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The Determination of Iodide in Brine

INTRODUCTION

Feed brines for chlor-alkali cells must be relatively free of alkaline earth metals and iodide. Brines high in alkaline earth metals shorten membrane life due to the interaction of these metals with iodide at the membrane surface.

In this Application Update, ion chromatography coupled with pulsed amperometric detection is used to determine iodide in brine (approximately 30% sodium chloride). This method is specific, sensitive, and rapid. Sample preparation is a simple sample dilution. Iodide is separated on the IonPac® AS11 column, which contains a hydrophilic resin that is well suited to the chromatography of iodide, a relatively hydrophobic anion. Using a nitric acid eluent, the iodide ion elutes from the column in under five minutes. Although iodide can be detected by direct current (dc) amperometry on a silver working electrode, a pulsed amperometric waveform is used to improve the reproducibility of iodide analysis.¹ The linearity and reproducibility of iodide detection by pulsed amperometry have been demonstrated.² The detection limit of iodide using pulsed amperometric detection is in the low µg/L range.

EQUIPMENT

Dionex DX-500 Chromatography system consisting of:

- GP40 Gradient Pump with vacuum degas option
- LC25 or LC30 Liquid Chromatography Module
- ED40 Electrochemical Detector
- EO1 Eluent Organizer
- AS3500 Autosampler

Dionex PeakNet Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water, 17.8 MΩ-cm resistivity or better
Concentrated nitric acid (16 M), ultrapure (J.T. Baker)
Potassium iodide (Fisher Scientific)

CONDITIONS

Column: IonPac AS11 Analytical, 4 x 250 mm (P/N 44076)
IonPac AG11 Guard, 4 x 50 mm (P/N 44078)

Expected Operating Pressure: 6.5 MPa (950 psi)

Degas Interval: 10 min

Injection Volume: 50 µL

Injection Loop: 100 µL

Eluent: 50 mM Nitric acid

Flow Rate: 1.5 mL/min

Detection: Pulsed amperometry, silver working electrode, Ag/AgCl reference

Waveform for the ED40 Detector:

<u>Time (sec)</u>	<u>Potential (V)</u>	<u>Integration</u>
0.00	+0.1	
0.20	+0.1	Begin
0.90	+0.1	End
0.91	-0.8	
0.93	-0.3	
1.00	-0.3	

Collection Rate: 1 Hz
Expected
Background: 7–20 nC
Temperature: 30 °C
Autosampler
Cycle Time: 11 min
Injection Mode: Pull
Needle Height: 2 mm
Flush Volume: 400 µL

PREPARATION OF SOLUTIONS AND REAGENTS

50 mM Nitric Acid

Add 6.25 mL of concentrated nitric acid to approximately 1000 mL of degassed 17.8 MΩ-cm deionized water in a 2-L volumetric flask. Dilute to the mark with degassed deionized water.

IODIDE STANDARDS

1000 mg/L Standard

Dissolve 1.31 g of potassium iodide in 1000 mL of deionized water. Use this primary standard to prepare a 10 mg/L secondary standard, from which working standards can be prepared on the day of analysis. Freeze the primary and secondary standards. Because iodide is light-sensitive, exposure to light should be minimized.

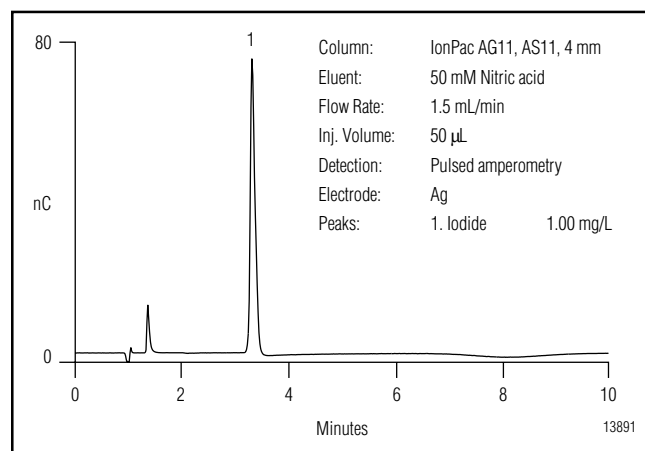


Figure 1 Determination of iodide by ion chromatography with pulsed amperometric detection

Electrode Preparation

Polish the silver electrode with the white fine polishing compound. Rinse the electrode well with deionized water and wipe with a damp paper towel. After this initial polish, the electrode should only be polished if it becomes discolored or if it has not been used for a month or longer.

Sample Preparation

Dilute a brine sample 1 to 10 with deionized water. The concentration of the diluted brine should be ≤ 0.52 M (3% sodium chloride). To evaluate recovery in the matrix, add appropriate volumes of a 1 mg/L iodide standard to the brine prior to dilution to yield concentrations of 25, 50, 100, 150, and 200 µg/L of added iodide.

