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Assay of Brines for Common Radiolysis Products

C. S. MacDougall

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NUCLEAR WASTE PROGRAMS
Study of Radiation Chemistry of Salt Mine Brines
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ASSAY OF BRINES FOR COMMON RADIOLYSIS PRODUCTS

C. S. MacDougall

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C. S. MacDougall

ABSTRACT

Brines are assayed for four common products of radiolytic reaction. Free chlorine is determined spectrophotometrically after reaction with *o*-tolidine. The test is specific for chlorine, and quantities of chlorine from 0.1 to 6 μg in the test aliquot are determined with a precision of about ±5%. Hydrogen peroxide is reacted with xylenol orange and determined spectrophotometrically with a precision of ±5% on 2-μg quantities of peroxide. A spectrophotometric method using thiocyanate is employed in the chlorate assay. After subtracting the bias caused by any H_2O_2 or Cl_2, 1-μg quantities of chlorate can be determined with a precision of ±10%. Perchlorate ion quantities of 1 ppm can be determined directly in brines by ion chromatography with a precision of about ±15%.

INTRODUCTION

One technique proposed for disposal of both high- and low-level radioactive waste is storage in a geologically suitable salt repository. Long-term safety considerations have thus spurred interest in the products formed by radiolysis of concentrated solutions of brines. A large body of information has previously been reported concerning the radiation chemistry of materials around waste canisters in salt.[1-4] However, complete elucidation of the radiation chemistry of the salt-mine brines requires additional laboratory work. It was the purpose of this project to provide the analytical methodology necessary to support the radiolysis studies.

Primary products of radiolysis of water are known to be $e^-(aq)$, $H\cdot$, $\cdot OH$, H_2O_2, H_2, and H_3O^+. The number of a species produced per 100 eV of absorbed radiation energy is represented by $G(H_2)$, $G(H\cdot)$, etc. These primary products may further react with each other or with other solutes present in solution. The overall molecular product concentrations (expressed as G values) depend on these further reactions. It was in the molecular product concentrations produced by irradiation of brine solutions that we were interested. Hydrogen is known to be the only reduced non-radical species formed in irradiated brine solutions.[2] Several oxidized species have been postulated, and the relationship between conceivable species—oxidized and reduced—is given by the following equation:

$$\begin{aligned} 2G(H_2) = {} & 2G(Cl_2) + 5G(ClO_2) + 2G(Cl_2O) \\ & + 4G(O_2) + 2G(H_2O_2) + 6G(ClO_3^-) \\ & + 8G(ClO_4^-) + 4G(ClO_2^-) \quad . \end{aligned} \tag{1}$$

In order to fully elucidate the radiation chemistry of these brine solutions, microanalytical techniques for free Cl_2, H_2O_2, ClO_3^-, and ClO_4^- (believed to be the major oxidized species formed during irradiation) had to be developed, adapted, and tested. Concentrations of the species of interest were not expected to exceed ~30 ppm in saturated brine,[1] which greatly limited the choice of analytical methods.

EXPERIMENTAL

All spectrophotometric measurements were made using a Perkin-Elmer model 570 spectrophotometer with standard 1-cm quartz cuvettes. Ion chromatographic assays were performed with a Dionex System 10 ion chromatograph. Comparable instruments could be substituted in either analysis. Explicit directions for Cl_2, H_2O_2, ClO_3^-, and ClO_4^- assays are detailed in Appendices A–D. Preparations of reagents and standards are also described in each Appendix.

RESULTS AND DISCUSSION

Free Chlorine

A spectrophotometric technique utilizing *o*-tolidine was chosen for the determination of free chlorine. In neutral solutions, *o*-tolidine reacts with free chlorine to form a green-colored complex. The absorbance of the color-developed solution obeys Beer's law at 625 nm. A variation of this technique has been used for some time to analyze environmental samples.[5] However, several modifications to the basic technique were necessary to adapt this method to the assay of saturated brines containing a variety of significant impurities (including nitrates and bromides). Normally, a buffer-stabilizer would be utilized to minimize low-pH interference or high-pH fading. However, the buffer formed a turbid solution when brine was added. Therefore, no buffer was used, and all color development was carefully timed. The technique consists of adding 0.5 mL of *o*-tolidine reagent to a 10-mL volumetric flask and diluting to approximately 8 mL with deionized water; the chloride concentration is adjusted to 1.09 *M* by addition of saturated $MgCl_2$ solution. To this mixture is added an aliquot of sample containing ~0.1 to 6 μg free chlorine. The solution is diluted to the mark with deionized water, and the solution absorbance is immediately measured against a reagent blank at 625 nm. Although no appreciable change in the absorbance of the colored complex was noted in the presence of brine (Fig. 1), the total quantity of chloride ion was maintained at 1.09 *M* in the color-developed test solution by addition of saturated $MgCl_2$. We wished to keep the redox potentials of the color-developed sample and standard solutions as nearly identical as possible in order to minimize interferences by impurities in the sample. The highest concentration of chloride expected in the brines was 10.9 *M* (saturated $MgCl_2$). Sample volumes averaged 1 mL, which when assayed by the described technique, were diluted tenfold in the color-developed solution, giving a final chloride concentration of 1.09 *M*. Some saturated stock $MgCl_2$ is added to brines having a lower chloride content, such as saturated NaCl, to adjust final chloride content at 1.09 *M*. Since chlorate and hydrogen peroxide were expected to be products of the radiolysis of brine, their effects upon the assay for free chlorine were examined. Chlorate ion up to 10 μg/mL does not interfere with the chlorine analysis (Fig. 2). Hydrogen peroxide does not interfere in the analysis per se. However, H_2O_2 does quantitatively react with free chlorine under radiolysis conditions according to the following equation:

