

AN INVESTIGATION OF NITRATE AND MERCURY CONCENTRATIONS
IN NATURAL WATERS THROUGH THE USE OF
ION-SELECTIVE ELECTRODES

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CHAPTER I

INTRODUCTION

Recently there has been much concern about the pollution of the environment by man. The purpose of this work was to establish the current level of nitrate and mercury concentrations of the Cottonwood and Neosho Rivers in the Emporia, Kansas, area and to explore the possibility of using nitrate and iodide sensitive electrodes as monitoring devices for these ions.

A measure of the nitrate and mercury concentrations would also show the effect that the city of Emporia, Kansas, has on these two rivers. To determine this effect, water samples were collected from sites which were situated both upstream and downstream from Emporia. The concentrations measured from the upstream sites could then be considered as normal, while those measured from the downstream sites could contain any added amounts of nitrate and mercury from the Emporia area. These concentrations would then be considered as abnormal.

Any study utilizing ion-selective electrodes must be concerned with the effects of interfering ions on the resulting data. Therefore, it was necessary to utilize some method of analysis for the determination of those ions which were most likely to interfere with the nitrate and iodide ion-selective electrodes.

This data would then determine the necessity of further calculation to obtain an accurate measure of the nitrate and mercury concentrations of the two rivers.

Both electrodes were used in conjunction with samples obtained during the period beginning January 28, 1971, and ending March 31, 1971.

CHAPTER II

THEORY

At the beginning of this century a new field of electrochemistry was introduced by Cremer¹ and Haber and Klemensiewicz² with the discovery that thin glass membranes were selective toward hydrogen ions. Later developments by Eisenman and his colleagues³ demonstrated that, by varying the composition of the membrane, the electrodes could be made selective toward cations such as Na^+ , K^+ , Ag^+ , and Li^+ . An excellent review of the work done with these electrodes is given by Rechnitz⁴ in his article in Chemical and Engineering News.

Later developments have brought us a divalent cation electrode and electrodes for a variety of anions. References for these developments may be found in the Department of Commerce publication, Ion-Selective Electrodes⁵.

In this study the nitrate and iodide electrodes were utilized in a direct determination of the nitrate ion and an indirect evaluation of the mercuric ion.

The Iodide Electrode

The iodide electrode used was a solid state electrode, in that it contains a crystal of silver iodide which is the means whereby a potential is developed as a direct measure of the activity of a solution (Figure 1).

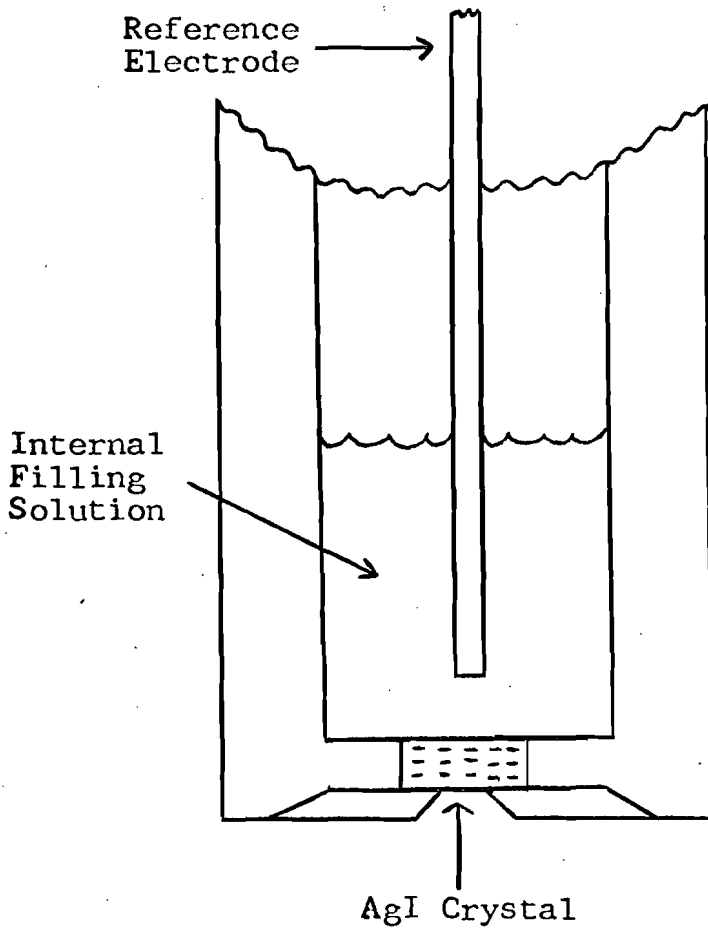


FIGURE 1
SOLID STATE MEMBRANE ELECTRODE

As explained by Eisenman³, the silver iodide crystal acts as a cation or anion exchanger and develops a Nernstian potential which is directly related to the activity of the ion to be measured. When a membrane of this type separates two solutions of a single salt at two different concentrations, the potential developed is given by the equation:

$$E = \frac{RT}{F} \ln \frac{a_i'}{a_i''} \quad (1)$$

The (') and (") represent the sample and internal filling solutions, R = the gas constant, F = the faraday, T = temperature in degrees Kelvin, and E = potential developed across the electrode. If the electrode is constructed as in Figure 1 and then filled with a solution of constant composition, equation (1) becomes:

$$E = \text{Constant} + \frac{RT}{F} \ln a_i' \quad (2)$$

which shows the potential to be solely dependent upon the activity of the solution to be measured.

The iodide electrode, like the nitrate electrode, is susceptible to interference from other ions. Sulfides and silver ions must be absent⁶, strong reducing agents must never be used, and the pH of the solution must never become too high. These factors all have destructive affects on the silver iodide membrane.

There are other ions which, when present, will also interfere with the normal action of the electrode; however, the nature of their interference is to produce an incorrect

potential readout. When an ion such as chloride is present, the potential developed follows equation (3):

$$E = \frac{RT}{F} \ln \left[\frac{a_i' + \left(\frac{u_j^*}{u_i^*} \right) K_{ij} a_j'}{a_j'' + \left(\frac{u_j^*}{u_i^*} \right) K_{ij} a_j''} \right] \quad (3)$$

The factor $\left(\frac{u_j^*}{u_i^*} \right) K_{ij}$ is characteristic of the selectivity of the membrane. In this case, the maximum allowable ratio of (chloride/iodide) is 10^6 .

If we set $\left(\frac{u_j^*}{u_i^*} \right) K_{ij}$ equal to K_j ⁷, we can define K_j as the selectivity constant for a particular ion. Again, by filling the electrode with a solution of constant composition, we can reduce equation (3) to:

$$E = \text{Constant} + \frac{RT}{F} \ln \left[a_i' + K_j a_j' \right] \quad (4)$$

which shows the potential developed to be dependent upon the activities of both ions in solution.

If a separate analysis is performed on the sample for the major interfering ions, then by substituting values into equation (4) a more correct value of the a_i' may be determined.

Even though the electrode measures activities, it is easier to make calculations on the basis of concentration. In dilute solutions, the activity of a species is equal to the concentration (i.e. the solution becomes more ideal). Equation (4) can be modified by remembering the relationship between activity and concentration⁸.

$$a_i = \gamma_i C_i \quad (\text{Figure 2})$$

and equation (4) becomes:

$$E = \text{Constant} + \frac{RT}{F} \ln \left[C_i' + K_j C_j' \right] \quad (5)$$

The Nitrate Electrode

The nitrate electrode is a liquid membrane electrode. The construction is similar to Figure 3. The potential developed in this electrode is due to the difference in activity of the nitrate ion between the sample and the internal filling solution.

Figure 4 is representative of the situation which exists in the nitrate electrode. The arrows show the cation, R^+ , is trapped within the membrane, while the anion species, X^- , is freely permeable. This is accomplished by making R^+ insoluble in water.

When the cationic species is freely permeable, Conti and Eisonman⁹ have shown the potential developed across the electrode is given by:

$$E = \frac{RT}{F} \ln \left[\frac{a_i' + (u_j^*/u_i^*) K_{ij} a_j'}{a_i'' + (u_j^*/u_i^*) K_{ij} a_j''} \right] \quad (6)$$

where the (*) indicates the solvent phase of the membrane. This equation is identical to equation (3).