RESULTS AND DISCUSSION

Chromatography of Iodide

Figure 1 shows the separation of 1 mg/L iodide on the IonPac AS11 column set using a 50 mM nitric acid eluent. Iodide elutes in under 4 minutes and is well separated from the void volume. Compared to other anion-exchange columns, the IonPac AS11 contains a very hydrophilic pellicular resin that produces improved peak shape for the hydrophobic iodide ion. The choice of the nitric acid eluent also improves peak shape.

Chloride elutes at approximately 1.5 minutes. The baseline dip at approximately 8 minutes is due to dissolved oxygen. This dip is from the previous injection (elution time of approximately 19 minutes) and varies from column to column. An 11-minute injection-to-injection time (autosampler cycle time) was chosen to place the dip where it does not interfere with iodide chromatography on either of the two column sets tested. Determine the dissolved oxygen elution time to ensure that 11 minutes is an appropriate cycle time. Although the iodide peak elutes earlier using higher eluent concentrations, the separation is subject to interferences from early eluting compounds and consequently is not as reproducible as separations using lower eluent concentrations.

Iodide is detected using an amperometric detector with a silver working electrode. The iodide from the sample combines with the silver of the working electrode surface to form silver iodide precipitate, oxidizing silver in the process. Pulsed amperometric detection allows for detection in the µg/L range and has high specificity for the iodide ion.

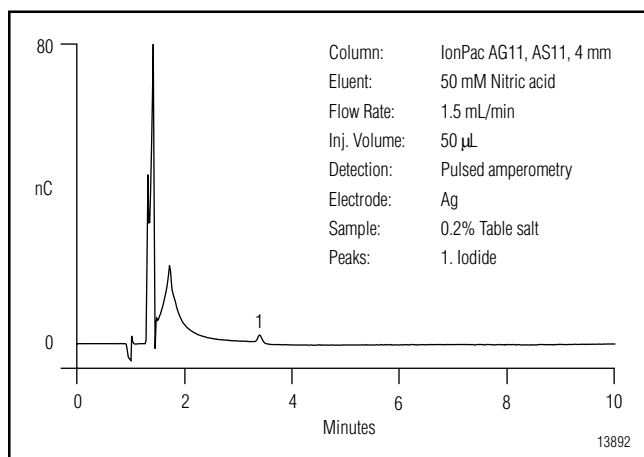


Figure 2 Determination of iodide in table salt

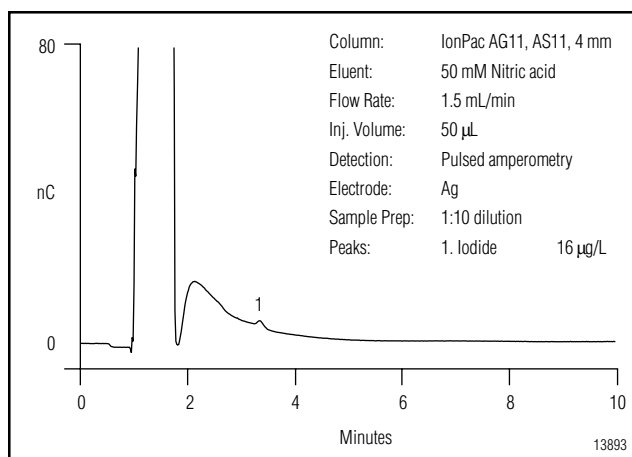


Figure 3 Determination of iodide in brine (30% NaCl)

The other halides are detected in the same manner, but less efficiently. Because the formation of the AgI precipitate is reversible, a small dip is observed after iodide elution due to the dissolution of the AgI remaining on the electrode and concomitant reduction of silver. This dip is much smaller when using pulsed amperometry rather than dc amperometry, and should not be integrated as part of the iodide peak.

Sample Analysis

Figure 2 shows the analysis of iodized table salt. This sample contains enough iodide to be easily detected in a 0.2% solution. Using this dilution, chloride does not interfere with iodide analysis.

High-purity brines (30% sodium chloride) typically contain very low concentrations of iodide and therefore cannot be diluted as much as iodized table salt. Figure 3 shows that iodide can be detected in a 1:10 dilution of brine. The peak area RSD of 8 injections of this sample was 6.3%. To quantify the amount of iodide, the sample was spiked with 25, 50, 100, 150, and 200 µg/L of iodide.

Figure 4 shows the averages of four injections of each brine sample that was spiked with iodide plotted against the concentration of added iodide. This figure shows that iodide is recovered in the matrix. Therefore, the high sodium chloride concentration does not inhibit the detection of iodide. The diluted brine contained 16 µg/L iodide (calculated using the line in Figure 4). The concentration of iodide in the undiluted brine was 160 µg/L.

