

Determination of cations and amines in hydrogen peroxide by ion chromatography using a RFIC (reagent-free) system

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Introduction

Hydrogen peroxide is an essential chemical in the fabrication of integrated circuit and microcircuit devices. Maximum allowable contaminate levels for semiconductor grade hydrogen peroxide can be as low as <100 ppt (ng/L) per individual inorganic cation. A number of semiconductor manufacturers include specifications for maximum allowable levels of <1 ppb (µg/L) for trimethylamine and related amines.

It has been reported that a Thermo Scientific™ Dionex™ IonPac™ CS10 column with a 40 mM methanesulfonic acid mobile phase and suppressed conductivity detection successfully determined inorganic cations in hydrogen peroxide.¹ In addition, simple amines and alkanolamines were determined. While these separations did not use an organic solvent modifier in the eluent, the addition of organic solvent will improve amine peak shape on this column.

This application uses a Dionex IonPac CS17 column to determine trace cations and amines in hydrogen peroxide with a large-loop injection. The Dionex IonPac CS17 column separates amines without the organic solvent eluent modifier needed for separating amines when using older cation-exchange ion-chromatography (IC) columns. Using the Thermo Scientific™

Dionex™ Reagent-Free Ion Chromatography™ (RFIC™) system, this application easily determines sub- $\mu\text{g/L}$ concentrations of cations and amines.

Experimental Equipment

- Thermo Scientific™ Dionex™ ICS-2500* consisting of:
 - Thermo Scientific™ Dionex™ GP50 Gradient pump with vacuum degas option
 - Thermo Scientific™ Dionex™ EG50 Eluent Generator with Thermo Scientific™ Dionex™ CR-CTC Continuously Regenerated Cation Trap Column and Thermo Scientific™ Dionex™ EluGen™ EGC-MSA cartridge
 - Thermo Scientific™ Dionex™ ED50A Electrochemical Detector with conductivity cell
 - Thermo Scientific™ Dionex™ LC25 Chromatography Oven
- Thermo Scientific™ Chromeleon™ 6.6 Chromatography Workstation

*This application can be performed on any Dionex RFIC system. An autosampler was not used for the work presented in this AU, but either a Thermo Scientific™ Dionex™ AS40 Autosampler or Thermo Scientific™ Dionex™ AS Autosampler can be used as long as the proper precautions are taken to produce a clean blank. For these precautions see the Sample Loading and the Precautions sections of Thermo Scientific Application Note 153.²

Reagents and standards

- Deionized water (DI), Type I reagent grade, 18 M Ω ·cm resistivity.
- Lithium hydroxide (LiOH)
- Sodium chloride (NaCl)
- Ammonium acetate (CH₃COONH₄)
- Potassium chloride (KCl)
- Magnesium sulfate (MgSO₄)
- Calcium chloride (CaCl₂)
- Methylamine (CH₃NH₂)
- Ethylamine (C₂H₅NH₂)
- Dimethylamine (CH₃)₂NH
- Trimethylamine (CH₃)₃N

| Conditions | |
|--------------|---|
| Column: | Dionex IonPac CS17 4 × 250 mm (P/N060557) |
| Guard: | Dionex IonPac CG17 4 × 50 mm (P/N 060560) |
| Eluent: | Dionex EGC-MSA, 0.8 mM isocratic to 28.5 min, gradient to 4 mM at 37 min, gradient to 8 mM at 50 min |
| Flow Rate: | 1 mL/min |
| Temperature: | 30 °C |
| Detection: | Suppressed conductivity, Thermo Scientific™ Dionex™ Cation Atlas™ Electrolytic Suppressor (CAES™), recycle mode |
| Inj. Volume: | 1 mL |
| Background: | <1 μS |

Preparation of solutions and reagents

Eluent

The MSA eluent is prepared automatically by pumping DI water through the Dionex EG50 eluent generator equipped with a Dionex EGC-MSA cartridge.

