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Industrial Ion Chromatography application note compendium

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There is a broad range of industrial applications that are ideally suited for the use of ion chromatography (IC), which is reflected in the large quantity of application and technical notes that are available. This compendium presents summaries of the latest releases in each of the following areas:

- Chemicals

- Materials

- Batteries

- Electronics

- Oil and Gas

- Biofuels

- Power

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Chemicals

Monitoring for ionic contaminants in chemical production is essential to ensure high product quality, particularly when these chemicals are subsequently used in manufacturing processes that require ultra clean reagents such as in semiconductor fabrication. Ion chromatography enables trace level (part per billion (ppb)) determination of anions and cations in acids, bases, and organic solvents.

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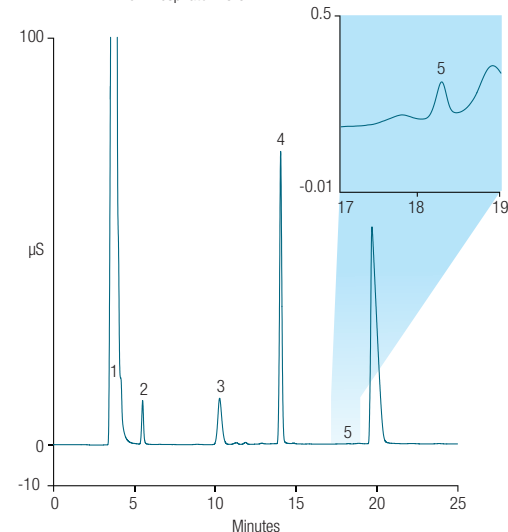## Determination of trace anions in hydrofluoric acid, ammonium fluoride, and a buffered oxide etchant

Concentrated hydrofluoric acid (HF) is used in the semiconductor and electronics industries, both alone and as one component of a buffered oxide etchant (BOE), to remove oxide layers during device production. This HF must be of high purity, especially with respect to anionic impurities that can damage the semiconductor. Simply diluting the HF to a concentration that will not overload the anion-exchange column does not allow enough sensitivity to determine the contaminating anions.

This technical note describes determination of low concentrations of strong acid anions in HF using ion exclusion (Thermo Scientific™ Dionex™ IonPac™ ICE-AS1) and anion exchange (Thermo Scientific™ Dionex™ IonPac™ AS11-HC) columns. The method design also allows determination of low concentrations of strong acid anions in an HF/ammonium fluoride mixture (BOE), and ammonium fluoride.

Sample: 8.33% $NH_4F.HF$
Peaks:
1. Fluoride —
2. Chloride 80.89 µg/L
3. Nitrate 341.6
4. Sulfate 1021
5. Phosphate 3.62

Determination of anions in ammonium fluoride.

Anion MDLs for each high fluoride sample.

Anion	MDL (µg/L)		
	Hydrofluoric Acid (12%)	Ammonium Fluoride (8.33%)	Simulated BOE (10x Dilution)
Chloride	1.23	0.81	0.71
Nitrate	1.01	2.25	3.17
Sulfate	2.49	5.48	1.81
Phosphate	9.86	4.83	1.14

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Determination of anionic impurities in sulfuric acid using ion chromatography

Trace ionic impurities in concentrated sulfuric acid can have a direct impact on the yield and reliability of chemical and semiconductor material processes such as wafer cleaning. However, the determination of anionic impurities in concentrated acids has been an analytical challenge. In sulfuric acid, the high concentration of sulfate limits the amount that can be injected into the anion-exchange column, thus limiting method sensitivity. In this application, sulfuric acid sample is diluted, and a volume that has been empirically determined to avoid overloading a high-capacity column is injected.

We developed two methods for this analysis: Method 1 uses a Thermo Scientific™ Dionex™ IonPac™ AS19 column with a hydroxide eluent to determine fluoride, chloride, bromide, nitrite, and nitrate; Method 2 uses a Thermo Scientific™ Dionex™ IonPac™ AS23-4µm column with a carbonate/bicarbonate eluent to determine phosphate.

Calibration, LOD, and LOQ of five anions using Method 1.