However, others^{10,11} have shown a different relationship for an anionic species. They give:

$$E = \text{Constant} + 2.3 \frac{RT}{z_i F} \log \left[a_i' + \sum_j K_j a_j' (z_j/z_i) \right] \quad (7)$$

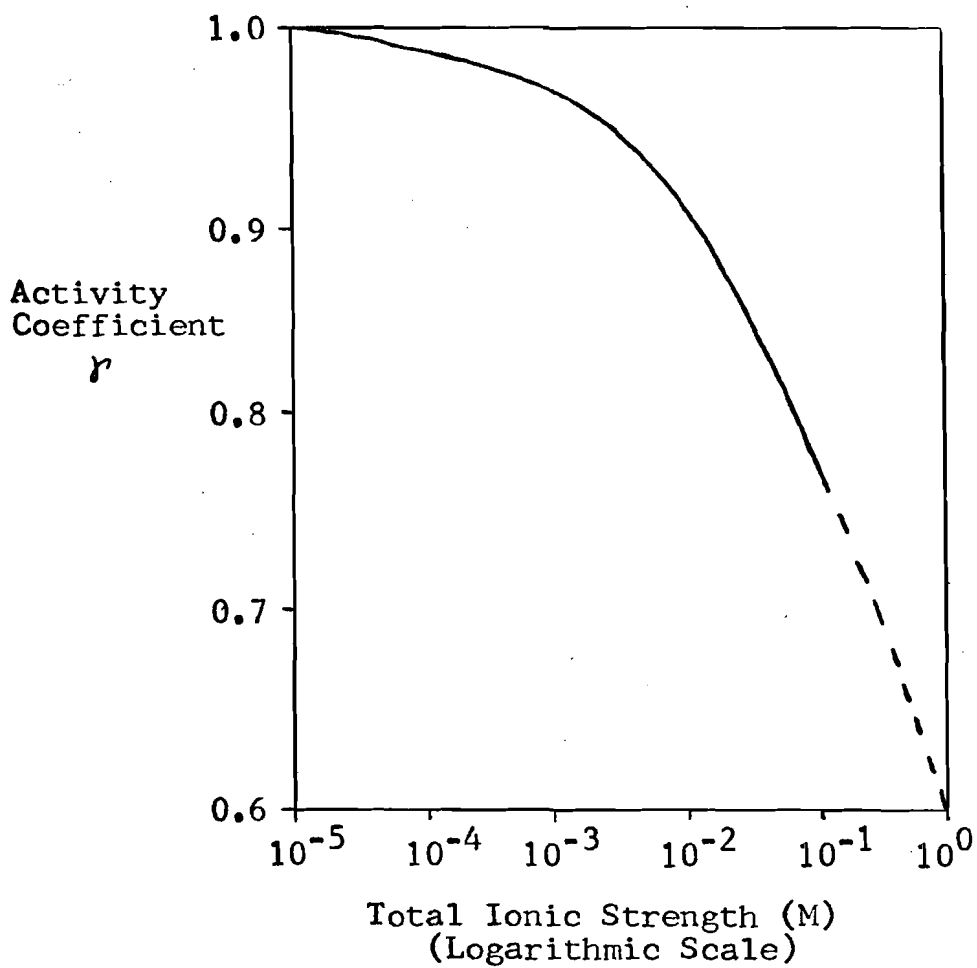


FIGURE 2

IONIC ACTIVITY COEFFICIENT OF NITRATE ION
VS. TOTAL IONIC STRENGTH IN PURE
SODIUM NITRATE SOLUTIONS¹¹

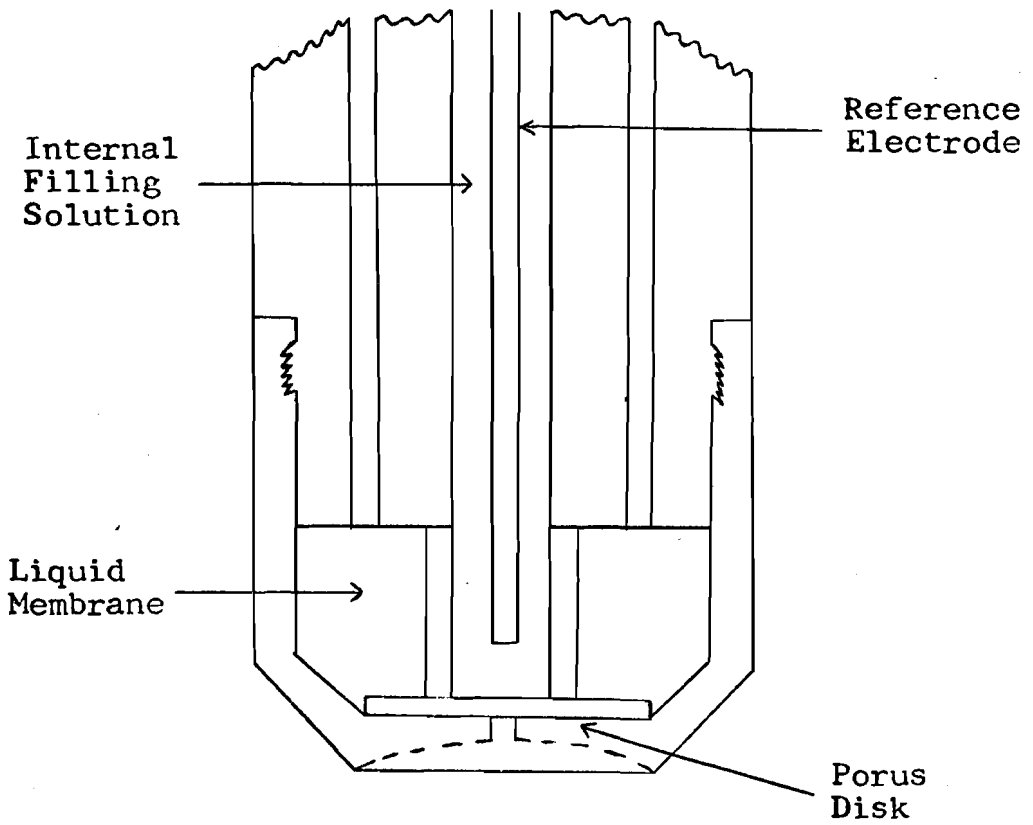


FIGURE 3

LIQUID - LIQUID MEMBRANE ELECTRODE

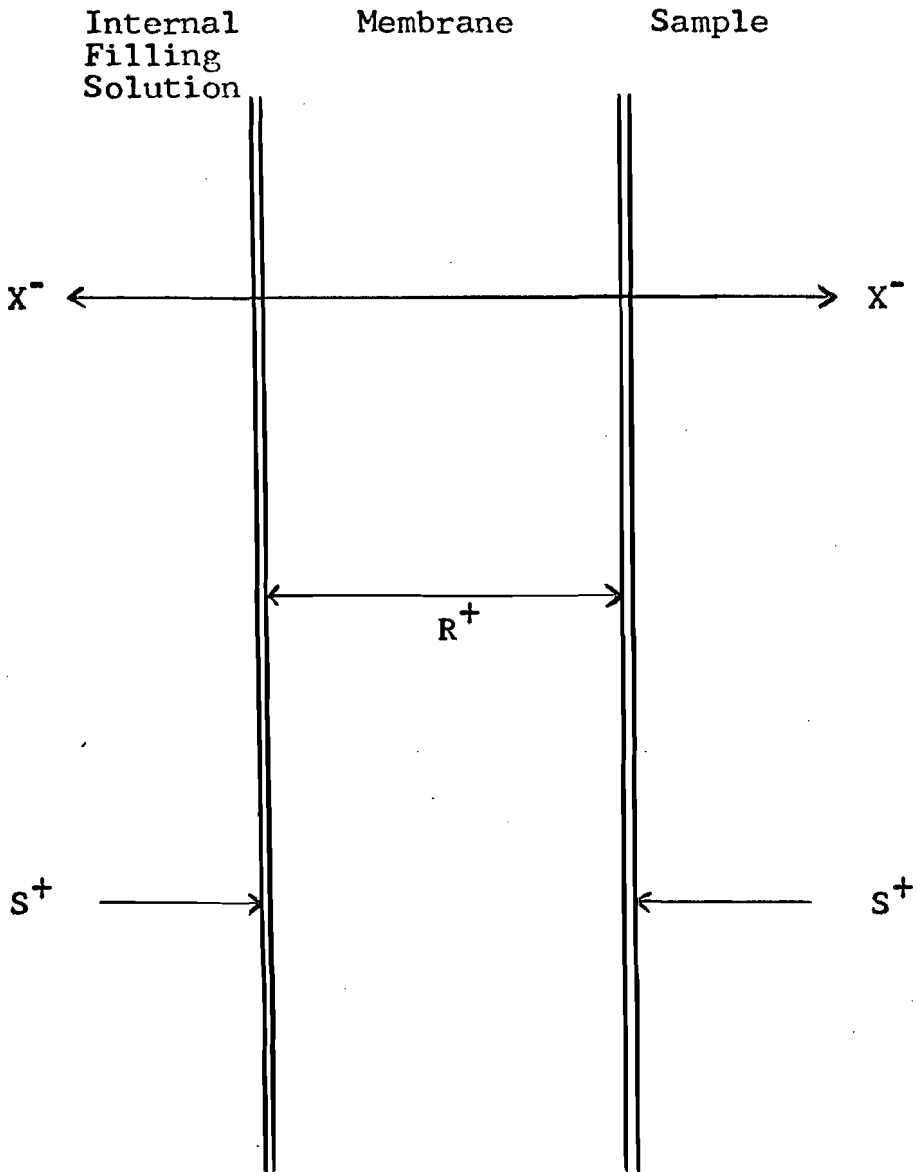


FIGURE 4

PERMEABILITY OF IONS THROUGH A LIQUID MEMBRANE

for two anionic species in solution where z_i and z_j are the electronic charges of the ions. The constant encompasses all other junction potentials in the system.