$$Cl_2 + H_2O_2 \rightarrow 2H^+ + 2Cl^- + O_2 \quad . \qquad (2)$$

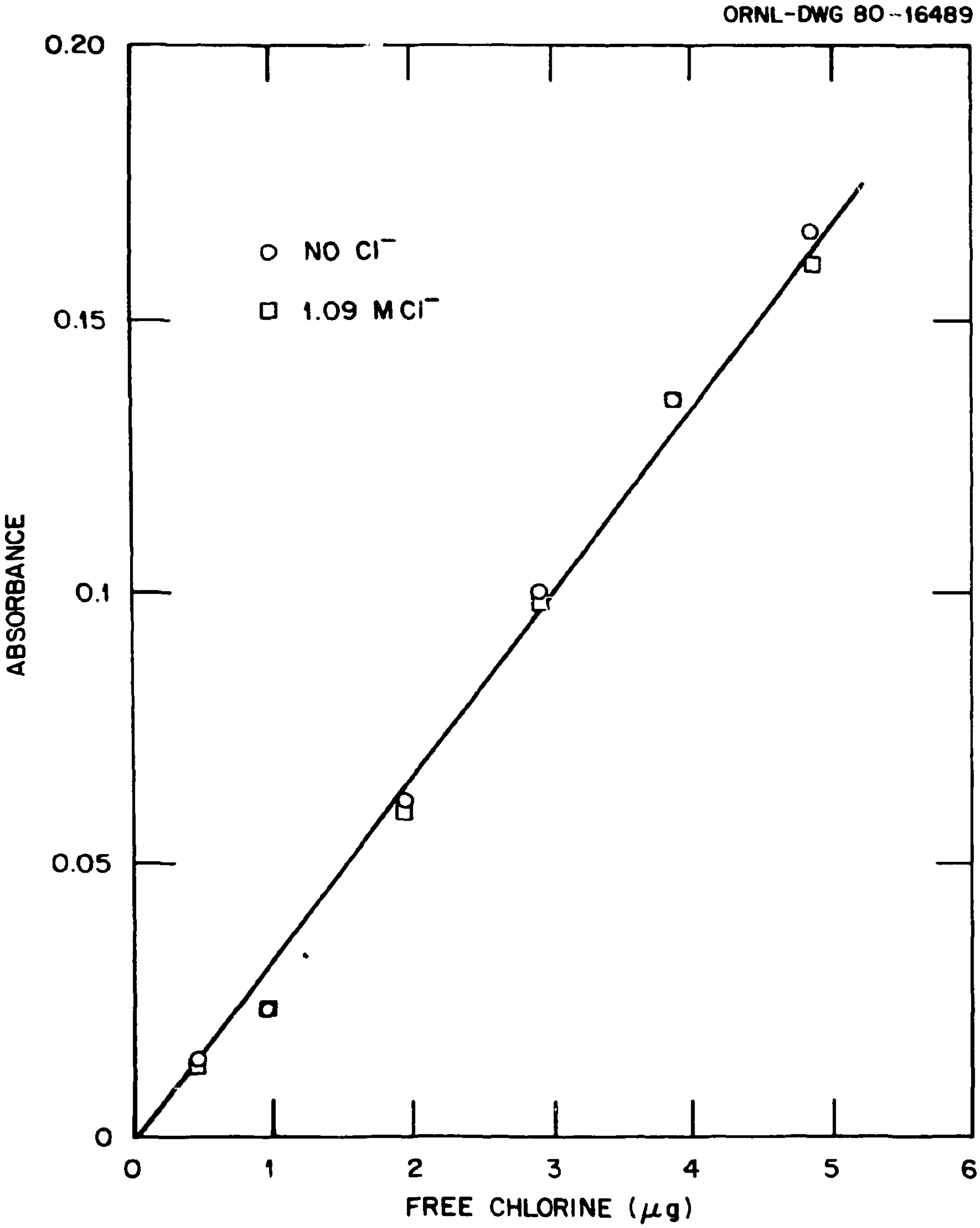

Fig. 1. Effect of chloride ion on free chlorine determination.