Standard solutions

Stock standards

Prepare 1,000 mg/L standards for each of the cations and amines in DI water. Standards should be prepared from the highest purity compounds available. Table 1 provides the amounts needed to prepare 100 mL of each standard. Concentrated standards are stable for at least one month when stored at 4°C.

Table 1. Mass or volume of compounds used to prepare 100 mL of 1,000 mg/L cation standards.

| Cation | Compound | Amount (g) |
|-----------|-------------------------------|-------------|
| Lithium | Lithium hydroxide | 0.343 |
| Sodium | Sodium chloride | 0.245 |
| Ammonium | Ammonium acetate | 0.427 |
| Potassium | Potassium chloride | 0.191 |
| Magnesium | Magnesium sulfate | 0.516 |
| Calcium | Calcium chloride | 0.277 |
| Amine | | Amount (mL) |
| | Methylamine (d=0.7 g/mL) | 0.143 |
| | Ethylamine (d= 0.81 g/mL) | 0.123 |
| | Dimethylamine (d= 0.68 g/mL) | 0.147 |
| | Trimethylamine (d= 0.63 g/mL) | 0.158 |

Composite Standard Solutions

Appropriate mixed standards are prepared from the 1,000 mg/L stock standards. First prepare 1 mg/L standards and then use these secondary standards to prepare the composite working standards at low $\mu\text{g/L}$ concentrations. For this application we prepared the composite standards listed in Table 2. Secondary standards should be prepared fresh weekly and working standards prepared fresh daily. If an accurate measurement of ammonium is required, run a separate ammonium standard because degradation of amine standards will produce ammonium.

Sample preparation

Hydrogen peroxide samples were treated with platinum to eliminate the hydrogen peroxide as described in reference 3.

Results and discussion

Chromatography

Separating inorganic cations and amines in the same sample has traditionally been a challenging application and has required the addition of organic solvents to achieve adequate peak shapes for the amines. Unfortunately, addition of an organic solvent to the eluent reduces detection sensitivity. Using advanced resin synthesis techniques, a cation-exchange column, the Dionex IonPac CS17 column, was produced that delivers good peak shapes for amines without the addition of an

organic solvent to the eluent. Using the Dionex IonPac CS17 column, a separation of the common inorganic cations, ammonium, and the four amines, mono-, di-, and trimethyl amine, and ethylamine was developed (Figure 1). This separation starts with a weak (0.8 mM MSA) eluent followed by two shallow gradients. Normally, such a separation could suffer from reproducibility problems due to eluent preparation errors, but the RFIC system eliminates this potential problem.

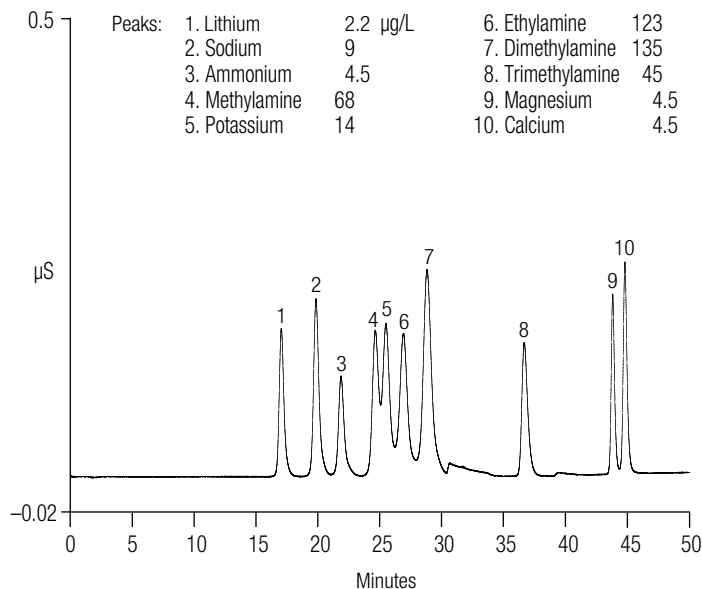


Figure 1. Separation of mixed cation and amine standard

Table 2. Standard concentrations for method calibration.