Here again, equation (7) can be modified to work directly with concentrations as follows:

$$E = \text{Constant} + 2.3 \frac{RT}{z_i F} \log \left[C_i' + \sum_j K_j C_j' (z_j/z_i)^{z_j/z_i} \right] \quad (8)$$

Data Analysis

The method for checking the operation of the electrodes is a simple calculation. Since equations (5) and (8) show a general form, $y = ax + b$, the slope of the line, $a = (2.3RT)/z_i F$, can be calculated. At 25°C, the slope of the line is $59.16/z_i$ millivolts. The slope of the line is dependent upon the temperature at the time the potential is measured and the number of electrons involved in the process. For accurate determinations, the samples and standards must all be at the same temperature. Each time the electrode is rebuilt, a new calibration curve must be made and the reliability of the curve tested in the same manner.

CHAPTER III

EXPERIMENTAL PROCEDURES

All chemicals used were American Chemical Society reagent grade and all solutions were prepared from distilled and deionized water. All glassware was cleaned with chromic acid and rinsed six times with deionized water before use.

PREPARATION OF STANDARDS

Standard Hydrochloric Acid

A solution of standard hydrochloric acid was prepared by dilution of concentrated hydrochloric acid and a portion titrated with KHP standardized sodium hydroxide to determine the normality.

Standard Silver Nitrate

A standard silver nitrate solution was prepared from crystals which were dried for 24 hours at 110°C, allowed to cool in a desiccator, 17.5496 grams transferred to a one liter volumetric and following dissolution, diluted to the mark. This solution was then stored in a brown bottle in the dark.

Standard Potassium Nitrate

The potassium nitrate solution was prepared by drying the crystals overnight at 110°C and 0.2103 grams diluted to

two liters. An analysis of the potassium nitrate used is found in Table 1.

Standard Sodium Chloride

The sodium chloride solution was prepared by drying the crystals overnight at 110°C and dilution of 0.1565 grams to two liters.

Standard Mercuric Nitrate Solution

10.4439 grams of triple distilled mercury were dissolved in 25 milliliters of concentrated nitric acid, and the resulting solution diluted to 100 milliliters with deionized water. Subsequent dilutions were made to prepare a calibration curve.

SAMPLING TECHNIQUES AND SAMPLE ANALYSIS

Samples of the two rivers were obtained at the points designated in Figure 5. Most of the points were at bridges. A five-liter plastic bucket was lowered on a 75-foot nylon line to the water and allowed to rinse for several minutes before retrieval. The pH and temperature of the sample were taken using an Orion Ionalyzer equipped with a combination electrode and a -10°C to 110°C mercury thermometer. The temperature adjustment and standardization of the meter were made at the sampling site.

Experimental procedures were developed to promote speed as well as accuracy. As much as possible, samples were

TABLE 1
POTASSIUM NITRATE ANALYSIS

Fischer Certified Reagent	Molecular Weight
Lot Number 742785	101.108 grams/mole
Iron (Fe)	0.0002%
Heavy Metals (as Pb)	0.0001%
Sulfate (SO ₄)	0.002 %
Sodium (Na)	0.005 %
Nitrite, Iodate	to pass test
Insoluble Matter	0.001 %
Chlorine, Total (Cl)	0.001 %
Phosphate (PO ₄)	0.001 %
Calcium, Magnesium, and R ₂ O ₃ ppt	0.009 %
pH of a 5% Solution at 25°C	6.1

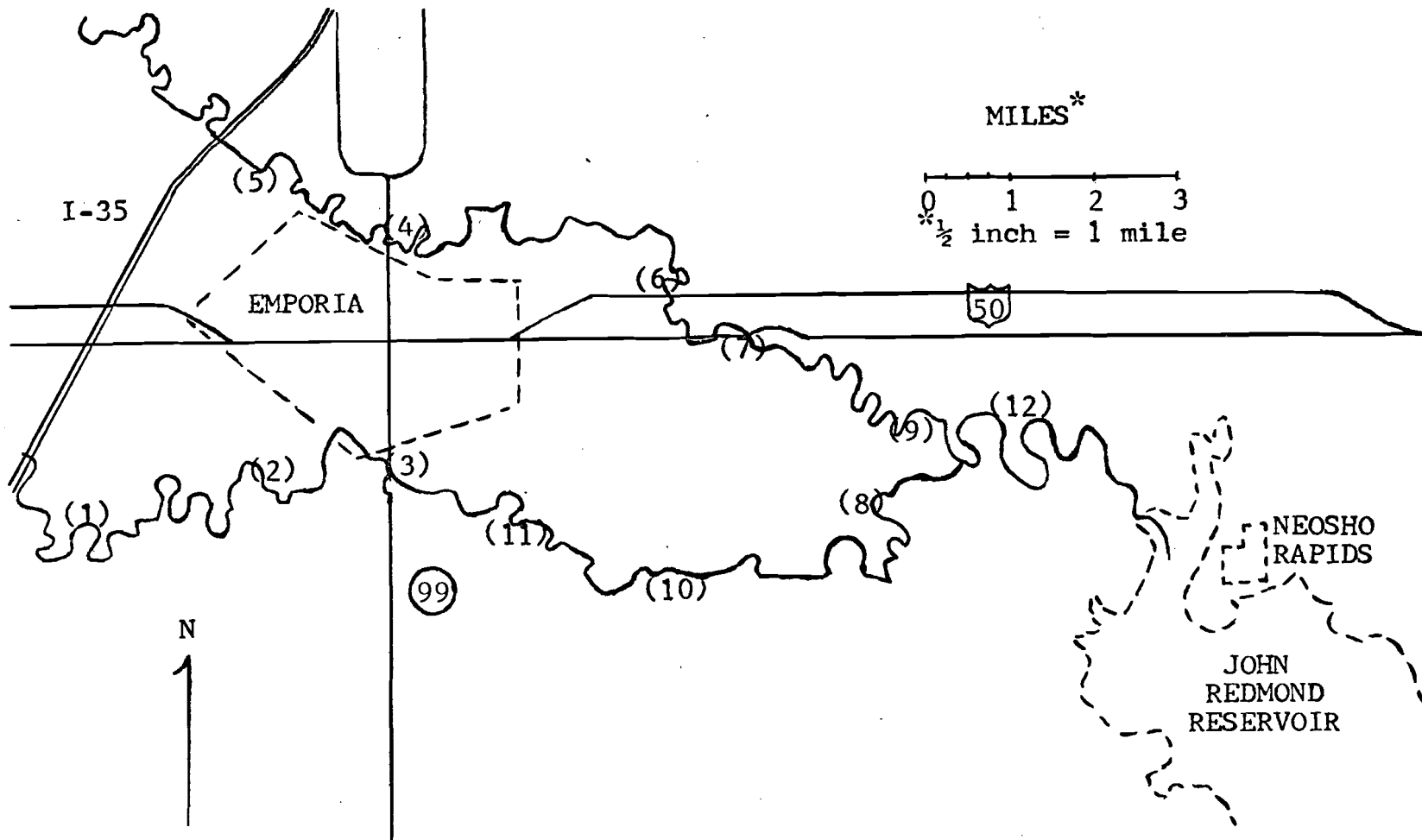


FIGURE 5

MAP OF SAMPLING STATIONS

(Reproduced from Lyon County, Kansas, General Highway Map)

TABLE 2

SAMPLING STATIONS

1. Two miles west on old Highway 50; turn south to the Cottonwood River.
2. From Sixth Street south on Prairie Street to the first bridge.
3. The spillway at Soden's Grove, the east wall upstream of the bridge.
4. First bridge north of Emporia on Highway 99.
5. The bridge by Water Works Pumping Station north of Emporia on Prairie Street.
6. First bridge east of Emporia on new Highway 50.
7. First bridge east of Emporia on old Highway 50.
8. Highway 99 south one mile, east on gravel road $5\frac{1}{2}$ miles, south on gravel road 1 mile, east on gravel road $\frac{1}{2}$ mile to bridge.
9. Highway 99 south to edge of Emporia, then east on gravel road ($4\frac{1}{2}$ miles to railroad tracks), proceed until river approaches road at north side before angle-iron barrier at edge of road. Bend in river has rock bar at bottom.
10. From Station 9, go back $2\frac{1}{2}$ miles west on gravel road, turn south on gravel road to first bridge.
11. From Station 10 go north to first mile road, turn west 2 miles, turn south on gravel road to first bridge.
12. Old Highway 50, six miles east of town, turn south on gravel road to river.

analyzed as received from the field with as little preparation as possible.

