and Santa Fe Railroad. The analysis showed the Cottonwood River at Emporia to contain 19 ppm chloride and that at Clements and Strong City to be 12 ppm each.⁴

Later in 1905, the United States Geological Survey conducted the first full-fledged analysis of the Cottonwood River. At this time, they sampled the river and its tributaries at thirteen locations. This study showed the water to have a low chloride concentration.³

Further analysis of the Cottonwood River was done beginning in December 4, 1906, to December 3, 1907. The analysis included silica, iron, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulfate, nitrate and chloride. The study showed the water to contain low concentrations of chloride, nitrate, carbonate and iron.⁴ There has been no attempts made to corroborate the data taken in 1905-07 until 1965 when Drs. Prophet and Scobee made the first corroboration in an unpublished project on Cottonwood River Analysis.³ Their analysis included... bicarbonate, carbonate, sulfate, chloride, nitrate and fluoride. The chloride concentration was found to vary from a low of 33 ppm at station 1 to a high of 140 at station 6.³

In Bolton's 1967 water study, there was no investigation of ground water in the river basin. Up until now, no correlation of the surface water and ground water in the river basin has been made because of the large number of wells that must be analyzed to establish such a correlation.

The maximum concentration of chloride and nitrate in drinking water recommended by the United States Public Health Service is 250 ppm and 100 ppm respectively.⁵ Determination of the levels of these species in water becomes a prime indicator of water quality.

In this water analysis, the first step in determining chloride concentration was the selection of a suitable method. Reference books indicated at least eleven different methods available for the determination of chloride concentration. These standard methods are: 1) Volhard Method; 2) Mohr Method; 3) Mercuric Nitrate Method (tentative); 4) Orthotolidine Method; 5) Orthotolidine Flash Test Method; 6) Orthotolidine-Arsenite (OTA) Method; 7) Drop Dilution Method for Field Use; 8) Method for Differentiation of Monochloramine and Dichloramine by Amperometric Titration (tentative); 9) Palin Method for Differential Titration for Free Available Chlorine, Monochloramine, Dichloramine, and an Estimation of Nitrogen trichloride (tentative); 10) Iodometric Method; 11) Gravimetric Method; 12) Potentiometric Method. All these standard methods require some sort of standardization before they can effectively be used to give valid results. Some of the methods require preliminary treating or checking of water samples to eliminate ions which interfere with the particular method used. Some of the methods, such as Gravimetric Method, require 5,000 ppm of chloride concentration before they can be used effectively.³ Since, the chloride content of the Cottonwood River is less than 5,000 ppm, the gravimetric method could not be used. The potentiometric method was chosen because the different titration curves due to the interference ions could be used in the determination of the quantity of the interference ions. Furthermore, the availability of the instruments and reagents necessary for the study made the choice possible.

The potentiometric method makes use of the fact that chloride ions may be treated with an equal number of silver ions. These two ions react to form silver chloride. The addition of more silver ions decreases the solubility of silver chloride which then precipitates. It also makes use of the fact that an increase occurs in the rate of change of potential with added titrant. A maximum in change of potential per unit volume of the titrant occurs at the equivalence point of the titration. Furthermore, the coprecipitation phenomena of chloride, bromide, iodide, etc. do not affect the total amount of silver nitrate used to titrate the water sample.¹¹ However, it affects the shape of the curve.

CHAPTER III

APPARATUS AND PROCEDURE

Potentiometric Analysis

A potentiometric method of chloride analysis of the water samples from the Cottonwood River Basin was chosen. The potential of a galvanic cell consisting of a reference electrode, a salt bridge, and an indicating electrode was measured as titration reagent was added to the sample being analyzed. Galvanic cells are systems which are arranged to permit the energy of chemical reactions to be converted to electrical energy. The potential drop, or emf, of a galvanic system is dependent upon a number of factors, such as the nature of electrodes, the temperature and the concentration of the substances participating in the reactions at the electrodes.

Galvanic cells consist of two half-cells. Oxidation occurs in the anode half-cell where, a substance loses electrons which the anode electrode picks up. At the electrode of the cathode half-cell, a reduction of a substance occurs. The substance takes up electrons from the cathode electrode. If both of the electrodes are joined in a circuit, the electrons given up to the electrode in the anode half-cell are transferred to the electrode in the other to effect the reduction there. This transfer of electrons constitutes the electric current which the galvanic cell produces. With proper choice of electrodes and reagents the potential developed is dependent upon the concentration of the substance being analyzed.

Standard Calomel Electrode

One of the reference electrodes used in this study was the Standard Calomel Electrode. It consists of a potassium chloride solution over solid

mercurous chloride and metallic mercury. The potential of this cell is governed by the half-cell reaction: $2 \text{Hg} = \text{Hg}_2^{++} + 2\text{e}^-$. The activity of the mercurous ion is determined by the solubility of mercurous chloride in the chloride solution. It has relatively low resistance (2,000 - 3,000 ohms) and a very limited current carrying capacity before exhibiting severe polarization. At temperatures above 80°C , calomel electrodes become unstable.¹⁰

Several calomel electrodes are available commercially. An electrode typical of the type used in this study is illustrated in Figure 1. The above half-cell reaction equation indicates that oxidation takes place at the Calomel electrode. In other words, the electrons given up by the mercury to the calomel electrode are transferred to the other half-cell of the silver/silver electrode where reduction occurs.

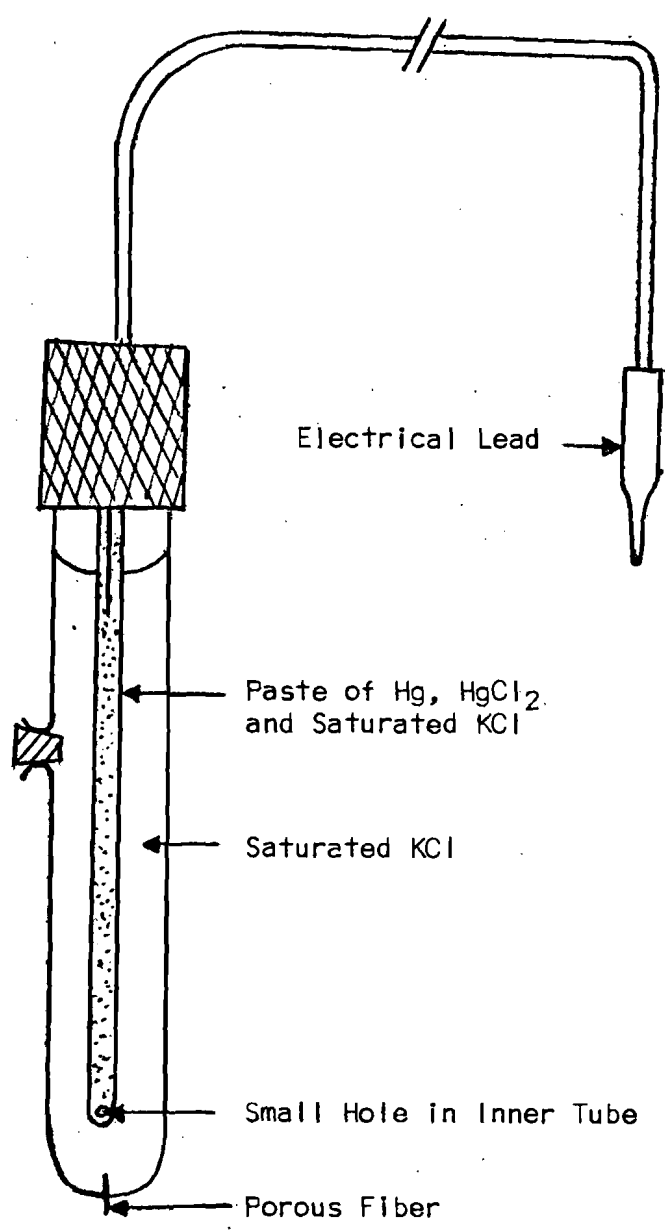
The E° of the saturated calomel electrode for the oxidation reaction is -0.246 V .⁸

Indicator Electrode

A silver/slightly soluble silver salt electrode was used as an indicator electrode. It consists of metallic silver in contact with a layer of silver chloride or a slightly soluble silver salt and immersed in an anion solution of unknown concentration. If the cell is Ag/AgCl, the half-cell reaction is:



This is a small compact electrode and can be used in any orientation. The reduction which occurs here is brought about by the transfer of electrons from the calomel electrode through the salt bridge to the silver/silver chloride electrode. The potential of this indicator electrode can be written as:



A COMMERCIAL FIBER-TYPE SATURATED CALOMEL ELECTRODE

FIGURE 1

$$E = E^{\circ} - 0.0591 \log \frac{1}{\text{act. Ag}^+}$$

$$\text{and as } K_{sp} = C_{\text{Ag}^+} \cdot C_{\text{Cl}^-}$$

$$E = E^{\circ} - 0.0591 \log \frac{C_{\text{Cl}^-}}{K_{sp}}$$

Where: E is the observed potential

E° equals reduction potential for $\text{Ag}^+ + 1e^- = \text{Ag}$

K_{sp} is the solubility product

The above equation (Nernst) indicates that a large increase in the concentration of chloride will decrease the observed E and vice versa. Since the solubility product of silver chloride, bromide, and iodide are 1.82×10^{-10} , 7.7×10^{-13} , 8.3×10^{-17} respectively,⁹ the observed E° would be as shown below:

Indicating electrode	E° Indicating electrode ⁹	Calculated cell potential with saturated Calomel ref. elec.
Ag/AgCl	+0.222	-0.0661
Ag/AgBr	+0.095	0.7195
Ag/AgI	-0.151	1.249

With both half-cells connected (Calomel electrode and silver/silver salt electrode), an observed potential equals the difference between the two half-cells. With E° Calomel electrode fixed, any change in the potential for the indicating silver electrode is indicated by a change in the potentiometer readings. To obtain a positive result for the silver/silver chloride electrode a change in polarity is necessary such that the reference electrode becomes the anode. The calculated potential with saturated Calomel electrode indicates this change of polarity by the change in sign for the calculated potentials.