Analyte	Range (µg/L)	Coefficient of Determination (r^2) Linear Fitting	LOD (µg/L)	LOQ (µg/L)	LOD in Concentrated Sulfuric Acid (mg/L)	LOQ in Concentrated Sulfuric Acid (mg/L)	LOD in 10% (w/w) Sulfuric Acid (µg/L)	LOQ in 10% (w/w) Sulfuric Acid (µg/L)
Fluoride	1–50	0.9998	0.19	0.64	0.19	0.64	19.4	65.3
Chloride	0.5–50	0.9999	0.05	0.17	0.05	0.17	5.10	17.3
Nitrite	2–50	0.9998	0.37	1.23	0.37	1.23	37.8	126
Bromide	5–50	0.9998	1.50	5.00	1.50	5.00	153	510
Nitrate	2–50	0.9999	0.47	1.55	0.47	1.55	48.0	158

Calibration, LOD, and LOQ of phosphate using Method 2.

Analyte	Range (µg/L)	Coefficient of Determination (r^2) Linear fitting	LOD (µg/L)	LOQ (µg/L)	LOD in Concentrated Sulfuric Acid (mg/L)	LOQ in Concentrated Sulfuric Acid (mg/L)	LOD in 10% (w/w) Sulfuric Acid (mg/L)	LOQ in 10% (w/w) Sulfuric Acid (mg/L)
Phosphate	50–500	0.9994	12.6	42	12.6	42	1.29	4.29

Peaks: 1. Fluoride
         2. Chloride
         3. Nitrite
         4. Bromide
         5. Nitrate
         6. Phosphate <LOD   48.1 µg/L

Samples: A. DI H_2O
          B. Sulfuric acid
          C. Sulfuric acid spiked with 50 ppb six anions
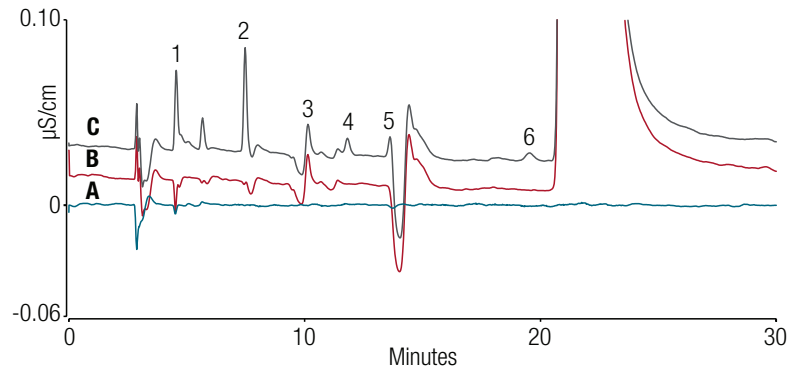
Overlay of chromatograms of sample vs. sample spiked with
50 µg/L of the six anions standards mix using Method 2.
Note: only phosphate was determined using this method.

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In-line sample preparation for the determination of anions in sodium hydroxide

Determination of anions in high pH samples is important for a variety of industries. For example, manufacturers of caustics need an accurate method to monitor the concentration of chlorate and other anions in the chlor-alkali process. In chlor-alkali processes, chlorine and sodium hydroxide are produced by the electrolysis of a saturated brine solution. A diaphragm is employed to separate the chlorine generated at the anode and the caustic soda produced at the cathode. Without the diaphragm to isolate the solutions, the chlorine and caustic would react and eventually produce sodium chlorate. Monitoring the chlorate, which results from sodium hydroxide coming into contact with chlorine gas, is critical to ensure the process is working correctly. However, anions in a high pH sample cannot be determined without proper sample pretreatment due to the high hydroxide concentration in the sample, which can act as an eluent.

This application update shows determination of mg/L concentration of anions in sodium hydroxide using automated inline sample preparation with Thermo Scientific™ Dionex™ Guardcap H vial caps and analyte separation using the Dionex IonPac AS23-4µm column.

Method linearity, retention time precision, and detection limit (MDL).

Analyte	Calibration Range (ppm)	Coefficient of Determination (r^2)	Retention Time Precision (RSD) *	MDL Standard (ppm)	MDL** (ppm)
Fluoride***	2-0.02	0.999	<0.1	0.002	2
Chlorite	10-0.01	0.998	<0.1	0.01	3
Bromate	10-0.01	1.000	<0.1	0.01	2
Chloride	10-0.01	0.997	<0.1	0.01	1
Nitrite	10-0.01	1.000	<0.1	0.01	1
Chlorate	10-0.01	0.999	<0.1	0.01	2
Bromide	10-0.01	0.999	<0.1	0.01	2
Nitrate	10-0.01	0.997	<0.1	0.01	1
Phosphate	20-0.02	0.999	<0.1	0.02	3
Sulfate	10-0.01	0.999	<0.2	0.01	2

*RSD = relative standard deviation of 7 levels, n = 3 for each level.