A bicarbonate determination¹² was made as soon as possible after returning from the field. The carbonate determination was not necessary because the pH indicated that no carbonate ion was present in the samples.

Thereafter, the samples were allowed to stand overnight to allow the particles of earth and organic material to settle out. If necessary, the samples were decanted to prevent interference from the organic substances.

Chloride¹² and sulfate¹³ determinations were also made to check possible interference occurring with respect to the nitrate electrode. (See Figure 6 for calibration curve for sulfate.)

The nitrate determinations were made by using an expanded scale Leeds and Northrup pH meter¹⁴ and an Orion nitrate-selective electrode in conjunction with a previously prepared calibration curve and a porous membrane-type standard reference electrode. Following the "pure sample method"¹¹, 100 milliliter samples were used under constant agitation at room temperature.

Electrodes such as this respond to many ions. This response to other ions is termed interference. The literature search showed the major interference to be the chloride ion^{11,15,16}. Dilutions with the standard nitrate solution were made of a standard chloride solution. Readings were taken again and a new calibration curve was drawn.

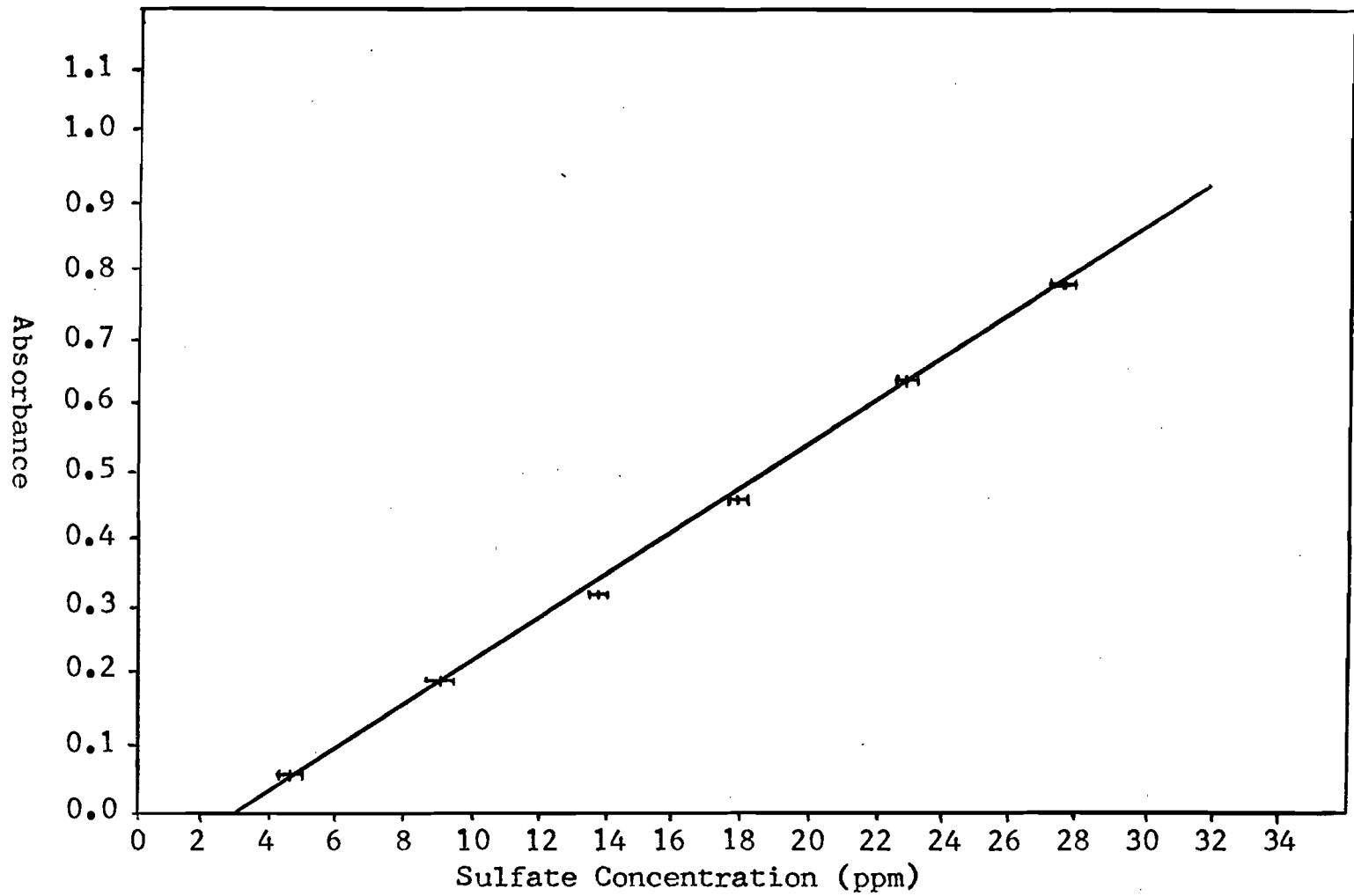


FIGURE 6

SULFATE CALIBRATION CURVE
(TURBIDIMETRIC DETERMINATION)

TABLE 3
SULFATE CALIBRATION DATA*

Standard Solution (ml)	H ₂ O (ml)	SO ₄ ⁼ (ppm)	Time			
			5 min.	6 min.	7 min.	8 min.
2	48	4.5	0.065	0.070	0.069	0.069
4	46	9.0	0.204	0.201	0.201	0.200
6	44	13.6	0.325	0.322	0.323	0.324
8	42	18.1	0.485	0.473	0.463	0.465
10	40	22.6	0.645	0.642	0.643	0.646
12	38	27.1	0.748	0.788	0.787	0.783
14	36	31.6	0.93+	0.93+	0.93+	-----

*Data taken by David Holdeman on February 25, 1971
Standard Sulfate Solution contains 113 ppm.

It was necessary to place a variable resistor across the Thermohm terminals and adjust the resistance while measuring a constant potential to expand the scale of the Leeds and Northrup pH meter. A Heathkit Millivolt Test Unit, in conjunction with a Heathkit Resistance Box, was used to supply the voltage. Measurements were made by setting a resistance of $1674\ \Omega$ on the resistance box. Then, the electrodes were immersed in deionized water and the meter switched from zero to measure. With the function switch in the automatic temperature position and the temperature compensation dial turned all the way down, the zero-standardization knob was used to set a reading of one pH unit. The deionized water then acted as a blank for the determinations. After wiping the electrodes to control any possible solution carry over, the samples were placed on the electrodes under conditions of constant agitation by the use of a magnetic stirrer. The electrodes were washed after each sample reading was taken and the zero setting checked with the deionized water sample.

No standard method of analysis was used to check the results of the electrode since Bunton and Crosby¹⁶ have shown there is no real correlation between standard and accepted methods. Since the chloride ion, bicarbonate ion, and sulfate ion are the major interferences when working with a nitrate electrode, in the absence of perchlorate ion and nitrite ion, subsequent calculations were made using the data obtained from the separate determinations and

equation (5) to give a more accurate analysis of the nitrate content of the samples.

The mercuric ion determinations were made according to the method outlined in the Orion Newsletter¹⁷. The same Leeds and Northrup pH meter and reference electrode were used; however, a salt bridge of 0.1 N potassium nitrate and eight per cent Agar-Agar was used to prevent contamination of the sample by the reference electrode.

The pH of the standards and samples must be maintained at a level of 3.5 - 4.0 to prevent the formation of mercuric and mercurous hydroxides. This was accomplished by adding one or two drops of concentrated HNO_3 to the liter sample.

CHAPTER IV

RESULTS AND DISCUSSION

The values in Table 4 show that an infinite number of scale expansions can be made with the Leeds and Northrup meter depending on the resistance chosen. A value of 1674Ω was chosen for this work because it allowed a full concentration range of 10^{-3} to 10^{-5} M NO_3^- to be measured with one calibration of the meter. This resistance also minimized any induced errors in the determination by reducing the amount of drift shown by the meter. Similar reasoning was employed in determining the resistive value to be used with the iodide electrode.