| Analyte | Level 1 ($\mu\text{g/L}$) | Level 2 ($\mu\text{g/L}$) | Level 3 ($\mu\text{g/L}$) | Level 4 ($\mu\text{g/L}$) | Level 5 ($\mu\text{g/L}$) |
|----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Lithium | 0.75 | 1.50 | 2.25 | 3.00 | 3.75 |
| Sodium | 3.00 | 6.00 | 9.00 | 12.00 | 15.00 |
| Ammonium | 1.50 | 3.00 | 4.50 | 6.00 | 7.50 |
| Methylamine | 22.50 | 45.00 | 67.50 | 90.00 | 112.50 |
| Potassium | 4.50 | 9.00 | 13.50 | 18.00 | 22.50 |
| Ethylamine | 7.50 | 15.00 | 22.50 | 30.00 | 37.50 |
| Dimethylamine | 45.00 | 90.00 | 135.00 | 180.00 | 225.00 |
| Trimethylamine | 15.00 | 30.00 | 45.00 | 60.00 | 75.00 |
| Magnesium | 1.50 | 3.00 | 4.50 | 6.00 | 7.50 |
| Calcium | 1.50 | 3.00 | 4.50 | 6.00 | 7.50 |

The eluent generator accurately produces the required eluent with high precision. Although potassium and methylamine are not baseline resolved, accurate quantification of these ions is possible using integration tools available in Chromeleon software. The unknown peaks at 30.60 and 39.50 min are likely a result of the gradient changes near those times in the eluent program. Overall, the baseline drift due to eluent concentration change is very low, which is a consequence of the high purity of the electrolytically generated MSA eluent.

Linearity and calibration

Prior to sample analysis we performed a method calibration of our RFIC system using the five mixed standards listed in Table 2. The ranges for each cation reflect the expected range for these cations in the hydrogen peroxide sample. Table 3 shows linear response for each cation in its chosen range.

Table 3. Method calibration results as reported by Chromeleon software.

| Analyte | % Corr. Coeff. | r ² | Offset | Slope |
|----------------|----------------|----------------|---------|--------|
| Lithium | 99.6549 | 99.311 | -0.0150 | 0.0253 |
| Sodium | 99.7025 | 99.406 | -0.0190 | 0.0085 |
| Ammonium | 99.8034 | 99.607 | -0.0082 | 0.0095 |
| Methylamine | 99.7243 | 99.449 | -0.0173 | 0.0010 |
| Potassium | 99.7612 | 99.523 | -0.0192 | 0.0061 |
| Ethylamine | 99.6417 | 99.285 | -0.0244 | 0.0041 |
| Dimethylamine | 99.7189 | 99.439 | -0.0340 | 0.0010 |
| Trimethylamine | 99.6124 | 99.226 | -0.0171 | 0.0014 |
| Magnesium | 99.9287 | 99.858 | -0.0032 | 0.0081 |
| Calcium | 99.6450 | 99.291 | -0.0029 | 0.0108 |

Minimum Detection Limit (MDL)

The MDL of each analyte was determined using seven injections of a low level standard (reported in Table 5). The amount determined, the RSD of that amount, and calculated MDL for each cation are shown in Table 4. These MDLs show that the method has the required sensitivity for this application.

Table 4. Determination of MDLs for cations and amines.

| Analyte | Average Amount (µg/L) | RSD (%) (µg/L) | MDL ^a (µg/L) |
|----------------|-----------------------|----------------|-------------------------|
| Lithium | 0.629 | 0.272 | 0.005 |
| Sodium | 2.502 | 0.324 | 0.025 |
| Ammonium | 1.125 | 1.877 | 0.066 |
| Methylamine | 18.100 | 0.184 | 0.105 |
| Potassium | 3.521 | 0.616 | 0.068 |
| Ethylamine | 6.263 | 0.549 | 0.108 |
| Dimethylamine | 36.040 | 0.292 | 0.330 |
| Trimethylamine | 12.870 | 0.342 | 0.138 |
| Magnesium | 0.735 | 2.575 | 0.059 |
| Calcium | 0.857 | 5.518 | 0.148 |

^a MDL = $\sigma t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$

Reproducibility

The short-term reproducibility was measured by injecting seven replicates of a low-level standard. The results reported in Table 5 show the excellent retention time reproducibility expected with the RFIC system, as well as good peak area reproducibility for a low-level standard.