** For 100 µL injection and 500 fold sample dilution, MDL = 500 × 3.14 × σ when n = 7.

*** MDL of fluoride is determined by the signal to noise ratio (S/N) of the level 2 standard.

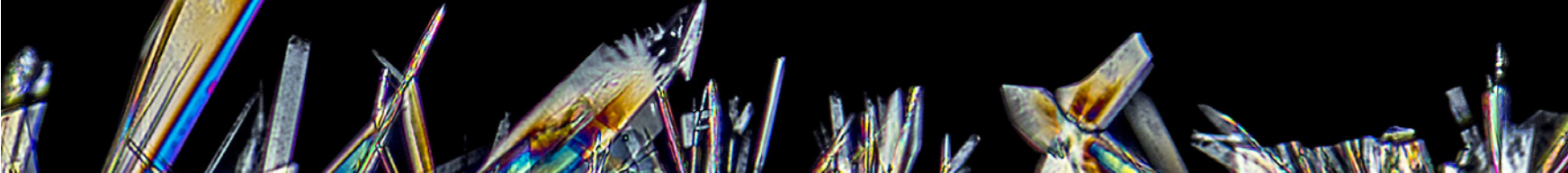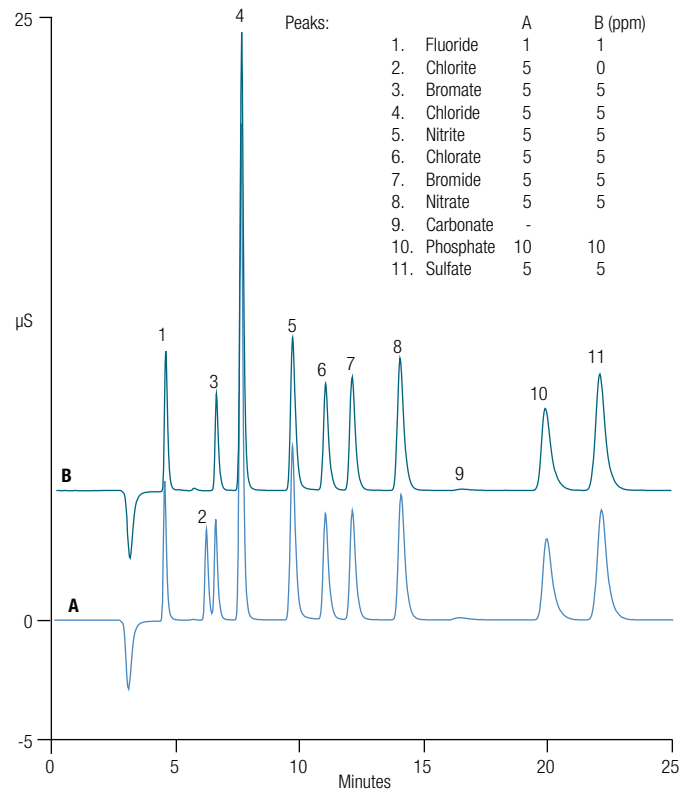Sample :   Mixed standard treated with
             Dionex Guardcap H
             A- in 500× diluted NaOH (0.0382N)
             B- in DI water

Peaks:		A	B (ppm)
1.	Fluoride	1	1
2.	Chlorite	5	0
3.	Bromate	5	5
4.	Chloride	5	5
5.	Nitrite	5	5
6.	Chlorate	5	5
7.	Bromide	5	5
8.	Nitrate	5	5
9.	Carbonate	-	
10.	Phosphate	10	10
11.	Sulfate	5	5

**Chromatograms of mixed anions samples in high-pH and in
neutral matrices.**

For more information click here

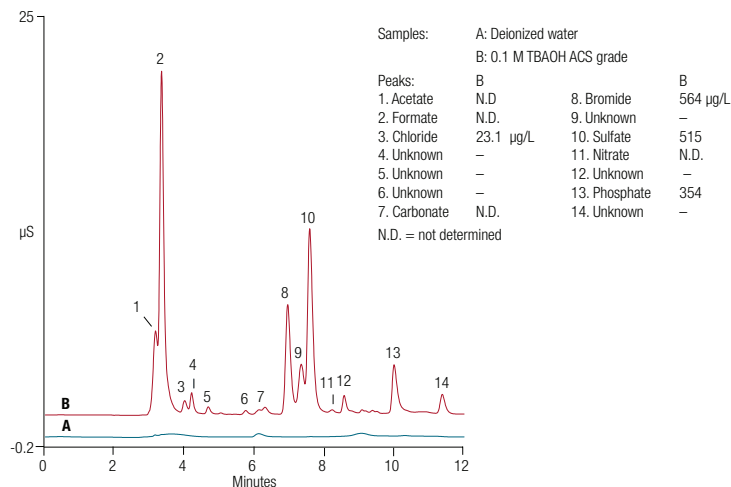# Determination of trace anions in basic solutions by single pass AutoNeutralization and ion chromatography