The calibration curve drawn (Figure 7) for the nitrate electrode shows a slope of 61 millivolts. This is an error of +1.64 per cent for a temperature of 23.5°C and can be attributed to a small leakage of the ion exchanger. This leakage was noticed even after rebuilding the electrode. As the lower limit of the electrode is approached, the error grows larger. The lower limit is set by the fact that the membrane contains nitrate; and as the solutions become more dilute, the nitrate ion actually passes from the membrane to the solution creating a counter potential in the electrode. The nitrate concentration level in the membrane is approximately 10^{-5} molar. Interfering ions tend to raise this

TABLE 4
EXPANDED SCALE pH READINGS*

Input (mv)	Resistance (Ω)							
	1674	1100	900	750	547	300	50	15
5	0.0	-----	-----	-----	-----	-----	-----	-----
10	0.5	-----	-----	-----	-----	-----	-----	-----
15	0.95	0.0	-----	-----	-----	-----	-----	-----
20	1.45	0.7	-----	-----	-----	-----	-----	-----
25	1.92	1.45	0.0	-----	-----	-----	-----	-----
30	2.42	2.2	0.9	-----	-----	-----	-----	-----
35	2.92	2.95	1.8	0.0	-----	-----	-----	-----
40	3.40	3.7	2.7	1.05	-----	-----	-----	-----
45	3.91	4.42	3.6	2.15	1.4	-----	-----	-----
50	4.40	5.18	4.5	3.20	2.8	0.0	-----	-----
55	4.90	5.9	5.4	4.30	4.2	2.6	-----	-----
60	5.39	6.65	6.3	5.40	5.6	5.2	-----	0.0
65	5.86	7.38	7.2	6.44	7.0	7.7	0.0	4.8
70	6.33	8.10	8.1	7.50	8.4	10.3	11.5	9.6

*The scale expansion is readily noticed by comparing the lists for 1674 Ω and 15 Ω ; for 1674 Ω it takes a 70 mv. change in input to produce a 6.33 pH unit scale change, while for 15 Ω only a 10 mv. change in input to produce a 9.6 pH unit change of scale reading.

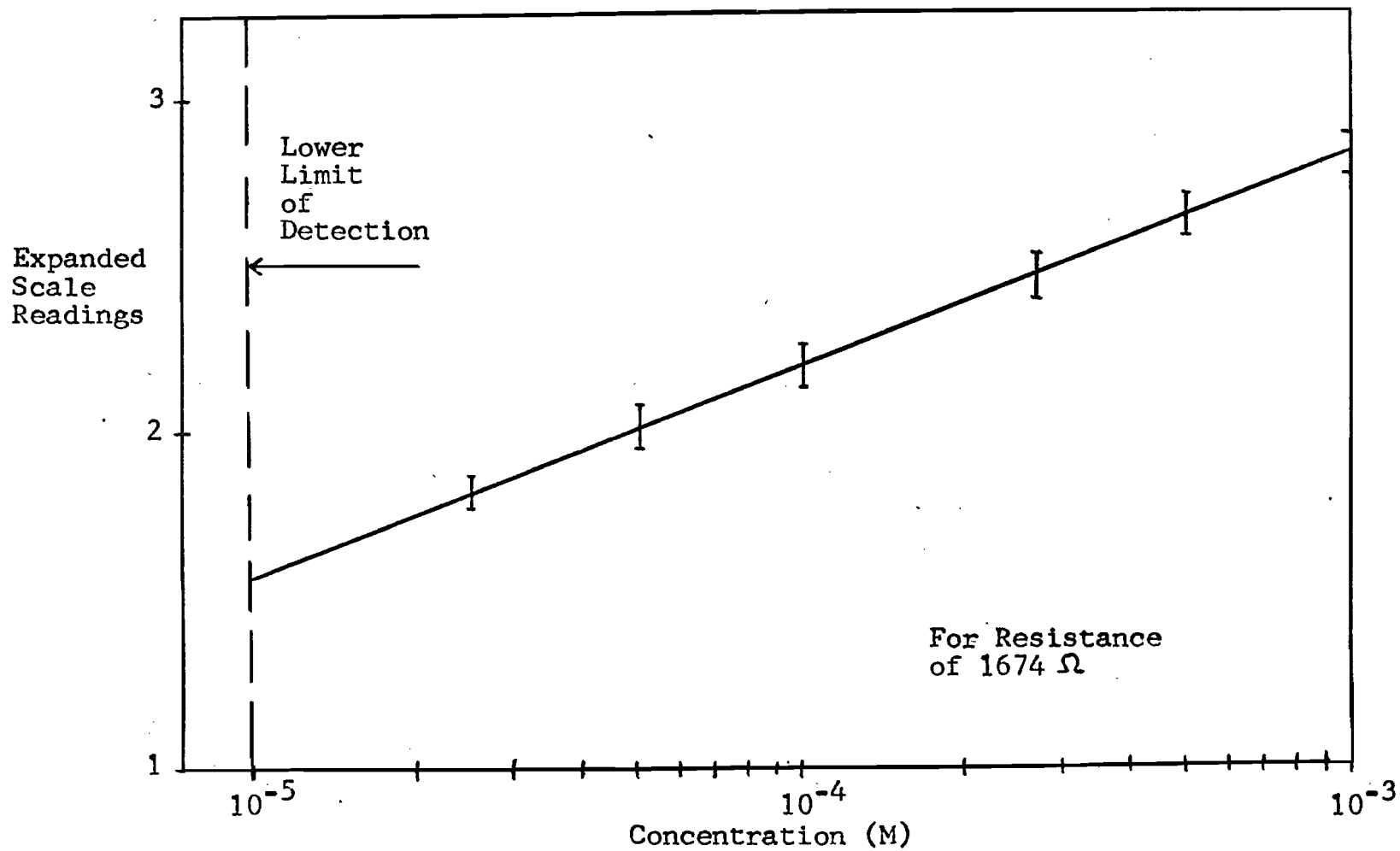


FIGURE 7

CALIBRATION CURVE FOR THE NITRATE ELECTRODE

TABLE 5
NITRATE CALIBRATION DATA

Stock Solution (ml)	Diluted to (ml)	Molarity (M)	Scale Reading (0-14)	Concentration (ppm)
100	100	1.0399×10^{-3}	2.83 \pm 0.01	64.5
50	100	0.5199×10^{-3}	2.65 \pm 0.01	32.2
25	100	0.2600×10^{-3}	2.45 \pm 0.02	16.1
25	250	1.0399×10^{-4}	2.22 \pm 0.01	6.5
5	100	0.5199×10^{-4}	2.00 \pm 0.01	3.2
25	1000	0.2600×10^{-4}	1.81 \pm 0.02	1.6
20	2000	1.0399×10^{-5}	1.40 \pm 0.01	0.6
0	100	Deionized water	1.00 \pm 0.03	----

limit. A significant loss of reproducibility and accuracy has been reported by Keeney, Brynes, and Genson¹⁵ in samples of ten milligrams per liter of dissolved nitrate. The last two data sets in Table 6 (p. 27) agree with Bunton and Crosby¹⁶ who have detected a lower value of five milligrams per liter.

Results taken from a graph such as Figure 7 must not be considered completely accurate because of the effects of interfering ions. Equations (5) and (8) can be rearranged to show the effects of interfering ions if two assumptions are first made: (1) there is only one interfering ion, and (2) it has the same electronic charge as the species to be measured. By an algebraic rearrangement, we arrive at the following equation:

$$\text{antilog} \left(\frac{\Delta E}{S} \right) - \sum_j K_j C_j = C_i$$

where

$$S = \frac{2.303RT}{F}$$

If we now allow only C_j to change, we can see that a higher value for C_j will give a lower C_i . Figure 8 shows the Cl^- interference with the nitrate electrode. Since the slope of the line is very close to zero, the error induced by contribution of the Cl^- would be negligible. Inspection of the Nernst equation shows that a one millivolt change in potential induced a four per cent error in the calculation of the concentration measured. However, this value only becomes significant at high $[\text{Cl}^-]/[\text{NO}_3^-]$ ratios.

TABLE 6
COMPARISON OF SAMPLE ANALYSIS*

Sample Sites	Sample Set	Conductance	Ion Content as ppm			
			HCO ₃ ⁻	Cl ⁻	SO ₄ ⁼	NO ₃ ⁻
Cottonwood River						
1	A	840	373	26.6	113	30
	B	430	240	UD	14.9	2.3
	C	622	300	137.0	29.0	2.7
2	A	-	-	-	-	-
	B	449	209	UD	15.8	2.3
	C	692	309	56.8	26.2	2.3
3	A	860	373	26.6	162.5	30
	B	360	220	UD	13.7	2.1
	C	700	311	95.0	26.3	2.5
11	A	926	361	38.5	167.5	39
	B	470	215	UD	15.3	2.3
	C	699	309	52.0	25.1	2.7
10	A	399	523	72.0	48.5	49
	B	410	212	UD	14.8	2.3
	C	705	314	39.0	25.3	2.6
8	A	650	373	62.0	111.5	24
	B	460	210	UD	14.4	2.1
	C	700	317	48.0	25.0	2.8
Neosho River						
5	A	555	317	310.0	54.5	24
	B	350	195	UD	10.6	1.2
	C	471	292	UD	16.0	2.1
4	A	730	488	106.0	28.5	25
	B	345	189	UD	9.6	1.1
	C	465	257	UD	15.9	2.0
6	A	410	306	312.0	52.5	35
	B	360	188	UD	10.4	0.9
	C	480	259	UD	17.6	2.1
7	A	399	312	101.0	53.0	31
	B	342	196	UD	10.2	1.4
	C	480	259	UD	17.6	2.3
9	A	399	308	438.0	53.5	32
	B	350	191	UD	10.6	0.8
	C	482	264	UD	17.1	2.1
12	A	-	-	-	-	-
	B	410	237	UD	19.6	2.1
	C	658	309	37.0	23.4	2.7

*Sampling date for Set A = January 28, 1971; Set B = March 5, 1971; Set C = March 31, 1971. Sites tabled from upstream to downstream. Site 12 is downstream from the joining of the rivers.