Preparation of Salt Bridge

Experiments have shown that liquid junction potential between two electrolytes can ordinarily be reduced to a small and often insignificant quantity by interposing a concentrated electrolyte solution called a salt bridge between them.⁹

To construct the salt bridge used in the study, one molar potassium nitrate solution was prepared by dissolving 25.28 grams of pure dry potassium nitrate with distilled water and dilute to 250 ml. volume.

Glass tubings of desirable length were bent in U-form. The tubes were filled with a warm mixture of 10% agar and one molar potassium nitrate. A small cotton plug was introduced at each end of the tube to add more strength to the agar. The tubes were cooled and then stored in a solution of one molar potassium nitrate.

Measurement of Cell emf

A Leeds and Northrup Millivolt Potentiometer Model No. 8691 was used in the potentiometric measurement of the chloride content of the Cottonwood River. The 8691 Millivolt Potentiometer is a double range, two dial portable instrument. It has a low operating range of 0 to 111 m. Volt and high range of 0 to 1110 m. Volts.

The instrument includes a built-in pointer type of galvanometer, standard cell and battery. It is supplied in a metal case with a slip-hinged lid, snap latch and handle.¹²

For conductivity measurements, the cell containing the two electrodes is made one arm of Wheatstone Bridge circuit. A D.C. potential is applied across the Bridge and the circuit can be balanced to yield zero potential across the galvanometer. After the potentiometer is standardized the cell emf is read directly off the scale.

Determination of pH

The hydrogen ion concentration (pH) of the water samples was determined before titration. A corning pH meter Model 5 was used. The instrument was first calibrated with a standard buffer solution of pH 6.8.

Determination of Resistance

The resistance of the water samples was determined before titration using a dip type conductivity cell and an Industrial Instrument Inc. Conductivity Bridge Model RC 16B2. The instrument was turned on and left for about seven minutes in order to warm up. The sensitivity knob was adjusted to maximum. With the electrode in the water sample, the eye-piece knob was adjusted until the eye-piece showed full expansion. The resistance was noted for each sample tested.

The resistances of different concentrations of sodium chloride were determined with the conductivity cell to relate resistance to total electrolyte concentration. A calibration curve of resistance versus concentration was a straight line. Using this calibration curve, one has an indication of electrolyte concentration.

Reagents and Standard Solution of Halides

Standard Sodium Chloride Solution

About 7 grams of 100% sodium chloride was dried in an oven at 110°C overnight. The dry sample was put in a desiccator for two hours. Using a Mettler Balance Model H16, 5.8461 grams of sodium chloride was obtained from the dry sample. The weighed sample was dissolved in deionized water and diluted to one liter. The concentration of the solution in moles was

obtained by dividing 5.8461 grams by the molecular weight of sodium chloride. This gave the value of 0.1000 M NaCl. Standard sodium chloride solutions of other concentrations were prepared by quantitative dilution of this solution with deionized water:

Similarly, the standard solutions of potassium bromide and potassium iodide were made by using appropriate weights respectively.

Standard Silver Nitrate Solution

About 17 grams of silver nitrate was dried in an oven at 110°C for one hour. The dry sample was put in a desiccator for three hours. The following weights were obtained using Mettler Balance Model H16:

Weight of sample and container	28.2910 grams
Weight of container	<u>12.7236 grams</u>
Weight of Silver Nitrate	16.1055 grams

The above weight of silver nitrate was dissolved in deionized water and diluted to one liter. The resultant solution was stored in a brown bottle and placed in a dark place. The calculated molarity was .0949.

Determination of the Concentration of Silver Nitrate by Fajans Method

A total of 25.00 ml. of 0.1000 M sodium chloride stock solution was pipetted into a 100 ml. wide mouth erlenmeyer flask. In addition, 25 ml. of deionized water was added to the flask. A small pinch of dextrin (about 0.1 g.) and a few drops of dichlorofluorescein were added as an absorption indicator.⁸ Silver nitrate solution from a burette was added drop by drop until the first permanent color change remained after stirring. The volume of silver nitrate solution used was recorded.

The concentration, N_1 of silver nitrate, was calculated by using the following relations.

$$N_1 V_1 = N_2 V_2$$

$$N_1 = \frac{N_2 V_2}{V_1}$$

Where: N_1 Normality of silver nitrate solution
 V_1 Volume of silver nitrate used
 N_2 Normality of sodium chloride solution
 V_2 Volume of sodium chloride used

The above procedure was repeated using 30.00 ml. and 50.00 ml. of sodium chloride standard solution. The blank-deionized water, was also titrated, requiring 0.0100 ml. silver nitrate. This 0.01 ml. AgNO_3 was so small compared to the volume used in the titration, that it was negligible. The average normality was determined together with the standard deviation. (See Table I) The Fajans Method in this determination was very useful as it gave a quick confirmation of the concentration of the standard solution.

TABLE I

Standard Sodium Chloride Versus Silver Nitrate Titration Data

Volume .1000 M NaCl	Volume X M AgNO_3	Calc M AgNO_3	Std. Dev.
25.00	26.20	.0954	
30.00	31.20	.0955	
50.00	52.60	.0953	
	Average	.0954 \pm	.00006

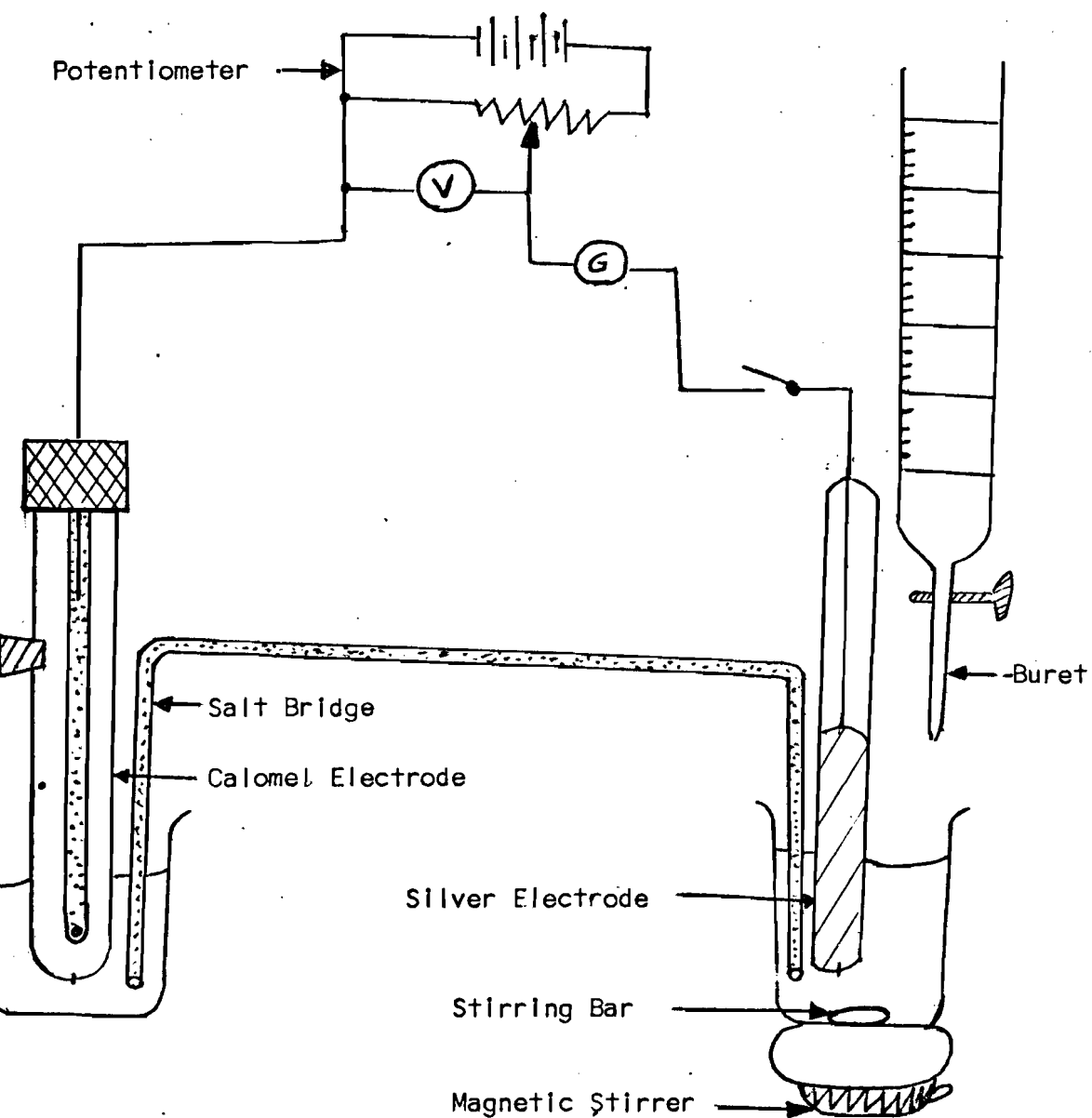
Chloride Determination

Apparatus used in the experiment were:

- 1) Leeds and Northrup Corporation Model No. 8691 Millivolt Potentiometer
- 2) A Coleman billet-type silver electrode
- 3) A saturated calomel electrode
- 4) A beckman magnetic stirrer
- 5) A ten milliliter buret

Procedure

A measured amount of water sample was pipetted into a 250 ml. beaker. The silver electrode was connected to the positive cell terminal of the potentiometer, Figure 2. It was then lowered about one centimeter deep into the solution. Into a 150 ml. beaker was introduced about 50 ml. of 1 M potassium nitrate. The calomel electrode was connected to the negative cell terminal of the potentiometer and lowered about one centimeter deep into the salt solution. A potassium nitrate salt bridge was placed between the calomel electrode and the silver electrode. The instrument was calibrated. A 10 ml. buret was filled with .1057 M AgNO_3 . A clean magnetic stirring bar was introduced into the water solution which was placed on the magnetic stirrer. The magnetic stirrer and the potentiometer were turned on, later turned on the "record position." The silver nitrate was added at increments of 0.1 ml. or any desired amount. After each addition, the resistance of the potentiometer was adjusted until the galvanometer showed no deflection when the tap key was depressed. The potential was then read from the scale of the potentiometer. The potential versus the volume of silver nitrate added was recorded.



APPARATUS FOR A POTENTIOMETRIC TITRATION

FIGURE 2

The above procedure was repeated using solutions of sodium chloride, sodium iodide and sodium bromide, and the various samples. A plot of potential versus volume of silver nitrate was prepared and interpreted. The data of typical titration are given in Table 2.

End Point Determination for Potentiometric Titration

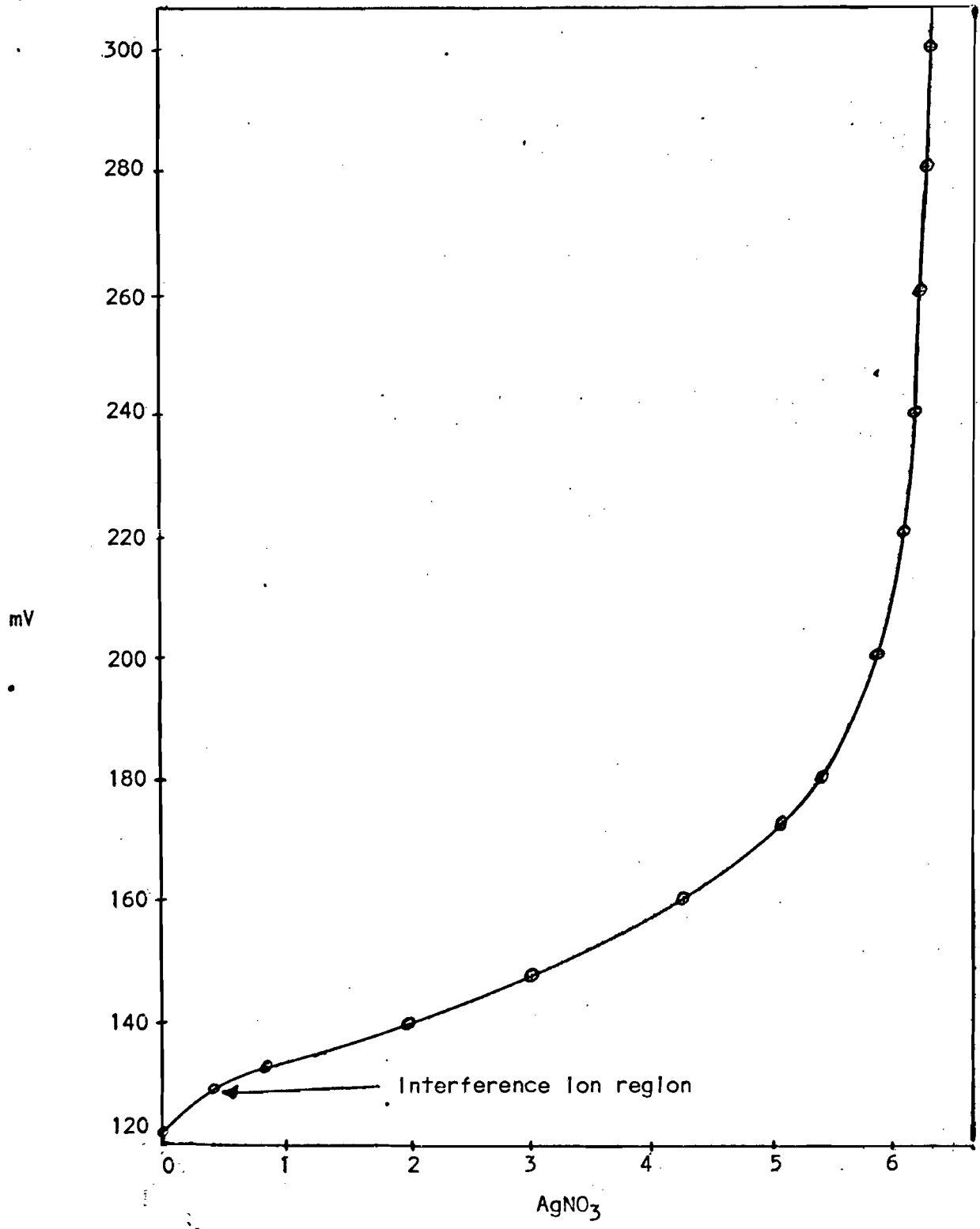
The titration curve was obtained by plotting as ordinate successive values of the cell electromotive force versus the corresponding volume in milliliters of titrant added. Analysis of typical data, Table 2, shows that over most of the titration range, the cell electromotive force (emf) varies gradually. Near and at the end point abrupt and rapid variations occurred. The resultant titration curve for one of the experiments is shown in Figure 3. The equivalent point lies in this region where the change in cell potential was the greatest per unit volume of titrant added. The midpoint of the steeply rising portion of the titration curve was estimated visually. This gave the estimated end point.

An end point may be located more precisely by plotting successive values of the rate of change of cell emf versus each increment of titrant ($\Delta E/\Delta V$) in the vicinity of the inflection point. This plot is the first derivative curve. The position of the maximum on the first derivative curve, Figure 4, corresponds to the inflection point on the normal titration curve, Figure 3. With the end point volume determined, the corresponding cell emf at the equivalent point was obtained by extrapolation from the original titration curve. The cell emf at the equivalence point was calculated for the titration, and was used to indicate end points for the analysis of water samples (Appendix 1). The chloride content of the sample was calculated using the chloride titer of the silver nitrate and reported in parts per million. (Appendix 2)

TABLE II.