The electronics industries need analytical methods to determine trace anions in concentrated bases. Anions at very low concentrations can cause corrosion, deposition defects, and shorts in electronic devices. Ion chromatography with suppressed conductivity detection is the preferred and well-established method for determining ionic species, especially at µg/L and ng/L concentrations. Direct analysis of concentrated base samples is challenging because the high concentrations of the base anion overloads the column, resulting in poor chromatography and quantification. Diluting the concentrated bases prior to anion analysis reduces the column overload issues. However, this dilution sacrifices anion determinations at µg/L and ng/L concentrations.

This application note discusses a Single Pass AutoNeutralization method that uses the Thermo Scientific™ Dionex™ IonPac™ AS18-Fast-4µm column set with the high static capacity of a 4 mm Thermo Scientific™ Dionex™ AERS™ 500 Carbonate Electrolytically Regenerated Suppressor to neutralize the base samples in a single pass.

Samples:
A: Deionized water
B: 0.1 M TBAOH ACS grade

Peaks:	B		B
1. Acetate	N.D	8. Bromide	564 µg/L
2. Formate	N.D.	9. Unknown	–
3. Chloride	23.1 µg/L	10. Sulfate	515
4. Unknown	–	11. Nitrate	N.D.
5. Unknown	–	12. Unknown	–
6. Unknown	–	13. Phosphate	354
7. Carbonate	N.D.	14. Unknown	–

N.D. = not determined

Trace anions in 0.1 M tetrabutylammonium hydroxide (TBAOH) ACS grade solution.

Calculated coefficients of determination and method detection limits (MDLs).

	Linear Range (µg/L)*	Coefficient of Determination (r^2)	MDL** (µg/L)
Fluoride	0–10	0.9957	6.0***
Chloride	0–50	0.9999	0.34
Nitrite	0–50	0.9996	0.46
Sulfate	0–50	0.9996	8.7***
Bromide	0–50	0.9994	0.88
Nitrate	0–50	0.9999	0.92
Phosphate	0–100	0.9997	0.52

*DI water was used as Standard 0; linear with offset was selected for calibration.
**3.14 × average amount × %RSD/100.
***3 × system blank.

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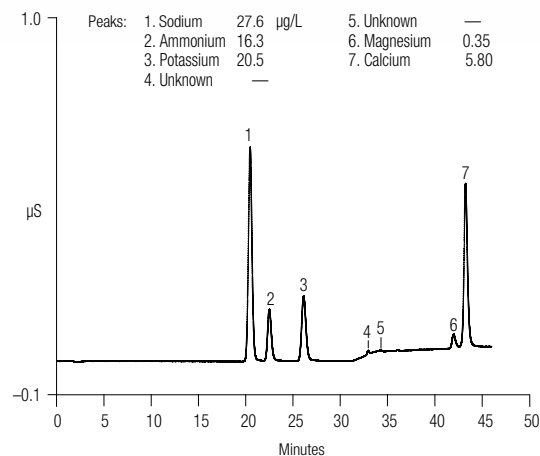# Determination of cations and amines in hydrogen peroxide by ion chromatography using a RFIC (reagent-free) system

Hydrogen peroxide is an essential chemical in the fabrication of integrated circuit and microcircuit devices. Maximum allowable contaminant 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.

This application note describes the use of a Thermo Scientific™ 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 IC columns. Using Reagent-Free™ IC (RFIC™) system, this application easily determines sub-μg/L concentrations of cations and amines.

Peaks:				
1. Sodium	27.6	μg/L	5. Unknown	—
2. Ammonium	16.3		6. Magnesium	0.35
3. Potassium	20.5		7. Calcium	5.80
4. Unknown	—			

RFIC Analysis of hydrogen peroxide Sample #1.

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.