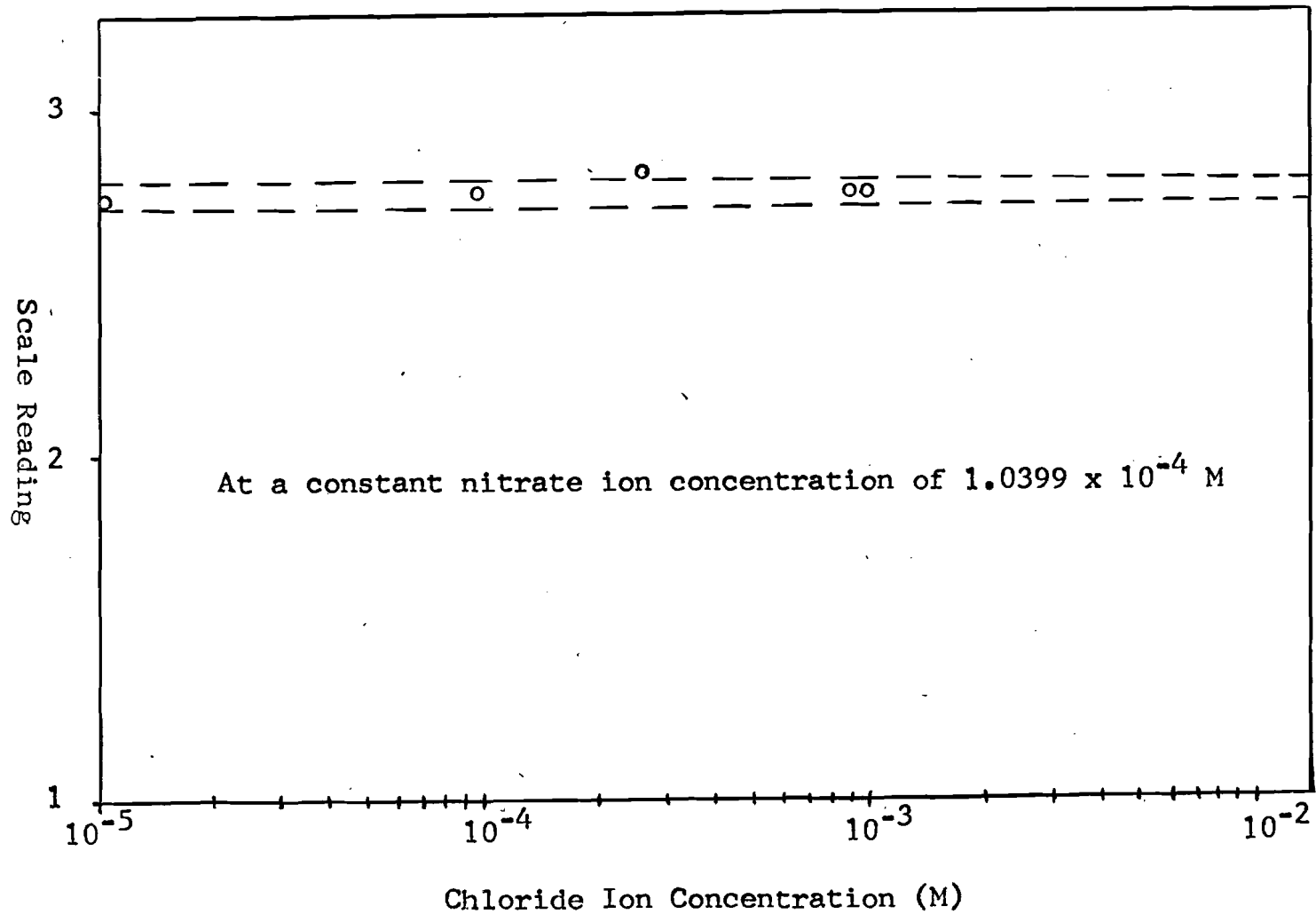


FIGURE 8

CHLORIDE INTERFERENCE WITH THE NITRATE ELECTRODE

TABLE 7
 DATA FOR CHLORIDE INTERFERENCE
 WITH NITRATE ELECTRODE

Cl ⁻ Solution added	Molarity Cl ⁻ (approximate)	Scale Reading
(1.3387 x 10 ⁻³ M solution of NaCl)		
0	0	2.70 ± 0.01
0	0	2.70 ± 0.01
10.1	1 x 10 ⁻⁴	2.73 ± 0.01
10.1	1 x 10 ⁻⁴	2.76 ± 0.01
25	0.25 x 10 ⁻³	2.80 ± 0.01
25	0.25 x 10 ⁻³	2.83 ± 0.01
90	0.9 x 10 ⁻³	2.79 ± 0.01
90	0.9 x 10 ⁻³	2.80 ± 0.01
(0.1082 M solution of NaCl)		
1	1 x 10 ⁻³	2.80 ± 0.01
1	1 x 10 ⁻³	2.80 ± 0.01
10	1 x 10 ⁻²	2.80 ± 0.01
10	1 x 10 ⁻²	2.84 ± 0.01

TABLE 8
SELECTIVITY CONSTANTS FOR NITRATE ELECTRODE

Ion	Constant (K)
ClO_4^-	10^3
I^-	20
ClO_3^-	2
Br^-	1.3×10^{-1}
NO_2^-	4×10^{-2}
CN^-	1×10^{-2}
HCO_3^-	9×10^{-3}
Cl^-	4×10^{-3}
OAc^-	4×10^{-4}
$\text{CO}_3^{=}$	2×10^{-4}
S_2O_3^-	Destructive Effects
$\text{SO}_3^{=}$	Destructive Effects
F^-	6×10^{-5}
$\text{SO}_4^{=}$	3×10^{-5}
H_2PO_4^-	5×10^{-5}
PO_4^{-3}	1×10^{-4}
$\text{HPO}_4^{=}$	3×10^{-5}
HS^-	4×10^{-2}

The nitrate concentration reported in this paper was not corrected for the effects of interfering ions. Separate calculations have shown that the effect on the electrode potential by the HCO_3^- , Cl^- , and $\text{SO}_4^{=}$ ions may be disregarded in this investigation.

The following is an example of the calculations which show the insignificance of the interference for sample (1) taken on January 28, 1971: the $[\text{HCO}_3^-] = 6.11 \times 10^{-3}$ M, $[\text{Cl}^-] = 0.75 \times 10^{-3}$ M, and $[\text{SO}_4^{=}] = 1.18 \times 10^{-3}$ M. The selectivity constants are: $K_{\text{HCO}_3^-} = 9 \times 10^{-3}$, $K_{\text{Cl}^-} = 4 \times 10^{-3}$, and $K_{\text{SO}_4^{=}} = 3 \times 10^{-5}$. (See Table 8.)

Substituting these values into equation (8) and rearranging ($T = 296.5^\circ\text{K}$), we have:

$$[\text{NO}_3^-] = \text{antilog} \left[\frac{E - \text{Constant}}{\frac{2.303RT}{z_1 F}} \right] - \left[6.11 \times 10^{-3} (9 \times 10^{-3}) + 0.75 \times 10^{-3} (4 \times 10^{-3}) + [1.18 \times 10^{-3} (3 \times 10^{-5})^2] \right]$$

Since $E - \text{Constant} = \Delta E$ and a reading of 1.95 pH units is a ΔE of 33.47 millivolts, then the antilog term is in the order of 6×10^{-5} which is considered insignificant because the antilog term is approximately 0.23.

Therefore, the nitrate concentrations were read directly from the calibration curve and then converted to read as parts per million.

The drastic change in values between sample sets A and B in Table 6 may be accounted for by considering the precipitation data given in Table 14 (see Appendix). The

amount of precipitation received produced a considerable dilution of the two rivers. An inspection of the conductances for the three sets of data verifies this assumption. Sample set C shows an increase in dissolved content which should approach a norm barring any further precipitation. This set of samples should contain only those compounds which occur naturally. Any compounds which are dumped directly into the rivers should be detected in the samples taken at the downstream sites.