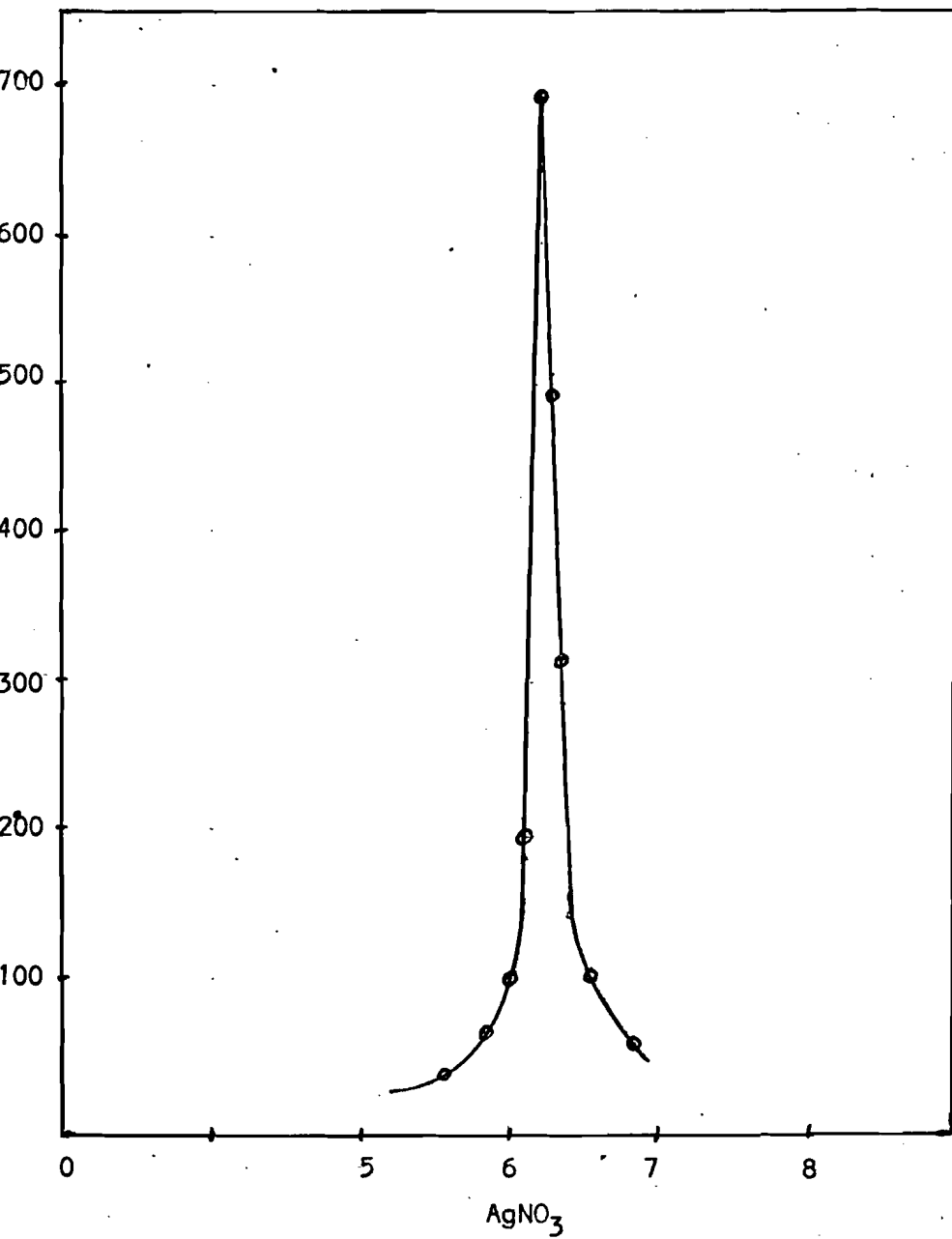
POTENTIOMETRIC DATA OF WELL WATER (E.C. CROSS), 1970

H ₂ O, ml	Ag ⁺ , ml	E, mV	$\frac{\Delta E}{\Delta V}$
100	.00	122.6	
	.25	128.0	
	.50	131.0	
	.75	132.4	
	1.00	134.0	
	1.50	136.6	
	2.00	139.8	
	3.00	147.6	
	4.00	157.4	
	5.00	172.0	21.6
	5.25	177.4	31.2
	5.50	185.0	40.0
	5.75	195.2	56.8
	6.00	209.4	184.4
	6.25	255.6	692.0
	6.30	290.2	496.0
	6.35	315.0	288.0
	6.40	329.4	212.0
	6.45	340.0	132.0
	6.50	346.6	106.0
	6.60	357.2	66.0
	6.70	363.8	



POTENTIAL VS VOLUME OF SILVER NITRATE, ML

FIGURE 3



CHANGE IN POTENTIAL PER CHANGE IN VOLUME VS VOLUME
OF SILVER NITRATE, ML

FIGURE 4

Collection of Water Samples from
the River and Wells

Water samples for analysis usually are collected at or near points on streams where gauging stations are maintained by the U.S. Geological Survey for measurement of water discharge. The methods of collecting water samples from the Cottonwood River is described by W. Bolton.³ One sample can define adequately the water quality at a given time if the mixture of solutes throughout the stream cross section is homogeneous. However, the concentration of solutes at different locations in the cross section may vary widely with different rates of water discharge, depending on the source of material and the turbulence and the mixing of the stream. Some streams must be sampled at several verticals across the channel to determine accurately the solute load.

In this study, samples of ground water were taken from wells by a method developed by Dr. Bridge.⁶ The water was drawn from the well by using the apparatus illustrated in Figure 5. The apparatus consisted of 1.5 volt battery, an ammeter, a probe, a wire and a bag fastener. The water taken by this method came from an indeterminate depth in the well, the apparatus making it possible to establish total water depth in the well only. Water was collected and stored in plastic bags and plastic bottles.

The plastic bag was attached to the fastening device and lowered slowly into the well. When the probe terminal touched the water in the well, the pointer of the ammeter deflected and a reading was taken of the distance from the top of the well to the surface of the water. The bag was lowered further until it filled and was then drawn from the well.

The depth of the well was measured using a graduated steel wire.⁶

Before sample collection, wells were pumped for several minutes. This ensured that water samples had not stood for any significant period in the well casing. Well numbers were used to label the samples. (These numbers give the location of the well. For example, well 24-20E-22DC is in SW SE SE Sec. 22, T.24S, R20E.⁷)

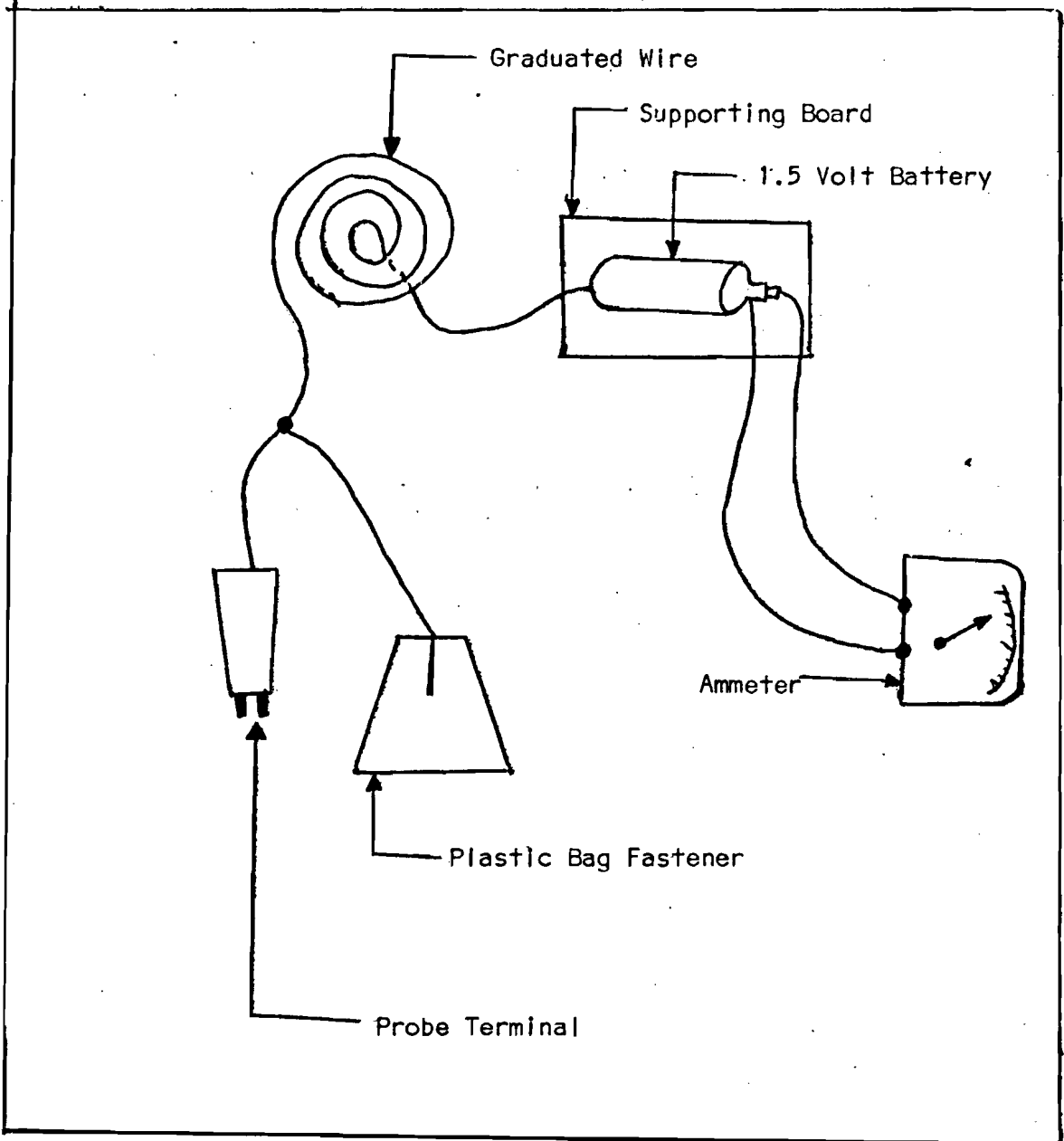


DIAGRAM OF WATER COLLECTING DEVICE

FIGURE 5

CHAPTER IV

RESULTS AND DISCUSSION

Selected samples collected by W. Bolton were analyzed for chloride by potentiometric titration with standard silver nitrate solution. The results, Table III, when compared to the results, based on Mohr Method, Table IV, indicate quite variable chloride concentrations with similar trend for both determinations. A plot of average values for each determination versus the corresponding location number indicate these trends as shown in Figure 6. The chloride contents of stations 25, 31, 33, 34 and 37 were found to be below 10.0 ppm. These station numbers were located on the tributaries of the Cottonwood River.³ The low chloride concentrations on the tributaries indicate that they flow through regions that contain small quantity of chloride.