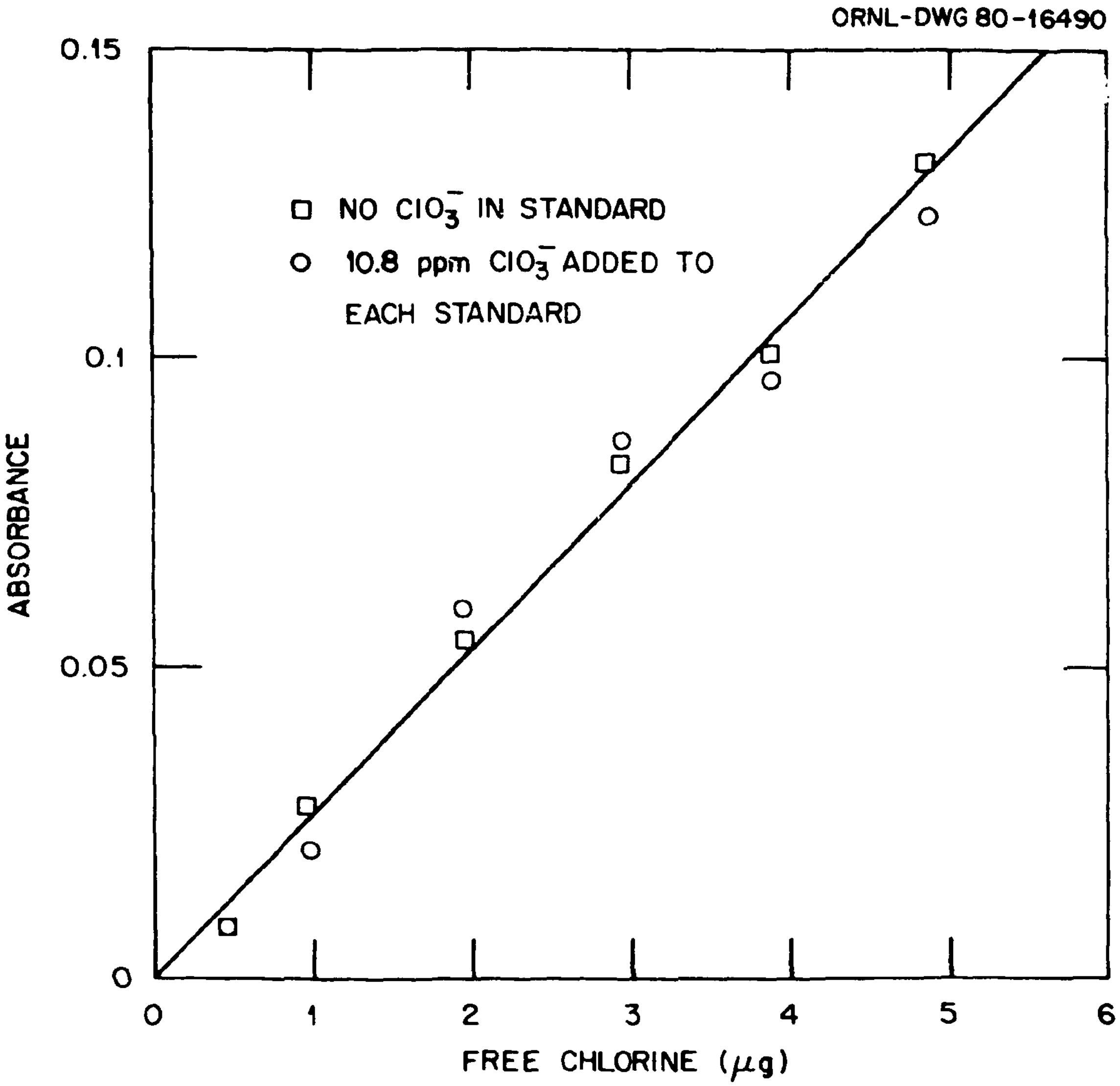

Fig. 2. Effect of chlorate ion on free Cl_2 assay.

Therefore, the presence of peroxide signals the absence of free chlorine and vice versa. Table 1 summarizes data supporting the above statement.

Table 1. Reaction of free chlorine with hydrogen peroxide

Run	H_2O_2 added (meq)	Cl added (meq)	Cl found (meq)
1	1.74 (29.6 mg)	0.137 (4.85 mg)	0
2	0.07 (1.18 mg)	0.137 (4.85 mg)	0.065 (97.4% recovery)
3	0.14 (2.36 mg)	0.137 (4.85 mg)	0

This technique is relatively specific for chlorine, and quantities of free chlorine from 0.1 to 6 μg in the test aliquot are determined with a precision of about ±5%.

Hydrogen Peroxide

A technique using the oxidation of Fe(II) with H_2O_2, followed by spectrophotometric determination of the Fe(III)/xylenol orange complex, was chosen for the determination of hydrogen peroxide.[6] Hydrogen peroxide, in dilute H_2SO_4 (0.05 *N*), oxidizes Fe(II) to Fe(III). Under these conditions, the Fe(III) forms a complex with xylenol orange (xo), which absorbs energy at the 540-nm wavelength. The absorbance is directly proportional to the Fe(III) concentration, which is in turn directly related to the original concentration of H_2O_2. A slight enhancement in Fe(III)/xo absorbance was noted in the presence of chloride (Fig. 3). Therefore, when analyzing brine for H_2O_2, the total quantity of Cl^- was maintained at 1.09 *M* in the color-developed solution, as explained in the previous section. Chlorate and perchlorate ions, typically present in irradiated brines, do not oxidize the Fe(II) under the conditions of this experiment.

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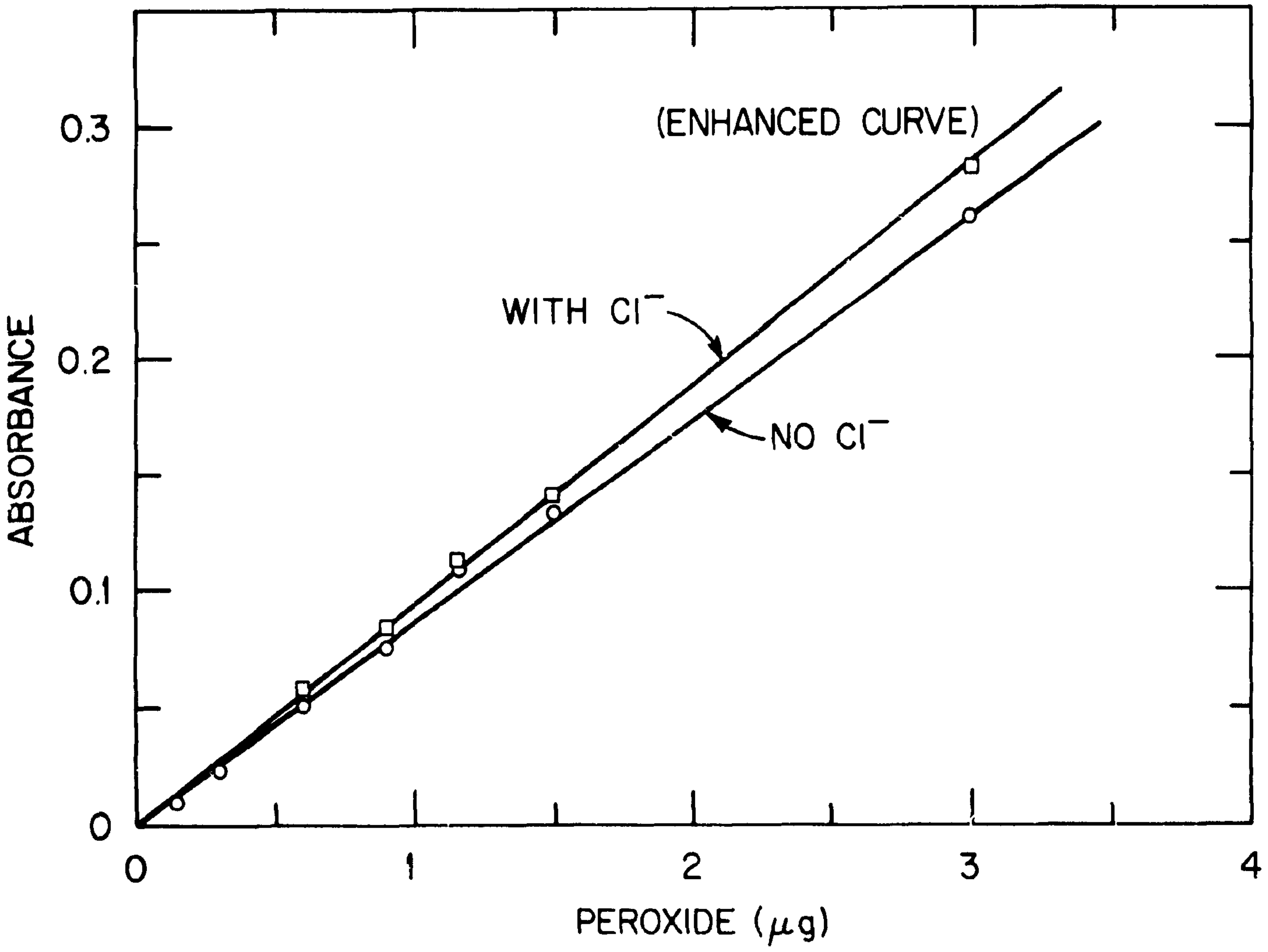