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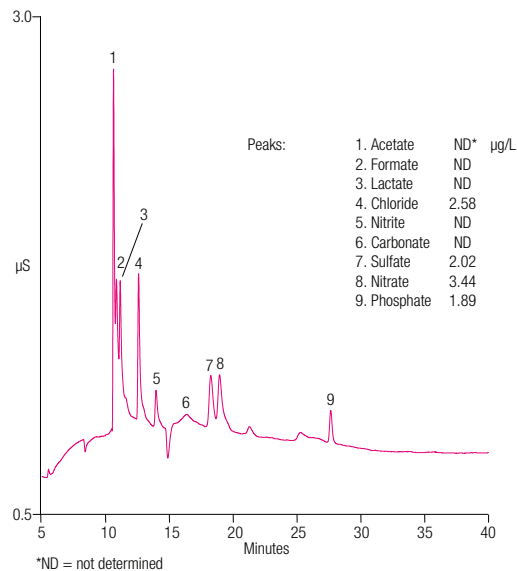# Determination of trace anions in organic solvents using matrix elimination and preconcentration

Anion contamination introduced during manufacturing processes can ruin semiconductors and computer components. Trace contaminants in solvents used during manufacturing can cause short circuits, defects in deposition, and corrosion. Component defects such as these reduce yields, which increases manufacturing costs and waste. As device geometries shrink, even lower levels of contamination become problematic.

This update to the Determination of trace anions in organic solvents using matrix elimination and preconcentration application note describes an automated method that improves consistency and lowers detection limits using the Thermo Scientific™ Dionex™ IonPac™ AS18 column set. This method successfully determines trace anions from high ng/L to low µg/L concentrations in isopropyl alcohol, methanol, acetone, and N-methyl-2-pyrrolidone, with improved method detection limits, from a 60% smaller sample injection.

Peaks:
1. Acetate ND* µg/L
2. Formate ND
3. Lactate ND
4. Chloride 2.58
5. Nitrite ND
6. Carbonate ND
7. Sulfate 2.02
8. Nitrate 3.44
9. Phosphate 1.89

*ND = not determined

Chromatogram of a chloride, sulfate, nitrate, and phosphate standard, 2 µg/L each, in methanol.

Method detection limits and SEMI specifications.

		SEMI Specifications			
Anion	2-Propanol MDL[a] (µg/L)	2-Propanol Grade 4[b] (µg/L)	Acetone Grade 1[c] (µg/L)	Methanol Grade 1[d] (µg/L)	n-Methyl-2-Pyrrolidone Grade 3[e] (µg/L)
Chloride	0.105	<50	<200	<200	<300
Sulfate	0.178	<50	–	<500	<250
Nitrate	0.448	<50	<100	–	<400
Phosphate	0.200	<50	–	–	<250

n = 5.
[a]Method detection limit based on least squares regression analysis in alcohol matrix according to SEMI C10-0305.

[b]SEMI specification C41-0705 (isopropyl alcohol).
[c]SEMI specification C19-0301 (acetone).
[d]SEMI specification C31-0301 (methanol).
[e]SEMI specification C33-0301 (n-methyl-2-pyrrolidone)

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Materials

Analysis of solid and semi-solid materials to determine halogen content can be challenging but pairing an IC system with a combustion unit simplifies this process by automating sample preparation and data acquisition to produce results with sensitivity, accuracy and consistency.

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Determination of chlorine, bromine, and sulfur in polyethylene materials using combustion IC with a carbonate/bicarbonate eluent

Polyethylene (PE) is a thermo-plastic created from the polymerization of ethylene, a process that produces long straight chains of hydrocarbon monomers. Plastic materials consist not only of plastic polymers, as many additives are used to improve different properties of the plastic. Halogen and sulfur-containing compounds are often added as plasticizers, flame retardants, and heat stabilizers. Due to the widespread use of plastic/polymers and their subsequent impact on the environment, it is important to know the content of the halogens and sulfur when polyethylene materials are disposed or recycled.

Plastic samples can be very difficult to analyze as sample preparation is required to extract analytes or remove interfering matrices, and these sample preparation techniques can be labor intensive. Combustion ion chromatography (CIC) has been demonstrated for the determination of halogens and sulfur in a variety of difficult samples.

Here we demonstrate that a Mitsubishi™ AQF-2100H combustion system combined with a Thermo Scientific™ Dionex™ Aquion™ IC System using a Dionex IonPac AS23 column set can be used for automated qualitative and quantitative analysis of halogens and sulfur in plastic samples.

Note: This application can also be run with hydroxide eluent. (see AN72349 for more info.)