Comparatively, stations 26, 27, 29, 30, 32, 35 and 36 were found to contain over 30.0 ppm of chloride with station 27 having the highest-- 57.0 ppm. These stations were located on the main stream. These values are much higher than the value reported in early analysis of water from the Cottonwood River Basin. The results are quite similar to values obtained by Prophet.¹³ Increased values indicate pollution of the main stream. Samples were collected in 1969 from selected sites in the Cottonwood Basin. These sites were located near the large feed-lots of the Emporia area, Table V. Based on preliminary data, the high chloride content of these samples may be caused by drainage from the industries of the area. Water from selected wells near Emporia was collected and analyzed for chloride concentration by Potentiometric Titration Method, Tables VI and VII.

TABLE III

CHLORIDE CONCENTRATION, pH AND RESISTANCE OF 1967 WATER
 SAMPLES FROM COTTONWOOD RIVER

Analyst: Ohaebosim, L. C. Date 1970

Conc. in ppm.

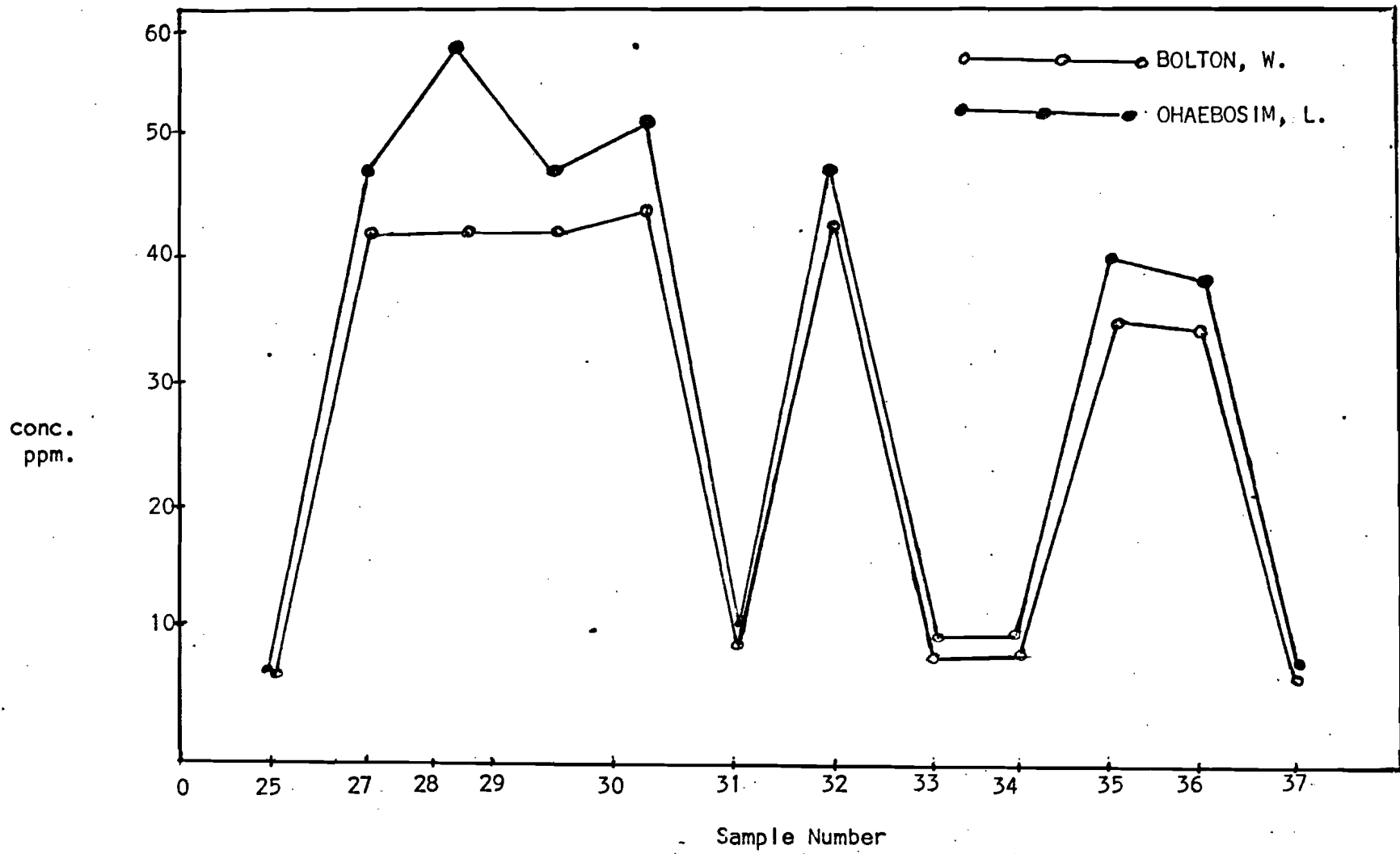
Sample	Run #1	Run #2	Average Conc. ppm	pH	Resistance
25	8.24	8.00	8.14	8.3	3550
26	47.4	47.1	47.3	8.1	1520
27	57.6	56.8	57.2	7.9	1330
29	47.0	47.0	47.0	8.2	1400
30	50.9	51.1	51.1	7.9	1520
31	10.5	10.2	10.3	8.2	3160
32	47.6	47.3	47.5	8.3	1430
33	9.6	9.8	9.7	8.3	3100
34	10.4	10.1	10.2	8.0	2000
35	40.2	40.1	40.2	8.1	1800
36	39.7	37.8	38.8	8.1	1740
39	7.4	7.0	7.2	8.0	3410

TABLE IV

CHLORIDE CONCENTRATION AND pH OF 1967 WATER SAMPLES
FROM COTTONWOOD RIVER³Analyst: Bolton, W. Date 1967

Conc. in ppm.

Sample	Run #1	Run #2	Average Conc. ppm	pH
25	7	7	7	7.6
26	42	42	42	7.9
27	43	42	42.5	8.0
29	42	42	42	8.0
30	44	44	44	8.1
31	10	8	9.0	7.9
32	41	40	40.5	8.1
33	8	8	8	8.0
34	8	8	8	7.9
35	35	35	35	8.1
36	34	34	34	8.1
39	6	6	6	7.9



CONCENTRATION PPM VS SAMPLE NUMBER

FIGURE 6

TABLE V

CHLORIDE CONCENTRATION, pH AND RESISTANCE
IN 1969 ON COTTONWOOD RIVER

Analyst: Ohaebosim, L. C. Date 1970

Sample	Date	Run #1	Run #2	Average Conc. ppm	pH	Resistance
1	5/4	287.3	285.1	286.2	7.9	710
1	4/15	275.5	280.2	277.8	7.6	720
1	4/20	275	278	276.5	7.8	727
2	4/15	233.2	231.3	232.2	7.7	760
2	7/20	229.8	226.5	228.2	7.6	740
3	5/4	196.0	191.5	193.7	6.0	920
4	4/15	5.07	4.5	4.75	7.8	760
6	4/15	105.8	102.9	104.4	7.8	897
6	4/20	110.8	107.8	109.3	7.9	1070
7	5/4	173.8	170.5	172.2	8.0	1100
8	5/4	300.3	308.9	304.6	7.8	495
12	4/20	70.3	72.7	71.5	7.8	1140
12	4/29	62.39	60.87	61.6	8.1	1250

TABLE VI

CHLORIDE CONCENTRATION, pH AND RESISTANCE OF 1970 WATER
SAMPLES FROM SOME WELLS NEAR THE COTTONWOOD RIVER

Analyst: Ohaebosim, L. C. Date 1970

Well No. or Name	Conc. in ppm	pH	Resistance
GRANT	59.91	8.1	1220
HEAD	189.1	8.0	700
CROSS	236.7	8.3	630
IVY	30.33	8.2	1368
HOPPER	285.4	7.6	578
TRACE	250.4	7.6	592
HEBERLY	5.110	8.0	1600
HERRICK	191.7	7.6	650

TABLE VII

DATA ON SOME GROUND WATER IN LYON COUNTY

Name	Miles (b)		Depth (ft)	Conc. Cl ⁻ ppm
	South	West		
Grant	0.5	2.5	*	59.9
Head	1.0	1.5	17.8	189.1
Cross	1.0	2.5	16.0	236.7
Ivy	1.5	2.5	26.0	30.3
Hopper	1.5	3.0	*	285.4
Trace	0.5	2.5	*	250.9
Herbely	1.5	3.5	*	5.1
Herrick	1.5	1.5	29.0	191.7
(a) Iowa Beef Packing Plant (IBP)	0.5	1.5		
(b) IBP Feedlot	0.5	3.0		

* Depth not available at this time

(a) Measurements taken by Dr. A. T. Ericson and L. C. Ohaebosim

(b) Measurements taken from the map produced by the United States Department of the Interior, Geological Survey of State of Kansas, 1967 Lyon County, with measurements taken relative to K.S.T.C.