Fig. 3. Effect of chloride ion on assay for H_2O_2.

Therefore, they do not interfere with the assay for H_2O_2. Although free chlorine would react with the Fe(II) added for color development and would hence interfere, H_2O_2 and Cl_2 are mutually incompatible in brine solutions, as explained in the section on free Cl_2. Therefore, if H_2O_2 is present to be measured, Cl_2 is not present and will not interfere. Of course, any other redox reagent that would interact with the Fe(III)/Fe(II) couple would interfere in the technique. Quantities of H_2O_2 from 0.1 to 3 μg in the test aliquot can be determined with a precision of about ±5%. The method is fairly specific for H_2O_2 in irradiated brines because possible interfering species are generally not present.

Chlorate

Chlorate ion, in moderately concentrated H_2SO_4 (3 *M*), oxidizes Fe(II) to Fe(III). A few drops of 0.1 *M* OsO_4 in H_2SO_4 are used to catalyze the oxidation.[7] The Fe(III) that is produced forms a complex with thiocyanate, which absorbs energy at the 480-nm wavelength. The absorbance is directly proportional to the Fe(III) concentration, which is in turn directly related to the original concentration of ClO_3^-. Fig. 4 shows a typical calibration curve for ClO_3^- in brine. Of course, any redox reagent that would interact with the Fe(III)/Fe(II) couple would interfere in the technique. Both H_2O_2 and free Cl_2 react with Fe(II) under the described conditions to positively bias the chlorate assay. Since each effect is quantitative, however, that bias may be subtracted and the chlorate assayed. Total quantity of Cl^- is maintained at 1.09 *M* in the color-developed solution to eliminate matrix effects in the color development.[8] Quantities of ClO_3^- from 0.2 to 10 μg in the test aliquot are determined with a precision of about ±10%.

Perchlorate

Perchlorate ion in brines can be assayed directly without prior separation from chloride by ion chromatography. A commercial column set procured from Dionex is used directly with no modifications. Fig. 5 shows a typical chromatogram of ClO_4^- in saturated brine. Anions, such as ClO_3^-,