Figure 5 shows that the analysis of brine samples (the injections that display no data points) does not alter the detection of the 1 mg/L iodide standard. The iodide peak area and retention time RSDs of the standard were 1.5%

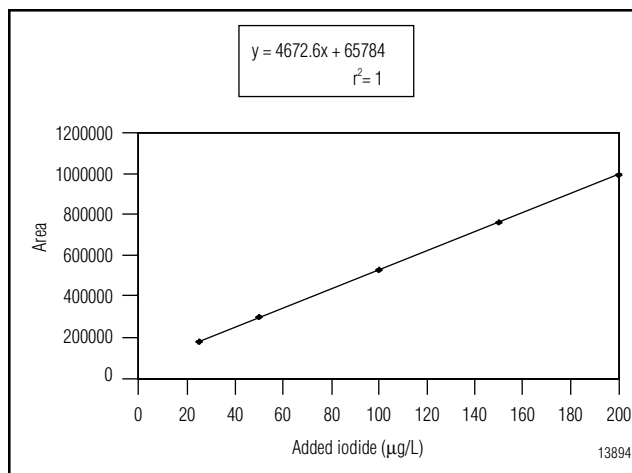


Figure 4 Linearity of iodide added to brine

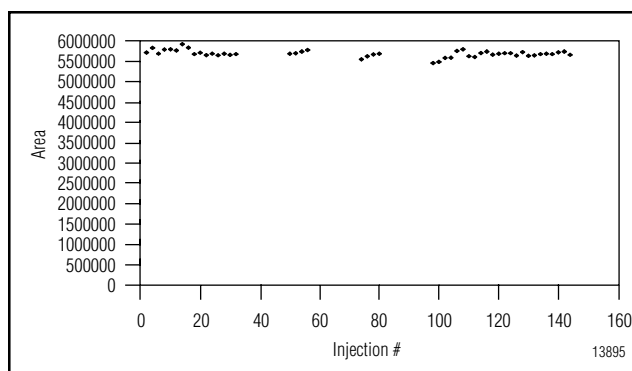


Figure 5 Reproducibility of an iodide standard (1 mg/L) during brine sample analysis. The injections that display no data points were injections of brine samples.

and 0.5%, respectively. In another experiment, 16 injections of a 1 mg/L standard were followed by 56 injections of brine, and then 16 additional injections of the standard. There was no significant change in the standard peak area response after 56 injections of brine. Both experiments show that repetitive analysis of diluted brine samples does not inhibit the response of iodide. Temperature control of the electrochemical cell and on-line degassing were critical to obtaining these low peak area RSDs.

PRECAUTIONS AND RECOMMENDATIONS

The IonPac AS11 column is packed in a sodium hydroxide solution. The column should be flushed with water for at least 30 minutes before equilibrating with the nitric acid eluent. If there is a loss of iodide retention time and/or peak efficiency, the column can be washed with a stronger nitric acid eluent. The AS11 column is stable in the 0–14 pH range, so strong base eluents can also be used for column cleaning. It is best to disconnect the column set from the detector during column cleaning. Changing the inlet column frit or the guard column may be a faster way to restore retention time and efficiency. Installation of a 4-L eluent bottle (P/N 39164) maximizes unattended operation. For best results, the Ag/AgCl reference electrode should be replaced every 6 months.

REFERENCES

1. Rocklin, R.D. and Johnson, E.L. *Anal. Chem.* **1982**, *55*, 4–7.
2. Dionex Corporation, *The Determination of Iodide in Milk Products*; Application Note 37; Sunnyvale, California.

LIST OF SUPPLIERS

Fisher Scientific, 711 Forbes Avenue,
Pittsburgh, Pennsylvania, 15219-4785, USA,
Tel: 1-800-766-7000.

J.T. Baker, Incorporated, 222 Red School Lane,
Phillipsburg, New Jersey, 08865, USA,
Tel: 1-800-582-2537.

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Dionex Corporation
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

Dionex Corporation
Salt Lake City Technical Center
1515 West 2200 South, Suite A
Salt Lake City, UT
84119-1484
(801) 972-9292

Dionex U.S. Regional Offices
Sunnyvale, CA (408) 737-8522
Westmont, IL (630) 789-3660
Houston, TX (281) 847-5652
Atlanta, GA (770) 432-8100
Marlton, NJ (609) 596-0600

Dionex International Subsidiaries
Austria (01) 616 51 25 *Belgium* (015) 203800 *Canada* (905) 844-9650 *France* 01 39 46 08 40 *Germany* 06126-991-0
Italy (06) 66030052 *Japan* (06) 885-1213 *The Netherlands* (0161) 6885-1213 *Switzerland* (062) 205 99 66 *United Kingdom* (01276) 691722
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