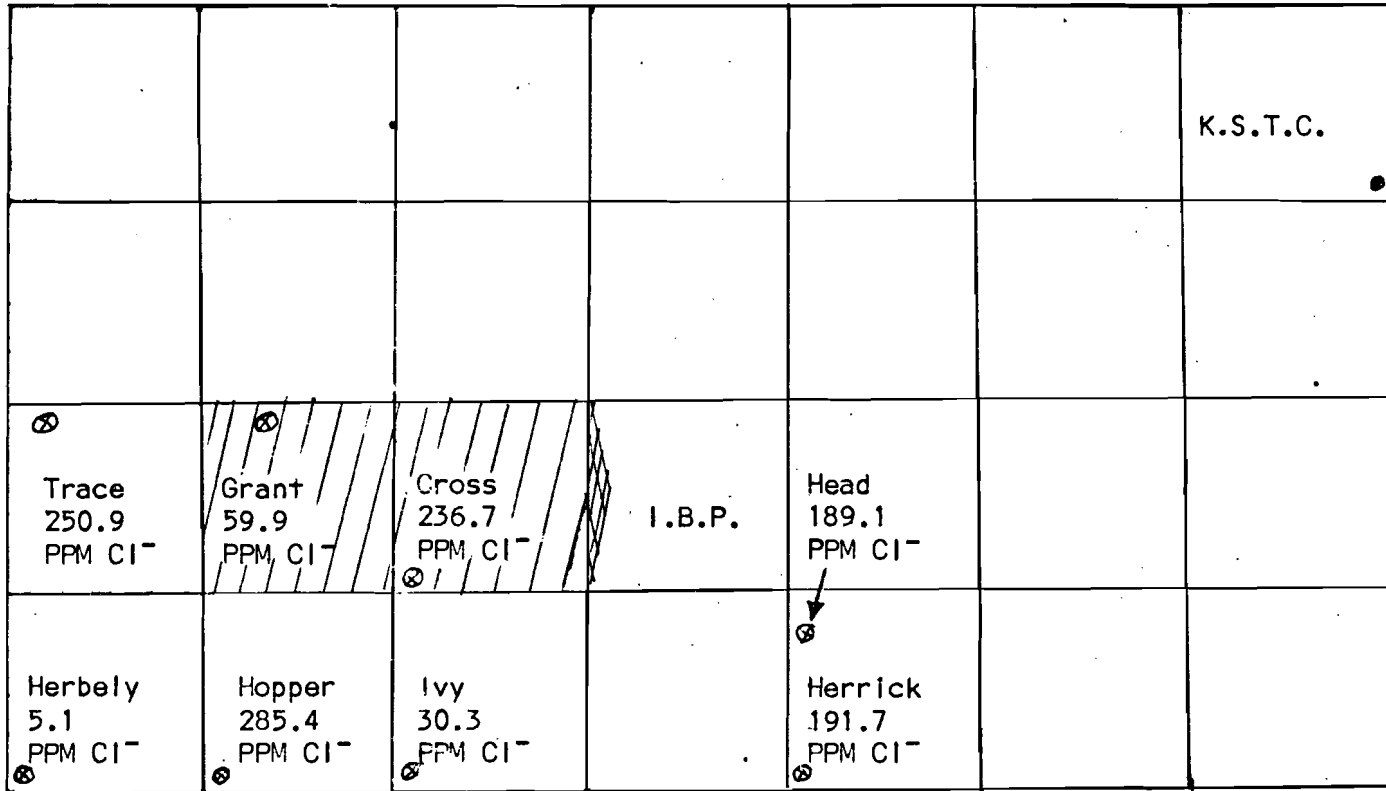
A plot of the ground water (wells) locations vs. chloride content, Figure 7, indicates some areas of very high chloride content which may be related to industrial activities of the area.

The titration curves for the water analysis showed little evidence of interference ions. In order to determine the concentration of these interference ions--bromide and iodide, the following steps were taken:

- 1) A known concentration of chloride, bromide and iodide was titrated using silver nitrate standard solution. A plot of potential versus the volume silver nitrate for each anion used was prepared, Figure 8.

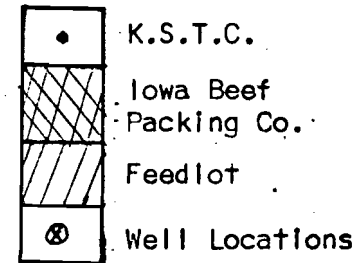
- 2) A potentiometric titration of mixtures of known concentrations of chloride and bromide; and also chloride and iodide was made. The titration curves for the mixtures are shown in Figures 9-11. These titration curves were used as calibration curves. Figure 12 represents interference ion curve which was drawn to the same scale as the calibration curves in Figures 10-11. Comparisons of Figures 10-11 and 12 show that the effect of the interference ions is too small to obtain any quantitative value for the concentration of bromide or iodide. Similar results were obtained when interference ion curves obtained from the samples collected by W. Bolton were compared to the curves in Figures 10-11. (Chloride end point was not shown in the curves.)

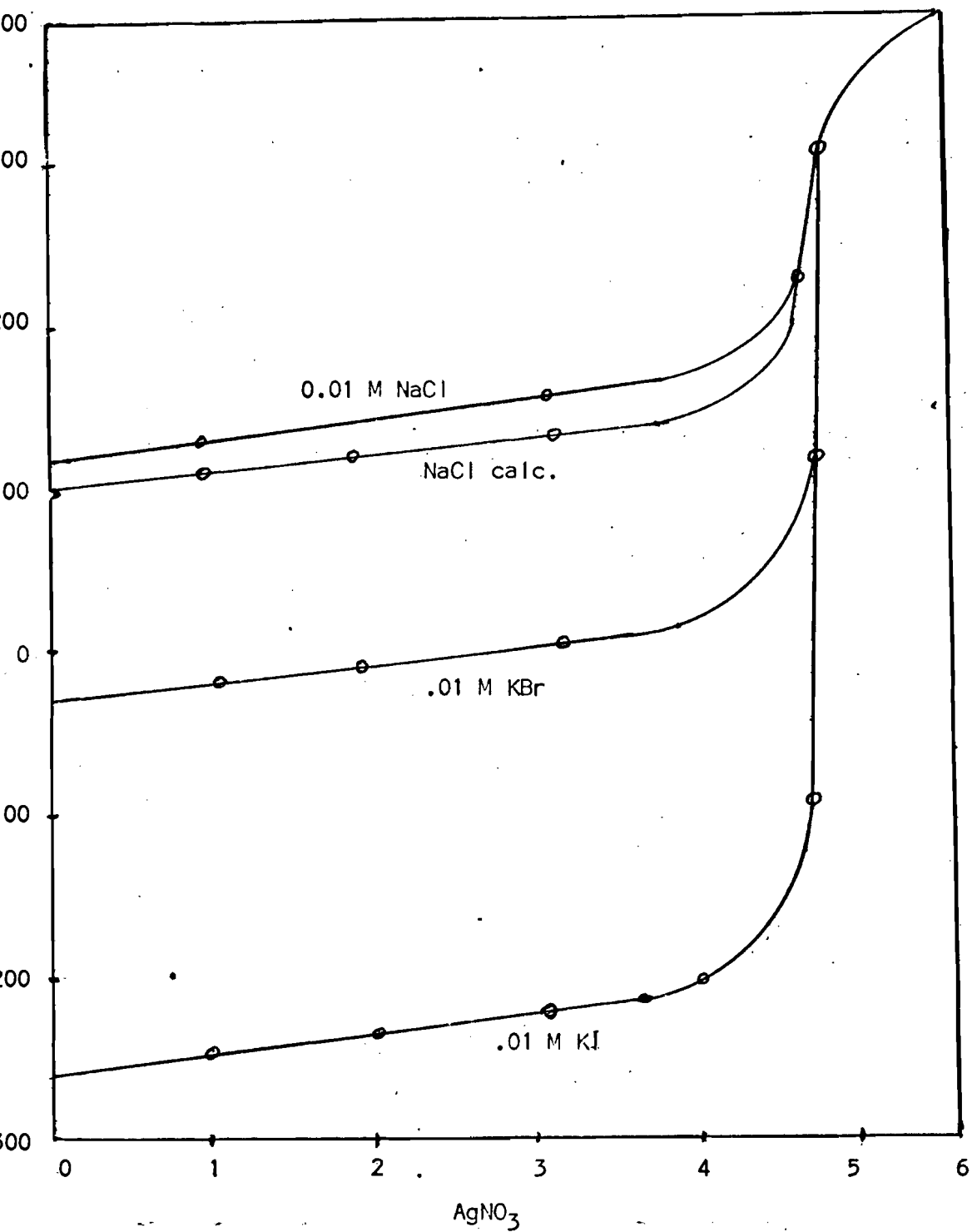
From the results thus obtained, it could be said that the titration method for chloride determination of the Cottonwood River used by Bolton was appropriate. The potentiometric determination did not indicate significant differences in concentrations to those previously reported. The concentration of bromide and/or iodide was less than .01 ppm in water samples analyzed. More sensitive methods will be required for quantitative determination of bromide or iodide in the water samples analyzed.