For more information click here
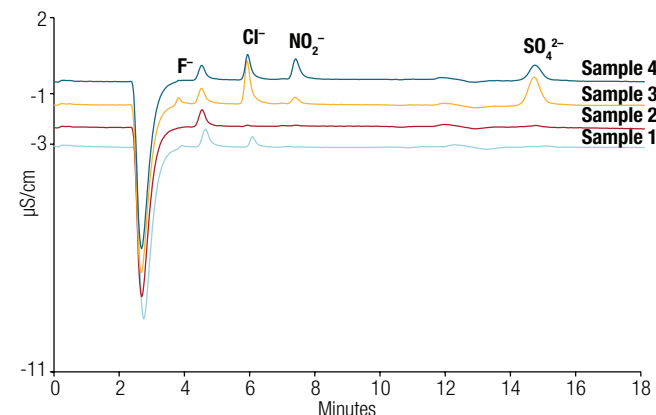
Chromatograms of polymer samples 1,2, 3, and 4.

Spike recovery for samples 1, 2, 3, and 4.

	Sample #1			
	Unspiked (ppm)	Added (ppm)	Spiked (ppm)	Recovery (%)
Chlorine	20.6	98.6	135	116
Sulfur	0	82.2	76.6	93.2
Sample #2				
Chlorine	3.09	95.8	106	107
Sulfur	2.30	79.5	75.5	92.1
Sample #3				
Chlorine	90.4	97.5	176	87.8
Sulfur	62.0	76.9	130	88.8
Sample #4				
Chlorine	55.3	98.1	181	128
Sulfur	30.8	79.9	108	96.4

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Batteries

Rechargeable lithium-ion batteries (LIBs) are key components for portable electronics, medical devices, industrial equipment and automobiles. Ion Chromatography can be used to gain insight into the fundamental processes and degradation mechanisms in LIBs and to ensure product quality during manufacturing.

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Determination of tetrafluoroborate, perchlorate, and hexafluorophosphate in a simulated electrolyte sample from lithium ion battery production

Lithium ion batteries are commonly used in portable consumer electronic devices. The electrolyte solution in these batteries consists of a lithium salt in an organic solvent. The anions of the added lithium salts can be determined by ion chromatography to ensure that the solutions have been prepared at the proper concentrations.

Here, the authors prepare simulated samples that contain either lithium tetrafluoroborate, lithium perchlorate, or lithium hexafluorophosphate in an equal mixture of ethylene carbonate, diethyl carbonate, and propylene carbonate, and demonstrate that the anionic content can be determined accurately using a Thermo Scientific™ Reagent-Free™ IC (RFIC™) system with a Thermo Scientific™ Dionex™ IonPac™ AS20 column.
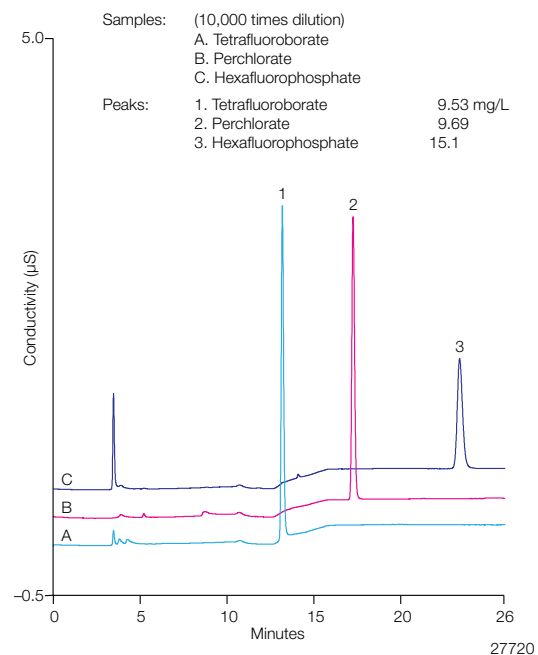
Chromatograms of samples (10,000 times dilution).

Assay results for the samples and spiked samples.