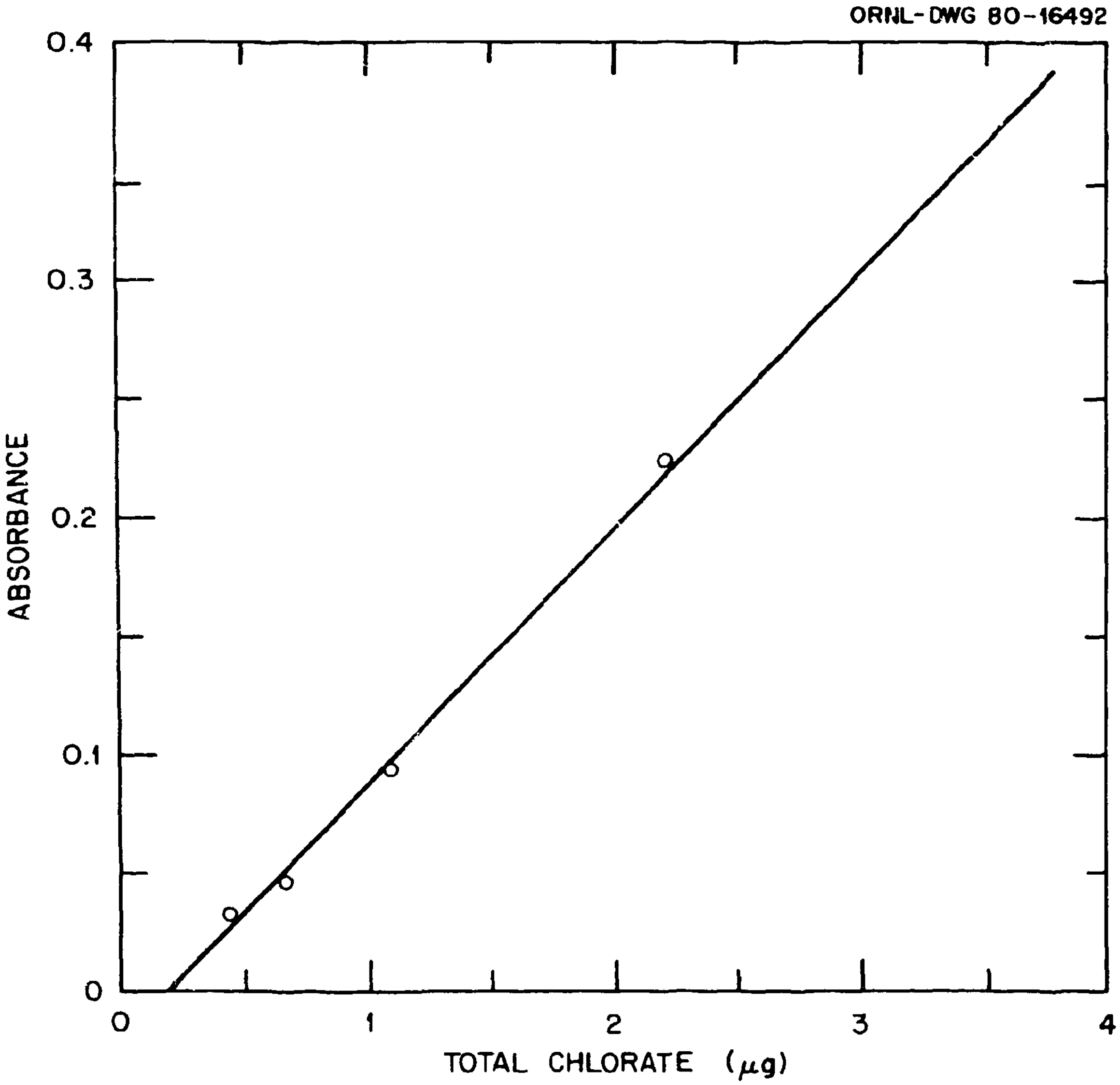

Fig. 4. Calibration curve for chlorate.

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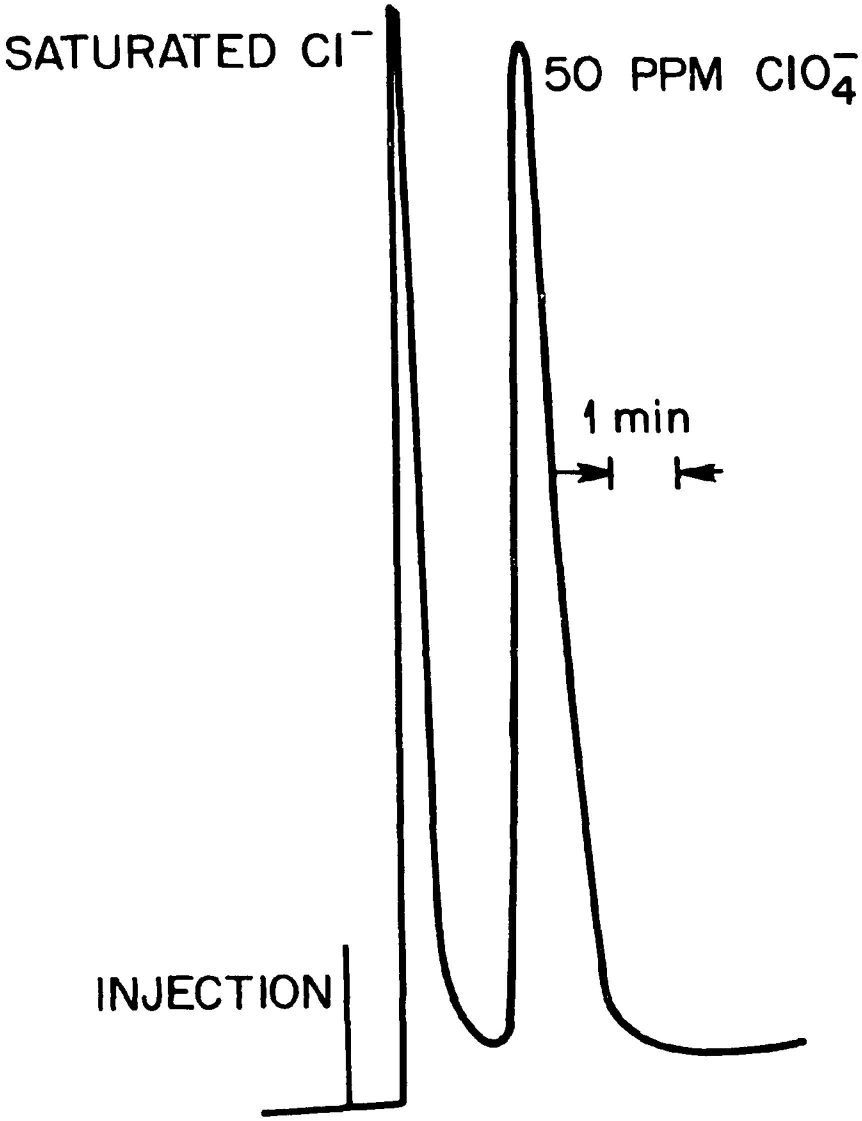

Fig. 5. Chromatogram of ClO_4^- in saturated $MgCl_2$.

NO_3^-, Cl^-, etc., are eluted with 0.005 *M* I at the beginning of the assay. The ClO_4^- ion, which is more tightly bound to the separator, is retained for about 4–6 min and is well separated from impurity peaks. Fig. 6 gives a typical calibration curve for ClO_4^-. Perchlorate can be detected in quantities as low as 0.3 ppm with an approximate precision of ±15%.

Overall Assay for Radiolysis Products in Brines

The following order of assay is recommended:

1. Assay for free Cl_2. The method described is relatively specific for free Cl_2. If no chlorine is found, proceed with step 2. If a test for chlorine is positive, go to step 3.

2. Assay for H_2O_2. If no free chlorine is present, some excess peroxide may or may not be in the sample. This technique is specific for H_2O_2 in brines containing no free chlorine.

3. Assay for ClO_3^-. This method will be sufficient for ClO_3^- in brines if the bias introduced by either free Cl_2 or H_2O_2 is calculated.