SOME LYON COUNTY GROUND WATER LOCATIONS
WITH REFERENCE TO K.S.T.C.

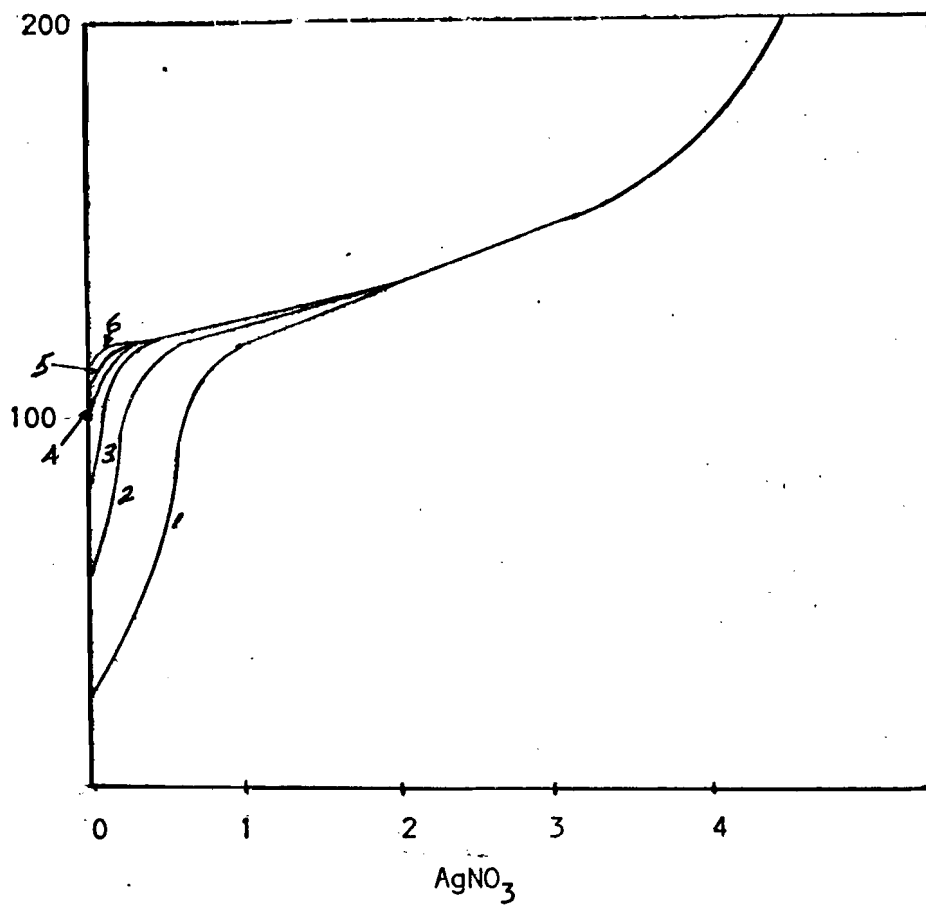
FIGURE 7





POTENTIAL VS VOLUME OF SILVER NITRATE, ML

FIGURE 8

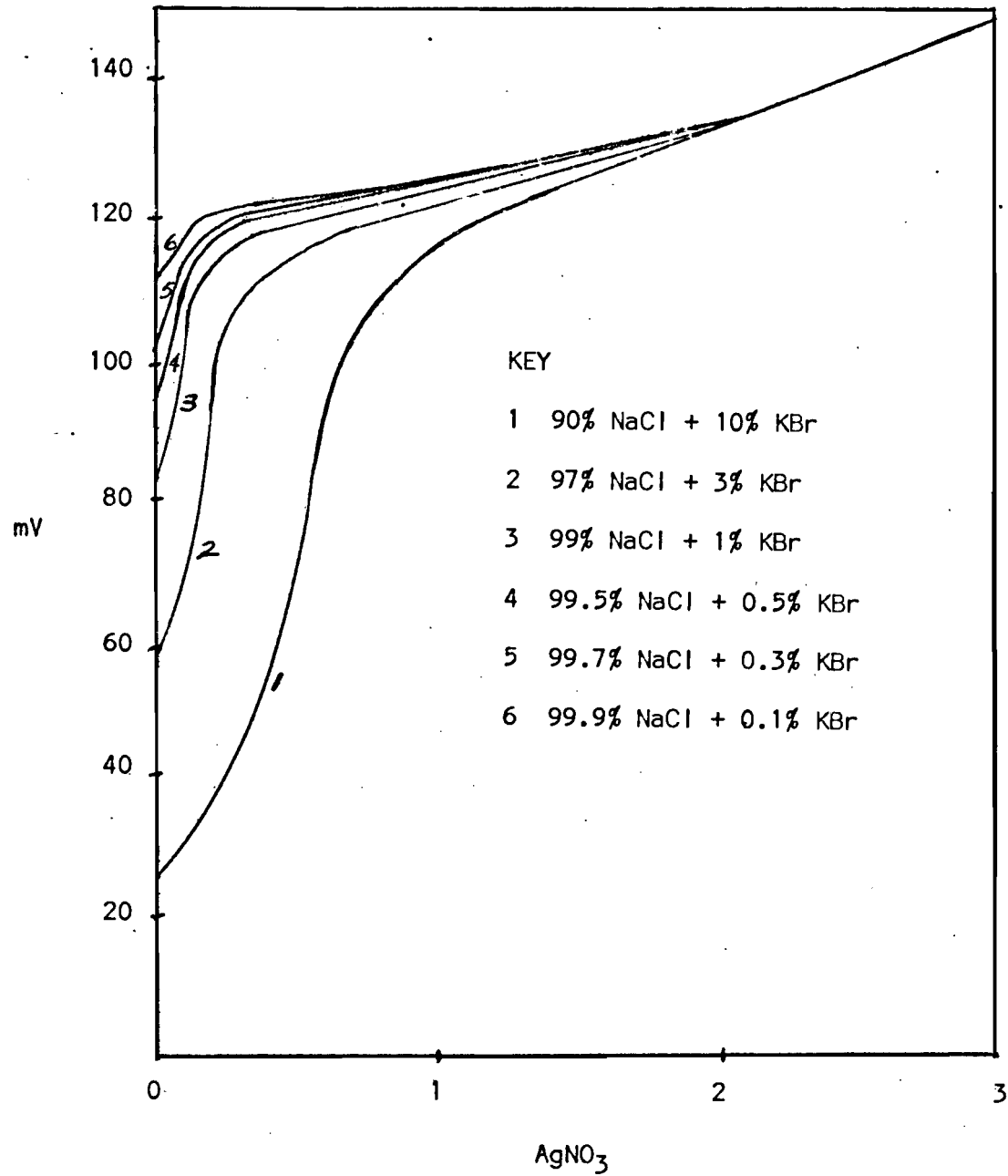


POTENTIAL VS VOLUME SILVER NITRATE

FIGURE 9

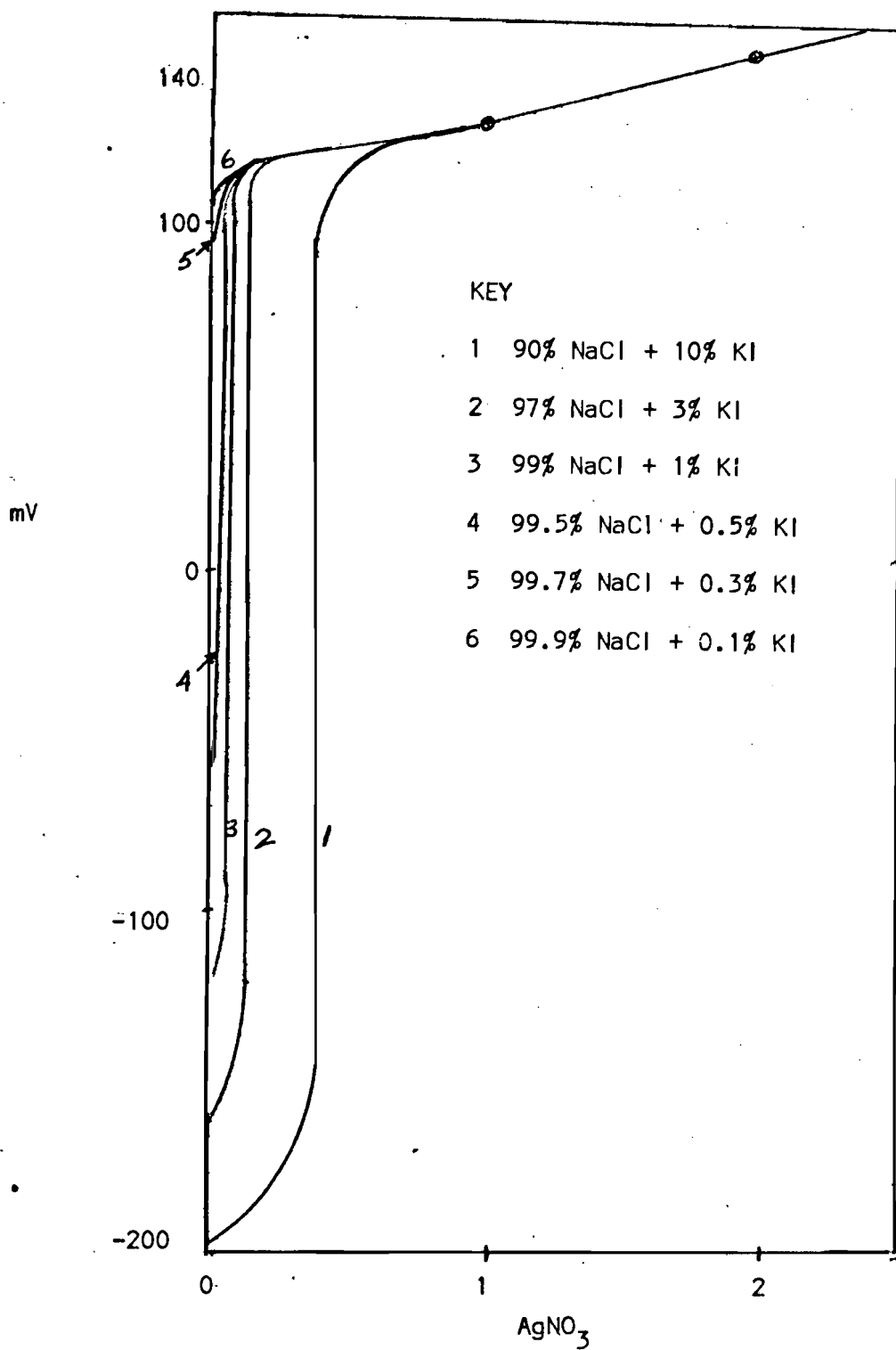
KEY

- 1 90% NaCl + 10% KBr
- 2 97% NaCl + 3% KBr
- 3 99% NaCl + 1% KBr
- 4 99.5% NaCl + 0.5% KBr
- 5 99.7% NaCl + 0.3% KBr
- 6 99.9% NaCl + 0.1% KBr



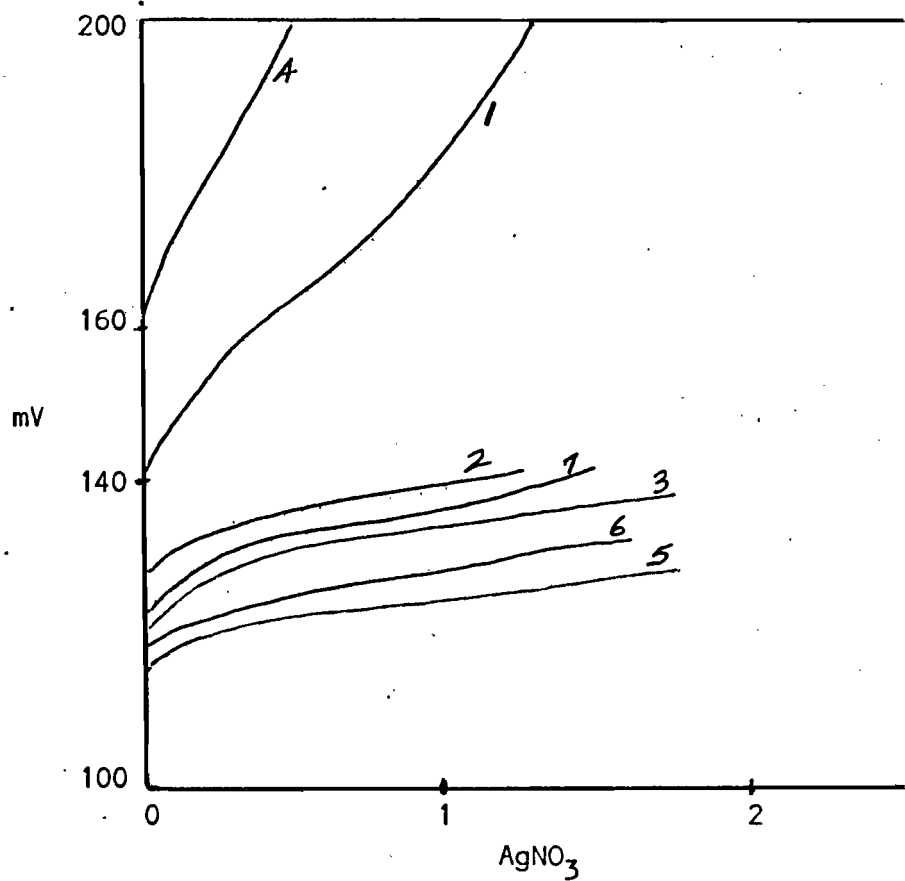
POTENTIAL VS VOLUME OF SILVER NITRATE, ML

FIGURE 10



POTENTIAL VS VOLUME OF SILVER NITRATE, ML

FIGURE 11



POTENTIAL VS VOLUME OF SILVER NITRATE, ML

FIGURE 12

KEY

- 1 Grant
- 2 Head
- 3 Cross
- 4 Ivy
- 5 Hopper
- 6 Trace
- 7 Herrick

CHAPTER V

CONCLUSION

In the study of the selected water samples collected by W. Bolton from the Cottonwood River and tributaries, different but consistent trends in the chloride contents of the samples was obtained using Potentiometric Titration Method of analysis for the chloride content of the water samples showed higher values than the Mohr Method of Analysis employed by W. Bolton. This difference might have been caused by storage and/or evaporation of the samples. The analysis also showed the tributaries to contain lower quantity of chloride than the main stream.

Similar analyses made on the ground water samples also revealed a variation of chloride content. The deeper wells were found to contain less chloride than the shallow ones, with the values ranging from 5.10 ppm to 285.4 ppm.

In the study of the effects of the interference ions-- Br^- and I^- , using Potentiometric Method of determination of the chloride content of the Cottonwood River Basin and the ground water, it was found that the concentrations of the interference ions were so small that they could not be measured quantitatively by this