Ion	Calculated Concentration after 10,000 Times Dilution (mg/L)	Average Found Concentration (mg/L)	Recovery (%)	Spiked Concentration (mg/L)	Average Found Concentration in Spiked Sample (mg/L)	Recovery (%)
Tetrafluoroborate	8.70	9.53	109	2	11.3	88.5
Perchlorate	9.95	9.69	97.4	2	11.8	106
Hexafluorophosphate	14.5	15.1	104	2	16.8	85.0

For more information click here

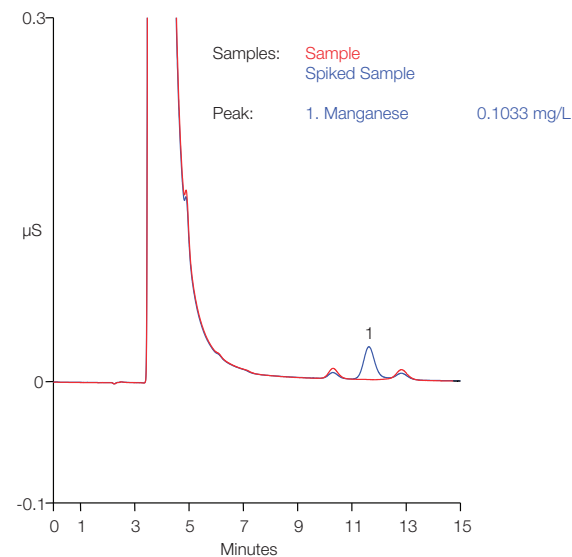# Determination of dissolved manganese in lithium/manganese oxide battery electrolyte

Lithium-ion batteries are widely used in products such as portable consumer electronic devices and electric vehicles. Lithium-ion batteries that are manganese-based are more environmentally friendly, have a good safety record, and can be made at a lower cost; however, they have a shorter lifetime than other types of lithium-ion batteries. One of the reported causes of lifetime loss is the dissolution of manganese from the cathode into the electrolyte during cycling.

The work shown here uses an RFIC system with suppressed conductivity detection to quantify dissolved manganese in the simulated electrolyte of a $Li/LiMn_2O_4$ battery. The method uses the Thermo Scientific™ Dionex™ IonPac™ CS12A column set, which was designed to deliver good peak shapes for cations such as manganese(II) (Mn^{2+}), with a simple methanesulfonic acid (MSA) eluent produced by an eluent generator. The combination of the RFIC system and a quality IC column yields a method that is sensitive, accurate, reproducible, and easy to execute, requiring only the addition of deionized water to the RFIC system.

Sample and spiked sample results.

Injection Number	Amount in Sample (mg/L)	Amount in Spiked Sample, Spiked Conc 0.1 mg/L (mg/L)
1	ND	0.1030
2	ND	0.1034
3	ND	0.1033
4	ND	0.1034
5	ND	0.1033
Average	ND	**0.1033**
RSD (%)	—	**0.15**
Recovery (%)	—	**103**

Overlay of chromatograms of unspiked and spiked samples.

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Electronics

Ionic contamination is a big concern in all aspects of the electronics manufacturing process because small amounts of contamination (parts-per-billion (ppb) to parts-per-million (ppm) concentrations) can cause corrosion, erosion, electromigration, and shorting. Ion chromatography is an efficient analytical technique that can quickly determine both trace and major constituents of a wide variety of process contaminants, providing a convenient means of quantifying common inorganic anions and cations.

Configuring the Dionex Modular HPIC system with an inline water purifier and inline calibration for trace anion determinations in ultrapure water

Anionic contaminants at ppb to ppt levels in water used by the electronics industry during manufacturing can cause corrosion-related failures, poor product quality, low product yields, and shortened product life. Ionic contamination is increasingly important and more challenging as devices decrease in size. Trace level determinations are challenging due to the potential introduction of contaminants from the environment that can occur during sample handling, which elevates the background level of anions, decreasing the limits of detection that can be achieved.

In this technical note, automated calibration and the Thermo Scientific™ Dionex™ EWP Electrolytic Water Purifier (EWP) are combined to minimize potential contamination to accurately and reproducibly determine anions at ppt levels using a Thermo Scientific™ Dionex™ IonPac™ AS17C™ column set and KOH electrolytic eluent generation.

Estimated method detection limits.

Analyte	Standard (ppt)	Limit of Detection, 3× S/N (ppt)
Fluoride	8.6*	26
Chloride	6.5*	20
Nitrite	8.0*	24
Bromide	50.0**	7
Nitrate	6.2*	19
Sulfate	51.7**	19
Phosphate	53.1**	43

* Estimated concentration in sample containers of a 10 mL sample injection.