A lower limit of 10^{-8} molar has been proposed for the iodide electrode¹⁷ for the detection of the mercuric ion. Below this value, the ionization constant of the membrane becomes important, i.e., the electrode senses the dissolution of the membrane. Extreme accuracy must be used in preparing the 10^{-6} to 10^{-8} molar solutions for the calibration curve. Figure 9 shows the calibration curve prepared for this work.

One would expect the slope of this curve to be different from that of the nitrate electrode since the electrode is used to measure a divalent ion, but the ionization of the silver iodide is the potential developing process because there is only one electron involved. The slope of the line is the same as that for the nitrate electrode and is dependent on the temperature of the solution. The method used requires the use of an ionic strength adjustor such as potassium perchlorate to maintain a constant level of activity in the solution. This

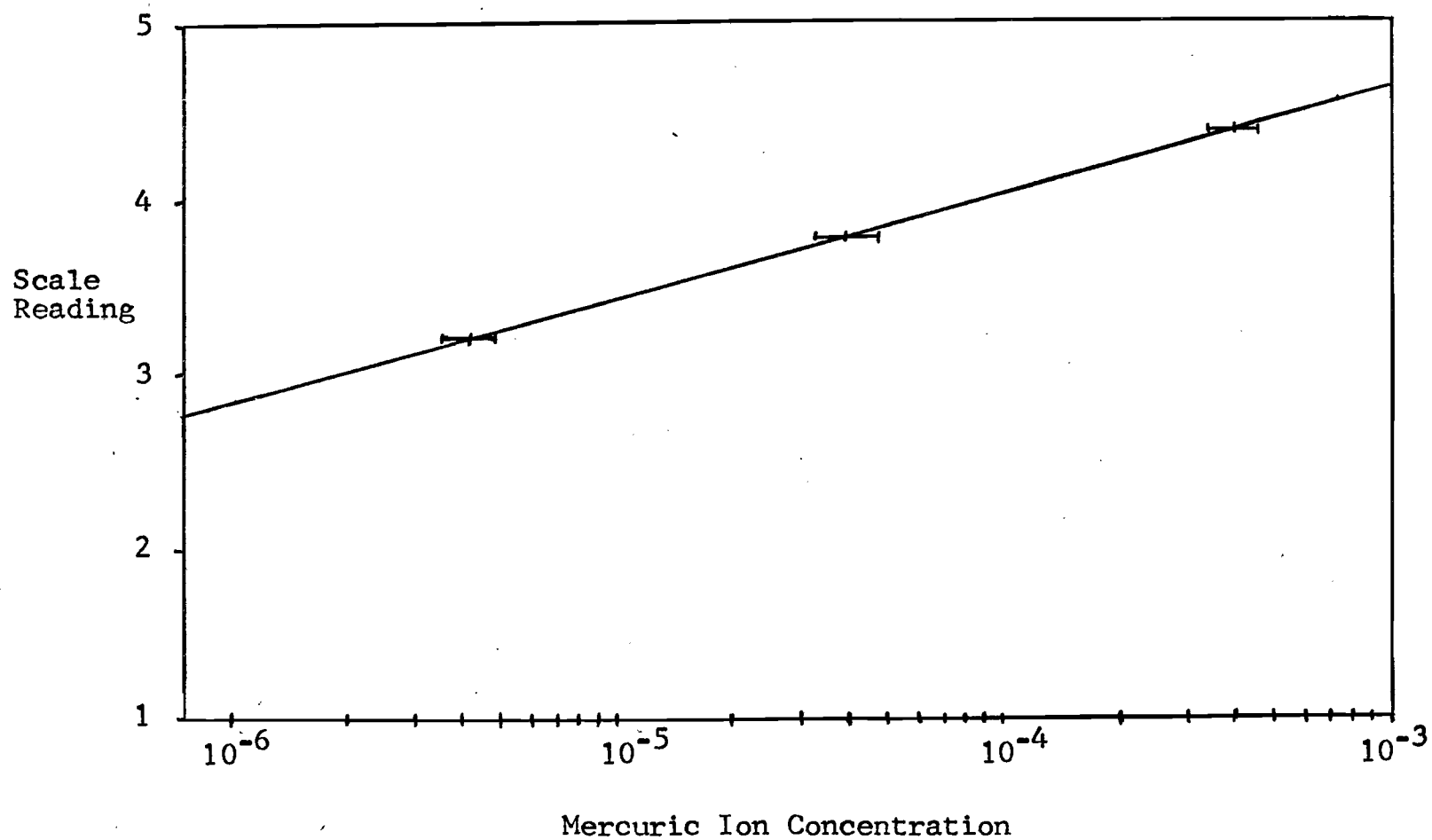


FIGURE 9

CALIBRATION CURVE FOR THE IODIDE ELECTRODE USED FOR
MEASURING MERCURIC ION CONCENTRATION

TABLE 9
 Hg^{++} CALIBRATION DATA

Molar Concentration one ml of solution added	Scale Reading	Effective Hg^{++} molar concentration
5.22×10^{-3}	3.35	$5.22 \times 10^{-6} \pm 1 \times 10^{-7}$
5.22×10^{-2}	3.89	$5.22 \times 10^{-5} \pm 1.1 \times 10^{-6}$
5.22×10^{-1}	4.50	$5.22 \times 10^{-4} \pm 1.11 \times 10^{-5}$

constant level of activity also allows the use of a salt bridge which is necessary to avoid contamination from the reference electrode.

The operation of the iodide electrode as a detector for the mercuric ion gives rise to the question of the effects of other ions on this electrode. Table 10 lists several ions which can cause incorrect measurements. Interferences that must be eliminated are Ag^+ and any strong reducing agents present in the sample. Strong reducing agents will transform the Hg^{++} ions to Hg^+ which will not attack the electrode membrane. Any amount of Ag^+ would tend to hinder the replacement⁵ of the Ag^+ in the membrane by Hg^{++} . The competing reactions are:



and



The results shown in Tables 11, 12, and 13 (See Appendix) are the final reports of the sample sets. The values do not represent the total nitrogen or mercury content of the samples. The nitrate electrode senses only the dissociated nitrate in the solution. It does not sense the bound or organic nitrate. Methods¹⁵ for the analysis of the total nitrate concentration have been proposed, but these methods are too involved to be used as a rapid analysis scheme. The iodide electrode is somewhat different from the nitrate electrode in that it will detect a species such as HgR^+ although it will not detect compounds of the HgR_2 form⁵.

TABLE 10
EFFECTS OF OTHER IONS ON MERCURIC ION DETERMINATIONS¹⁸

Ion	Effect on Electrode
S^{2-}	destructive effects
Cl^{-}	complexing species
Br^{-}	complexing species
CN^{-}	complexing species
I^{-}	impares Ag^{+} replacement reaction

Conclusions

Water quality records¹⁹ show a general agreement with the data in the last two sample sets pertaining to the nitrate levels of the two rivers. This fact, along with the simplicity of operation of the nitrate electrode, definitely makes it ideally suited for monitoring nitrate levels in the two rivers. Since the concentrations of the interfering ions in the Emporia area are low enough, there is no need to make separate determinations and calculations to determine the effects of the interfering ions on the nitrate determinations.

Having shown that it is possible to use the nitrate electrode to measure the level of dissolved ions in these rivers, the second purpose of this research was to determine the affect, if any, of Emporia on the two rivers. By comparing the data taken on Samples 1, 2, 3, 4, and 5, which were taken above Emporia, with the data for Samples 6, 7, 8, 9, 10, 11, and 12, it can be seen that the city of Emporia slightly increases the nitrate level of the Cottonwood River. However, the increase is so small as to be almost negligible. As expected, the increase is apparent only on the Cottonwood River and not the Neosho River since Emporia is essentially "down hill" from the Neosho River.

Emporia does affect the Neosho River as far as the other ions measured are concerned. This could possibly be due to the fact that the city water supply is taken from the Neosho River. The reduction in the level of the river is significant. Any ion concentrations in Dow and Badger

Creeks, which join the Neosho River below sites 4 and 10, will not be diluted as much as if Emporia were not removing some water from the river. Before any definite statement can be made concerning the Neosho River, a study of the two creeks would be necessary.

No significant mercury concentration was indicated through the use of the iodide electrode and the method described in the experimental section of the paper. Several assumptions can be made from this fact. (1) The mercuric ion content of the two rivers is not large enough to be measured in this manner. (2) The mercury present in the samples was not in ionic form but consisted of the HgR_2 form. (3) The method used in this study was inadequate.

Preliminary work indicates that the mercuric ion concentration may be high enough to be measured, but the chloride ion concentration is high enough to cause significant changes in the measurements (Table 15). A method has been described which uses a direct titration of the Hg^{++} with NaI using the iodide electrode as an indicator electrode²⁰ which may prove to be suitable for a monitoring operation. More work is clearly indicated in this area.