Table 5. Method reproducibility.

| Analyte | Conc. (µg/L) | Retention Time | RSD (%) | |
|----------------|--------------|----------------|---------|-------|
| | | | Amount | Area |
| Lithium | 0.63 | 0.286 | 0.272 | 5.051 |
| Sodium | 2.5 | 0.360 | 0.324 | 3.010 |
| Ammonium | 1.12 | 0.311 | 1.877 | 7.947 |
| Methylamine | 18 | 0.330 | 0.184 | 2.206 |
| Potassium | 3.5 | 0.351 | 0.616 | 5.654 |
| Ethylamine | 6.2 | 0.239 | 0.549 | 9.447 |
| Dimethylamine | 36 | 0.294 | 0.292 | 4.216 |
| Trimethylamine | 12.8 | 0.131 | 0.342 | 6.765 |
| Magnesium | 0.73 | 0.056 | 2.575 | 5.620 |
| Calcium | 0.85 | 0.071 | 5.518 | 8.044 |

Sample analysis

Three platinum-treated hydrogen peroxide samples were analyzed with the RFIC method (Figures 2–4). Of these samples, only samples 2 and 3 (Figures 3 and 4) had detectable amines, with a small amount of trimethylamine. Sample 1 contained alkali and alkaline earth cations and ammonium and Sample 3 contained ammonium and alkaline earth cations.

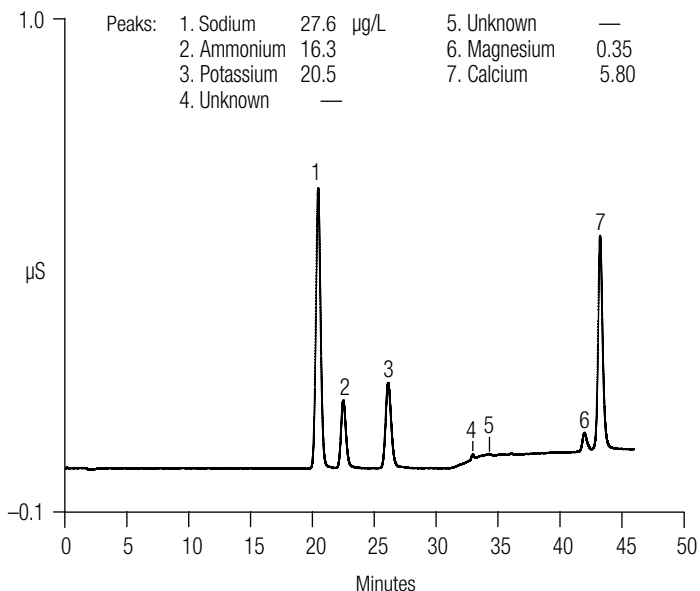


Figure 2. RFIC Analysis of hydrogen peroxide Sample #1.