method. The concentration of the interference ions was found to be less than 0.1% or 0.01 ppm. While other specific methods of analysis such as Iodometric Methods, Specific Ion Electrode Methods etc. could be used to determine their concentrations, it is felt these concentrations would prove negligible.

The study showed that the interference ions forming slightly soluble silver salts do not affect the total volume of silver nitrate used in the titration of each water sample.

The chloride content of the River varied from station to station.

There were variations of chloride content of the same station at different dates.

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APPENDIX I

CALCULATIONS OF VOLTAGE AT EQUIVALENT POINT

$$E = E^{\circ}_{\text{Ag}^+} - 0.0951 \log \frac{1}{C_{\text{Ag}^+}}$$

$$E^{\circ}_{\text{Ag}^+} = 0.7995 \text{ Volts}$$

$$E_{\text{calomel electrode}} = 0.2415 \text{ Volts}$$

$$K_{\text{sp}} \text{ silver chloride} = 1.82 \times 10^{-10}$$

$$C_{\text{Cl}^-} = \frac{\text{m. mole chloride remaining}}{\text{Volume solution}}$$

$$C_{\text{Ag}^+} = \frac{K_{\text{sp}}}{C_{\text{Cl}^-}}$$

At Equivalent Point

$$\text{Eq.pt} = E - E_{\text{calomel}} = E - 0.2415$$

$$\begin{aligned} E &= 0.7995 - 0.0951 \log \frac{1}{4.266 \times 10^{-5}} \\ &= 0.7995 - .25826 \text{ Volts} \\ &= 0.5412 \text{ Volts} \end{aligned}$$

$$\text{Eq.pt} = 0.5412 - 0.2415 \text{ Volts}$$

$$= .2997 \text{ Volts}$$

$$= 299.7 \text{ MV}$$

APPENDIX 2

CHLORIDE CONTENT CALCULATION
(E-L CROSS)

$$\begin{aligned} & \text{Content to Cl}^- \text{ titer} \\ &= (0.10567)(35.433) \frac{\text{mg Cl}^-}{\text{ml}} \\ &= 3.744 \frac{\text{mg Cl}^-}{\text{ml}} \end{aligned}$$

Vol. Aliquot used = 100 ml

Vol. AgNO₃ at eq. pt. = 6.32 ml

$$\text{Cl}^- = (3.744)(6.32) \left(\frac{1000}{100} \right) \text{ ppm}$$

$$\text{Cl}^- = 236.7 \text{ ppm}$$