4. Assay for ClO_4^-. This test is specific for ClO_4^-.

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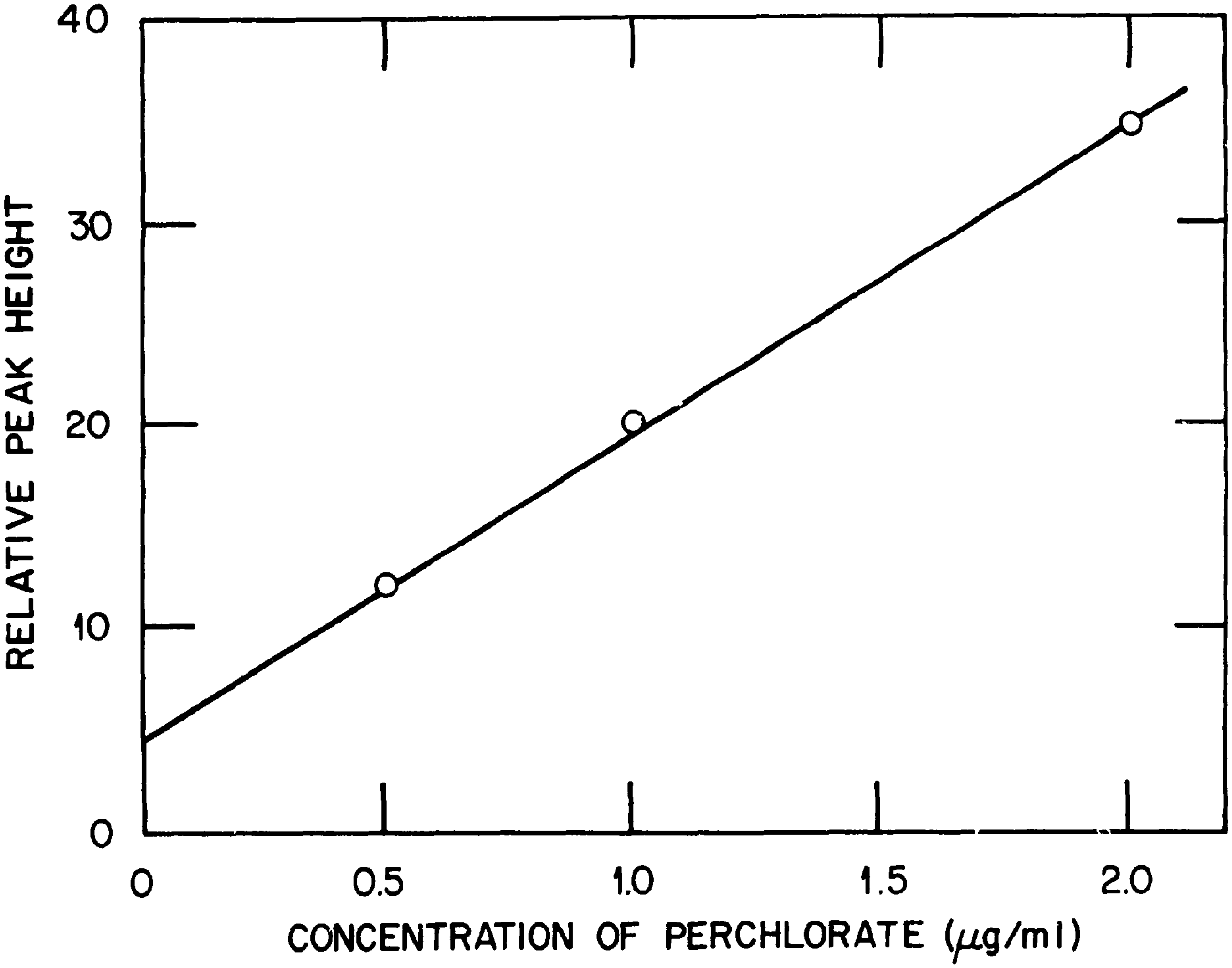

Fig. 6. Calibration curve for perchlorate by ion chronatography.

REFERENCES

1. G. H. Jenks, *Review of Information on the Radiation Chemistry of Materials Around Waste Canisters in Salt and Assessment of the Need for Additional Experimental Information*, ORNL-5607 (March 1980).

2. G. H. Jenks, *Radiolysis and Hydrolysis in Salt-Mine-Brines*, ORNL-TM-3717 (March 1972).

3. G. H. Jenks, *Effects of Temperature, Temperature Gradients, Stress, and Irradiation on Migration of Brine Inclusions in a Salt Repository*, ORNL-5526 (July 1979).

4. G. H. Jenks, E. Sonder, C. D. Bopp, J. R. Walton, and S. Lindenbaum, "Reaction Products and Stored Energy Released from Irradiated Sodium Chloride by Dissolution and by Heating," *J. Phys. Chem.* 79: 871 (1975).

5. *Standard Methods for the Examination of Water and Wastewater*, 14th ed., published by American Public Health Assoc., American Waste Works Assoc., and Water Pollution Control Federation, Washington, D. C., 1976.

6. B. L. Gupta, "Microdetermination Techniques for H_2O_2 in Irradiated Solutions," *Microchem. J.* 18: 363 (1973).

7. G. F. Smith and A. J. Veraguth, "The Determination of Chlorates in the Presence of Perchlorates. Reduction of Chlorates in Acid Solution Employing Excess Fe(II) or As(III)," *Anal. Chim. Acta* 17: 386 (1957).

8. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, New York, 1944.

APPENDICES

APPENDIX A. DETERMINATION OF FREE CHLORINE IN BRINE SOLUTIONS

1. Reagents

1. Thiosulfate, approx 0.025 *N*. Dissolve approx 6.2 g $Na_2S_2O_3 \cdot 5H_2O$ in recently boiled distilled water. To this, add 1 mL 0.1 *N* NaOH. Transfer mixture to a 1-liter volumetric flask, and dilute to the mark with distilled water. Allow the solution to age overnight. Standardize against NBS-136b ($K_2Cr_2O_7$) by the following technique:

   a. Weigh approx 0.02 g dichromate into a 125-mL Erlenmeyer flask.
   b. Add approx 50 mL deionized H_2O.
   c. Add 3 mg KI and then 6 mL concentrated HCl.
   d. Allow mixture to sit in the dark for 5 min.
   e. Titrate with $S_2O_3^{2-}$ from a red color to a light yellow-green.
   f. Add starch solution.
   g. Titrate from blue to a light green end point.