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BIBLIOGRAPHY

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APPENDIX

TABLE 11
ANALYSIS OF SAMPLES TAKEN ON JANUARY 28 AND 29, 1971

Sample	Temperature (°C)	pH	Conductance (mho)	River*
1	---	----	840	C
2	No Sample Taken			C
3	---	----	860	C
4	---	----	730	N
5	0.8	7.90	555	N
6	0.6	7.30	410	N
7	0.6	7.40	399	N
8	0.9	6.80	650	C
9	1.2	6.75	399	N
10	1.3	6.55	399	C
11	2.5	7.50	926	C
12	No Sample Taken			

*C = Cottonwood River; N = Neosho River; J = After Cottonwood and Neosho Rivers Join

TABLE 11.1
ANALYSIS OF SAMPLES TAKEN ON JANUARY 28 AND 29, 1971

Sample	Alkalinity HCO ₃ ⁻ (ppm)	Salinity Cl ⁻ (ppm)	SO ₄ ⁼ (ppm)	NO ₃ ⁻ (ppm)	Hg ^{++*}
1	373 [±] 4	26.6 [±] 0.1	113.0 [±] 5.5	30 [±] 3	---
2	No Sample Taken				
3	373 [±] 4	26.6 [±] 0.1	162.5 [±] 8.1	30 [±] 3	---
4	488 [±] 5	106.0 [±] 0.5	28.5 [±] 1.2	25 [±] 2	---
5	317 [±] 3	315.0 [±] 1.6	54.5 [±] 2.7	24 [±] 2	---
6	306 [±]	312.0 [±] 1.6	52.5 [±] 2.6	35 [±] 3	---
7	312 [±] 3	101.0 [±] 0.5	53.0 [±] 2.6	31 [±] 3	---
8	373 [±] 4	62.0 [±] 0.3	111.5 [±] 5.5	24 [±] 2	---
9	308 [±] 3	438.0 [±] 2.1	53.5 [±] 2.7	32 [±] 3	---
10	523 [±] 5	72.0 [±] 0.4	48.5 [±] 2.4	49 [±] 5	---
11	360 [±] 4	38.5 [±] 0.2	167.5 [±] 8.4	39 [±] 4	---
12	No Sample Taken				

*No Analysis Performed

TABLE 12
ANALYSIS OF SAMPLES TAKEN ON MARCH 5, 1971

Sample	Temperature (°C)	pH	Conductance (mho)	River*
1	3.5	6.90	430	C
2	3.8	6.90	449	C
3	3.4	7.00	360	C
4	2.0	7.00	345	N
5	2.7	6.90	350	N
6	5.4	7.05	360	N
7	3.9	7.20	342	N
8	5.3	7.20	460	C
9	4.5	7.28	350	N
10	4.7	6.90	410	C
11	5.3	7.00	470	C
12	4.2	7.15	410	J

*C = Cottonwood River; N = Neosho River; J = After Cottonwood and Neosho Rivers Join

TABLE 12.1
ANALYSIS OF SAMPLES TAKEN ON MARCH 5, 1971

Sample	Alkalinity HCO_3^- (ppm)	Salinity Cl^- (ppm)	$\text{SO}_4^{=}$ (ppm)	NO_3^- (ppm)	Hg^{++}
1	238 \pm 2	UD*	14.9 \pm 0.7	2.3 \pm 0.2	UD**
2	208 \pm 2	UD	15.8 \pm 0.8	2.3 \pm 0.2	UD
3	218 \pm 2	UD	13.7 \pm 0.7	2.1 \pm 0.2	UD
4	189 \pm 2	UD	9.6 \pm 0.5	1.1 \pm 0.1	UD
5	195 \pm 2	UD	10.6 \pm 0.5	1.2 \pm 0.1	UD
6	188 \pm 2	UD	10.5 \pm 0.5	0.9 \pm 0.1	UD
7	195 \pm 2	UD	10.1 \pm 0.5	1.4 \pm 0.1	UD
8	210 \pm 2	UD	14.4 \pm 0.7	2.1 \pm 0.2	UD
9	191 \pm 2	UD	10.7 \pm 0.5	0.8 \pm 0.1	UD
10	212 \pm 2	UD	14.8 \pm 0.7	2.3 \pm 0.2	UD
11	214 \pm 2	UD	15.2 \pm 0.8	2.3 \pm 0.2	UD
12	236 \pm 2	UD	19.6 \pm 0.9	2.1 \pm 0.2	UD

*Undetectable

An addition of 5 ml. of 0.1 N AgNO_3 produced no visible precipitate.

**Electrode shows negative response.

TABLE 13
ANALYSIS OF SAMPLES TAKEN ON MARCH 31, 1971

Sample	Temperature (°C)	pH	Conductance (mho)	River*
1	11.5	7.60	622	C
2	11.2	7.60	692	C
3	11.5	7.70	700	C
4	11.7	7.70	465	N
5	10.4	7.80	471	N
6	13.8	7.50	480	N
7	13.0	7.70	480	N
8	12.4	7.60	700	C
9	13.5	7.70	482	N
10	12.0	7.60	705	C
11	13.2	7.80	699	C
12	12.5	7.80	658	J

*C = Cottonwood River; N = Neosho River; J = After Cottonwood and Neosho Rivers Join

TABLE 13.1
ANALYSIS OF SAMPLES TAKEN ON MARCH 31, 1971

Sample	Alkalinity HCO_3^- (ppm)	Salinity Cl^- (ppm)	$\text{SO}_4^{=}$ (ppm)	NO_3^- (ppm)	Hg^{++}
1	300 \pm 3	137.0 \pm 0.7	29.0 \pm 1.4	2.7 \pm 0.3	UD**
2	309 \pm 3	56.8 \pm 0.3	26.2 \pm 1.3	2.3 \pm 0.2	UD
3	310 \pm 3	95.0 \pm 0.5	26.3 \pm 1.3	2.5 \pm 0.3	UD
4	257 \pm 3	UD**	15.9 \pm 0.8	2.0 \pm 0.2	UD
5	291 \pm 3	UD	16.0 \pm 0.8	2.1 \pm 0.2	UD
6	258 \pm 3	UD	17.6 \pm 0.9	2.1 \pm 0.2	UD
7	258 \pm 3	UD	17.6 \pm 0.9	2.3 \pm 0.2	UD
8	317 \pm 3	48.0 \pm 0.2	25.0 \pm 1.2	2.8 \pm 0.3	UD
9	264 \pm 3	UD	17.1 \pm 0.9	2.1 \pm 0.2	UD
10	314 \pm 3	39.0 \pm 0.2	25.3 \pm 1.3	2.6 \pm 0.3	UD
11	308 \pm 3	51.0 \pm 0.3	25.1 \pm 1.2	2.7 \pm 0.3	UD
12	308 \pm 3	37.0 \pm 0.2	23.4 \pm 1.1	2.7 \pm 0.3	UD

*Undetectable

An addition of 5 ml. of 0.1 N AgNO_3 produced no visible precipitate.

**Electrode shows negative response.

TABLE 14

PRECIPITATION IN THE EMPORIA AREA FROM JANUARY 28
THROUGH MARCH 31, 1971, AS REPORTED BY THE
FEDERAL AVIATION ADMINISTRATION WEATHER MONITOR

Date	Rainfall (inches)	Date	Rainfall (inches)
January		March	
28	0.00	1	trace
29	0.00	2	0.00
30	trace	3	0.00
31	trace	4	0.00
February		5	0.00
1	0.01	6	0.00
2	0.00	7	0.00
3	0.00	8	0.00
4	0.40	9	0.06
5	0.01	10	0.00
6	0.00	11	0.00
7	0.00	12	0.00
8	0.00	13	0.00
9	0.00	14	trace
10	0.00	15	0.00
11	0.06	16	0.00
12	0.00	17	0.00
13	0.00	18	trace
14	0.00	19	trace
15	0.00	20	0.00
16	0.00	21	0.00
17	0.00	22	0.00
18	0.26	23	0.00
19	trace	24	0.20
20	0.00	25	trace
21	0.56	26	0.00
22	0.23	27	0.00
23	0.00	28	0.00
24	0.00	29	0.00
25	0.00	30	0.00
26	0.00	31	0.00
27	0.00		
28	0.08		

TABLE 15
 DATA ON CHLORIDE INTERFERENCE
 USING AN IODIDE ELECTRODE FOR
 MERCURIC ION* DETERMINATIONS

NaCl added (gram)	Molarity of Cl ⁻ Ion	Scale Reading
0.00235	3.432×10^{-5}	6.85 \pm 0.04
0.00635	1.271×10^{-4}	6.45 \pm 0.02
0.05930	0.993×10^{-3}	5.72 \pm 0.01
0.57925	0.946×10^{-2}	4.9 \pm 0.00
0	0	6.85 \pm 0.04

*Mercuric ion concentration = $5.22 \times 10^{-5} \pm 5 \times 10^{-6}$;
 KClO₄ concentration = 13.85 gm/l.