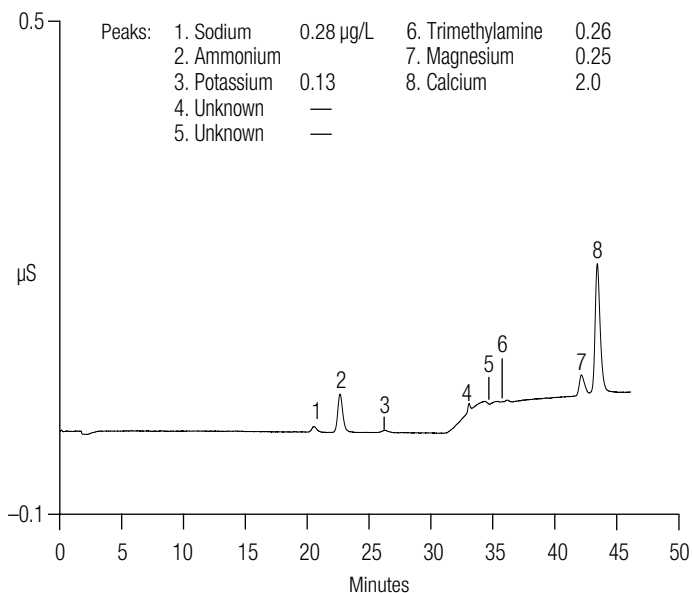


Figure 3. RFIC Analysis of hydrogen peroxide Sample #2.

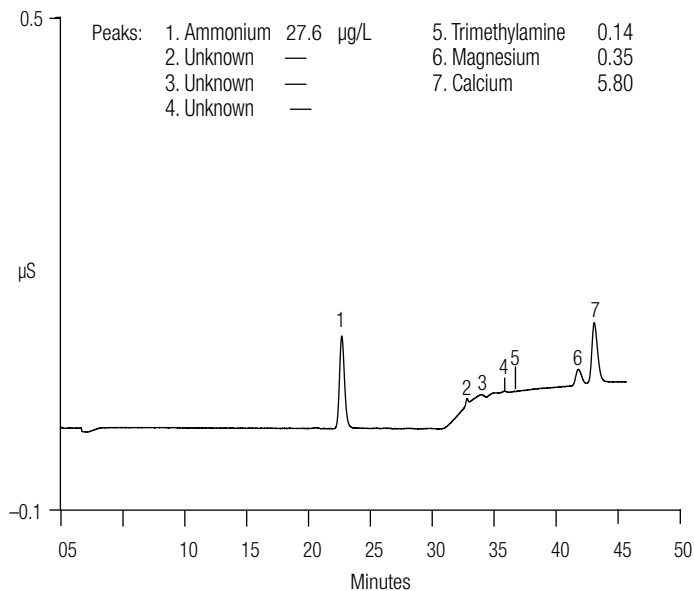


Figure 4. RFIC Analysis of hydrogen peroxide Sample #3.

Method accuracy

To evaluate the method accuracy, a standard of ethylamine, dimethylamine, and trimethylamine was spiked into the sample and the recovery determined. Results of the spike recovery are shown in Table 6. These results show good recovery at the low concentrations of each of these analytes.

Table 5. Method reproducibility.

| Ethylamine | Amount (µg/L) | | | |
|----------------|---------------|--------|----------------|------------|
| | Sample | Spike | Spike + Sample | % Recovery |
| Sample 2 | 0.0000 | 0.5000 | 0.6013 | 120.3 |
| Diethylamine | Amount (µg/L) | | | |
| | Sample | Spike | Spike + Sample | % Recovery |
| Sample 1 | 0.0000 | 1 | 0.9904 | 99.04 |
| Sample 3 | 0.0000 | 1 | 0.7792 | 77.92 |
| Trimethylamine | Amount (µg/L) | | | |
| | Sample | Spike | Spike + Sample | % Recovery |
| Sample 1 | 0 | 1 | 1.2678 | 126.8 |
| Sample 2 | 0.2592 | 1.5 | 1.4159 | 77.11 |
| Sample 3 | 0.1396 | 1.5 | 01.752 | 107.5 |

Summary

This application uses a Dionex IonPac CS17 column and a RFIC system to separate cations and amines in a hydrogen peroxide sample. These cations are determined at sub-µg/L concentrations using a large-loop direct injection.

References:

1. Kerth, J., Rattmann, C., Jensen D. *GIT-Labor-Fachz.* **2000**, 44(11), 1324–1327.
2. *Monitoring for Trace Anion Contamination in the Extracts of Electronic Components.* Application Note 153, Thermo Fisher Scientific, Sunnyvale, CA.
3. SEMI C30-06999 Specifications and Guidelines for Hydrogen Peroxide.

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