2. Standard chlorine, approx 1.0 mg free chlorine per mL. Pipet 2 mL of stock 5% NaOCl into a 1-liter flask, and dilute to the mark with deionized H_2O. Standardize against thiosulfate (solution 1) by the following technique:

   a. Into a 150-mL Erlenmeyer flask, pipet 2 mL concentrated acetic acid.
   b. Add 15–25 mL deionized H_2O.
   c. Add 1 g KI and swirl the mixture until the KI is dissolved.
   d. Pipet 25 mL of the standard chlorine solution into the flask.
   e. Titrate with $S_2O_3^{2-}$ to a pale yellow color.
   f. Add 2–5 mL starch solution.
   g. Continue the titration to the disappearance of the blue color.

3. Orthotolidine reagent. Add 5 mL of concentrated HCl to 100 mL of deionized H_2O. Add 10 mL of this solution, 20 mg $HgCl_2$, 30 mg $Na_2C_{10}H_{13}O_8N_2 \cdot 2H_2O$ (disodium salt of EDTA) and 1.5 g orthotolidine dihydrochloride to deionized H_2O; dilute to one liter. Store this solution in an opaque bottle. Replace reagent every six months.

4. Magnesium chloride, saturated.

2. Preparation of Standards Curve

1. Pipet 0.5 mL of orthotolidine reagent into each of seven 10-mL volumetric flasks.

2. Dilute to approximately 8 mL with deionized H_2O.

3. To six of the flasks (all except the blank), add 1 mL saturated $MgCl_2$.

4. Pipet 0, 5, 10, 20, 30, 40, and 50 μL aliquots of the free chlorine standard into the flasks.

5. Dilute to the marks with deionized H_2O.

6. Shake each standard, and allow 1 min for color development. (TIMING IS IMPORTANT.)

7. Measure the absorbance at 625 nm of each standard against the reagent blank (no Cl_2 added).

8. Prepare a standard curve by plotting absorbance values on the ordinate (y-axis) and total Cl_2 on the abscissa (x-axis).

3. Assay of Sample

1. Pipet 0.5 mL of orthotolidine reagent into a 10-mL volumetric flask, and dilute to approximately 5 mL with deionized H_2O.

2. Adjust the chloride content by adding an appropriate aliquot of saturated $MgCl_2$ to yield 1.09 M Cl^- in the color-developed solution.

3. To this mixture, add an aliquot of sample containing approx 0.1–6 μg free chlorine.

4. Proceed with steps 5–7 above.

5. Compare sample absorbance to the standard curve, and read the total μg Cl (X).

4. Calculations

Let

X = total μg free chlorine, as read from standards curve for the measured sample absorbance,

V = volume of sample aliquot in mL, and

C = concentration of Cl_2 in original sample in μg/mL.

Thus,

$$C = X/V \quad .$$

APPENDIX B. DETERMINATION OF H_2O_2 IN AQUEOUS OR BRINE SOLUTIONS

1. Reagents

1. Sulfuric acid, 0.1 *N*. Add 3 mL of concentrated H_2SO_4 to 500 mL H_2O and dilute to 1 liter.

2. Fe(II) solution, 2 × 10^{-3} *M* Fe(II) in 0.1 *N* H_2SO_4. Weigh 784 mg $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ into a 1-liter flask. Dilute to the mark with 0.1 *N* H_2SO_4 (solution #1).

3. Xylenol orange (XO). Dissolve 300 mg XO in 100 mL H_2O.

4. Potassium permanganate, 0.1 *N*. Weigh approximately 3.3 g $KMnO_4$ into a 1-liter flask. Dissolve the crystals in 200 mL hot distilled H_2O. Dilute the resultant solution to one liter with distilled H_2O and allow to stand overnight (preferably over the weekend). After aging, filter the solution through a fine glass frit and store the standard in a glass-stoppered bottle. Standardize this solution against NBS-40h sodium oxalate.

5. Stock H_2O_2, 3%. Dilute 10 mL of 30% H_2O_2 to 100 mL with deionized H_2O. Store in a refrigerator when not in use. Standardize this solution against the potassium permanganate (above) in the following manner:

   a. Place 75 mL of 3% v/v H_2SO_4/H_2O in a 250-mL beaker.

   b. Pipet in 1 mL of the 3% H_2O_2 solution.

   c. Titrate with standard $KMnO_4$ to a faint pink color. This will yield a stock solution with a titer of about 25 mg H_2O_2/mL.

6. Working H_2O_2 standard, approx 25 µg/mL. Dilute 1 mL of the stock H_2O_2 to 1 liter with deionized H_2O.

7. Magnesium chloride, saturated.

2. Preparation of Standards Curve

1. Pipet 4 mL of 0.1 *N* H_2SO_4 into eight 10-mL volumetric flasks.

2. Pipet 1 mL of XO color reagent into each flask.

3. Pipet 0, 5, 10, 20, 30, 40, 50, and 100 µL aliquots of the working H_2O_2 standard into the flasks.

4. To each standard, add 1 mL of saturated $MgCl_2$.

5. Pipet 1 mL of Fe(II) solution into each flask, and dilute each mixture to the mark with deionized H_2O.

6. Shake each standard, and allow 10 min for stabilization and color development.

7. Measure the absorbance at 540 nm of each standard against the reagent blank (no H_2O_2 added).

8. Prepare a standards curve by plotting absorbance values on the ordinate (y-axis) and total H_2O_2 on the abscissa (x-axis).

3. Assay of Sample

1. Pipet 4 mL of 0.1 *N* H_2SO_4 into a 10-mL volumetric flask.

2. Pipet 1 mL of XO color reagent into the flask.

3. To this volumetric flask, add an aliquot of sample containing from 0.1 to 3 μg H_2O_2.

4. Adjust the chloride content by adding an appropriate aliquot of saturated $MgCl_2$.

5. Proceed with steps 5–7 listed above.

6. Compare sample absorbance to the standards curve and read the total μg H_2O_2 (X).

4. Calculations

Let

X = total μg H_2O_2 for sample, as read from standards curve for the measured sample absorbance,

V = volume of sample aliquot in mL, and

C = concentration of H_2O_2 in original sample in μg/mL.

Thus,

$$C = X/V .$$

APPENDIX C. DETERMINATION OF CHLORATE IN BRINE SOLUTIONS

1. Reagents

1. Sulfuric acid, concentrated, reagent grade.

2. Sulfuric acid, 6 *M*. Take 360 mL of pure, concentrated H_2SO_4, sp gr 1.84, and pour it cautiously and slowly into about 1-2 volumes of water. Cool, mix thoroughly, and dilute to 1 liter.

3. Sulfuric acid, 0.1 *N*. Add 3 mL of concentrated H_2SO_4 to 500 mL H_2O and dilute to 1 liter.

4. Fe(II) solution, 2×10^{-3} *M* Fe(II) in 0.1 *N* H_2SO_4. Weigh 784 mg $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ into a 1-liter flask. Dilute to the mark with 0.1 *N* H_2SO_4 (solution #3).

5. Potassium thiocyanate, 1.5 *M*. Weigh 72.9 g KSCN into a 500-mL volumetric flask and dilute to the mark with distilled water.

6. Osmium tetroxide, 0.01 *M* in 0.1 *M* H_2SO_4, G. F. Smith or similar.

7. Magnesium chloride, saturated.

8. Ceric sulfate, 0.1 *N*. Weigh approximately 53 g $Ce(HSO_4)_4$ into a 1-liter flask. Add 23 mL of concentrated H_2SO_4 to 300 mL H_2O and add this mixture to the ceric salt. After dissolution, dilute the mixture to 1 liter and allow to stand overnight. Standardize against NBS-40h sodium oxalate.

9. Stock ClO_3^-. Weigh 3.5 g of $NaClO_3$ into a 1-liter flask, and dilute to the mark with H_2O. Standardize this solution against the ceric solution (#8) in the following manner:

   a. Pipet a 5-mL aliquot of chlorate solution into a 250-mL beaker.
   b. Add 125 mL H_2O and 5 mL conc H_2SO_4.
   c. Heat the mixture to boiling, and boil for 3 min.
   d. Add 20 mL 0.1 *N* ferrous ammonium sulfate and take the solution back to boiling.
   e. Cool the mixture to room temperature and titrate the excess Fe(II) with standard Ce^{+4} (potentiometrically).
   f. Determine a blank by titrating 20 mL ferrous solution in the same manner.
   g. This gives a stock solution with a titer of about 2 mg ClO_3^- per mL solution.

10. Working ClO_3^- standard, approx 200 μg ClO_3^-/mL. Dilute 10 mL of the stock ClO_3^- to 100 mL with deionized water.

2. Preparation of Standards Curve

1. Pipet 2, 3, 5, 10, and 20 μL of the working ClO_3^- standard into five 5-ml volumetric flasks.

2. Pipet 500 μL saturated $MgCl_2$ into the flasks.

3. Add 800 μL 6 *M* H_2SO_4.

4. Add 4 drops of OsO_4 from an eye dropper.

5. Pipet in 400 μL of ferrous solution (#4).

6. Swirl the solution and let sit for 60 min.

7. After oxidation of the Fe(II) by ClO_3^-, pipet in 1 mL KSCN (solution 5) and dilute to the mark with water.

8. Immediately measure the solution absorbance at 480 nm of each standard against a reagent blank (no ClO_3^- added).

9. Prepare a standards curve by plotting absorbance values on the ordinate (y-axis) and total ClO_3^- on the abscissa (x-axis).

3. Assay of Sample

1. Pipet an aliquot of sample containing from 0.2 to 10 μg ClO_3^- into a 5-mL volumetric flask.

2. Adjust the chloride content to 1.09 *M* (final solution) by adding an appropriate aliquot of saturated $MgCl_2$.

3. Proceed with steps 3–8 listed above.

4. Compare sample absorbance to the standards curve and read equivalent μg $[ClO_3^-]$.

4. Calculations

Let

$[ClO_3^-]$ = total equivalent μg ClO_3^-, as read from standards curve for measured sample absorbance,

[Cl] = total free chlorine in sample aliquot in μg,

$[H_2O_2]$ = total H_2O_2 in sample aliquot in μg,

C = concentration of ClO_3^- in original sample in µg/mL, and

V = volume of sample aliquot in mL.

Then,

$$C = \frac{\{[ClO_3^-] - 0.39[Cl] - 0.82[H_2O_2]\}}{V} \quad .$$

APPENDIX D. DETERMINATION OF PERCHLORATE IN BRINES

1. Reagents

1. Sodium iodide, 0.005 *M*. Weigh 1.499 g NaI into a 2-liter volumetric flask and dilute to volume with deionized water.

2. Stock perchlorate, approx 1.0 mg ClO_4^-/mL. Weigh 1.41 g $NaClO_4 \cdot H_2O$ into a 1-liter flask and dilute to volume with deionized H_2O.

3. Perchlorate, working standards, 0.5, 1.0, 2.0 µg ClO_4/mL. Dilute 0.5, 1.0, and 2.0 mL of stock solution #2 to 1 liter in saturated $MgCl_2$.

4. Magnesium chloride, saturated.

2. Preparation of Standards Curve and Sample Assay

1. Insert separator column #20232 and suppressor column #30583 into the ion chromatograph.

2. Preflush columns for 1/2 h with distilled water.

3. After samples and standards are prepared, begin flushing the sample train with 0.005 *M* NaI at a flow of 30% pump capacity.

4. Set mode switch to linear and the µmho sale at X 1.

5. Allow the baseline to stabilize.

6. Immediately upon baseline stabilization, fill the injection loop with the first standard and inject.

7. Record the peak height of the perchlorate peak.

8. Rinse out sample loop and inject other standards.

9. Record the corresponding perchlorate peak heights.

10. Prepare a standards curve by plotting peak height values on the ordinate (y-axis) and perchlorate values on the abscissa (x-axis).

11. Rinse out the sample loop and inject sample.

12. Record peak height for perchlorate in sample.

13. Compare sample peak height to the standards curve and read concentration ClO_4^- directly.