** Calibration standard 50 ppt.
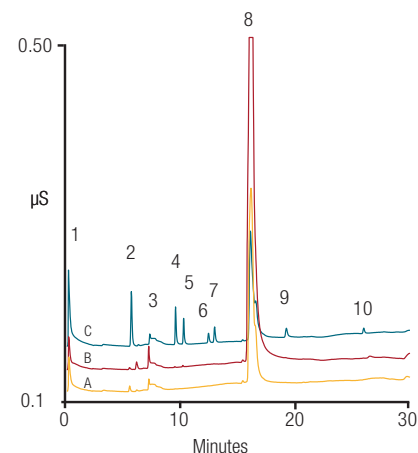
Sample: A: EWP system blank; B: Sample blank*
C: 50 ppt Standards
Vol.: B: 10 mL for container sample,
C: 10 µL for standards
Peaks: 1. System   6. Bromide
2. Fluoride   7. Nitrate
3. Contamination   8. Carbonate
4. Chloride   9. Sulfate
5. Nitrite   10. Phosphate

* Sample run time includes 21.5 min pre-injection time

Comparison of Dionex EWP water and container blanks with 50 ppt trace anions using Thermo Scientific™ Dionex™ AutoPrep™ System small loop.

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Determination of halogens in polymers and electronics using a combustion ion chromatography system

The widespread use of electronic products has drawn increased attention to their impact on the environment. In many countries this has resulted in the adaptation of regulations affecting wastes, substances, and energy use of electronic products. Combustion methods, such as combustion ion chromatography (CIC), have been developed that ensure complete decomposition of solid and semi-solid samples and concomitant release of halogens. CIC provides a fast and reliable method for measuring the halogen content of various consumer products and the associated waste streams.

This application note describes a simple CIC method to determine halogens in polymers for electrotechnical products and electronics. Polymer and electronic samples were homogenized by cryogenic grinding, combusted in the Mitsubishi AQF-2100H system, and then directly injected into a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system with a Thermo Scientific™ Dionex™ IonPac™ AS17-C column set.
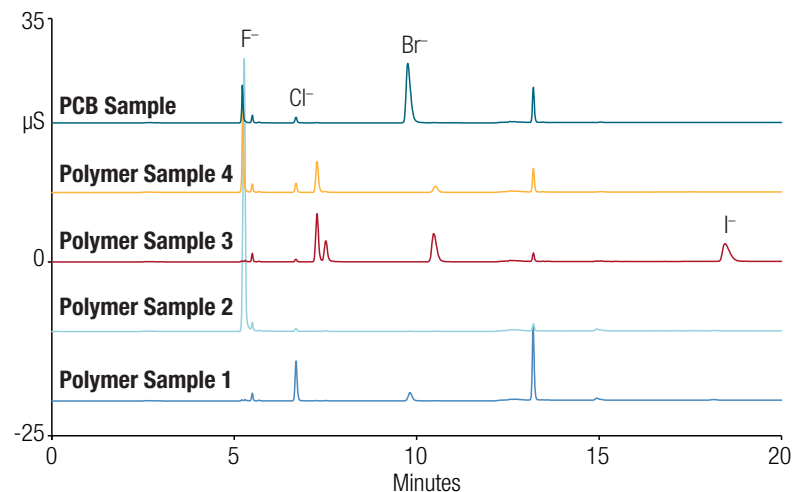
Chromatograms of four polymer samples and one PCB sample.

Method accuracy.

| Sample Name	Weight (mg)	Amount Spiked (mg)	Measured Halogen (Cl) (mg/kg)	Certified Value (mg/kg)	Recovery %
Polymer Sample 1	15.5	16.3	92.1	102.2	90.1
Polymer Sample 2	20.7	18.0	93.4	102.2	91.4
Polymer Sample 3	19.1	16.5	91.8	102.2	89.9
Polymer Sample 4	21.9	18.3	116.7	102.2	114
PCB Sample	4.4	15.7	95.2	102.2	93.1

For more information click here

Water used in the production of electronic devices must be extremely pure. In particular, it must be free of ionic compounds. Typically, manufacturers aim to have the concentration of each ion below 1 µg/L. Another water contaminant that manufacturers seek to minimize is urea, which has been shown to cause problems with semiconductor production. While anions and cations are routinely measured in ultrapure water (UPW) by ion chromatography, the determination of urea is more challenging due to its poor retention by ion-exchange phases and the lack of a suitable detection technique for low concentrations.

This application note describes a method to determine urea that meets these challenges. Urea is retained on the Thermo Scientific™ Dionex™ IonPac™ CS16-Fast-4µm column and detected by triple-quadrupole mass spectrometry (MS).
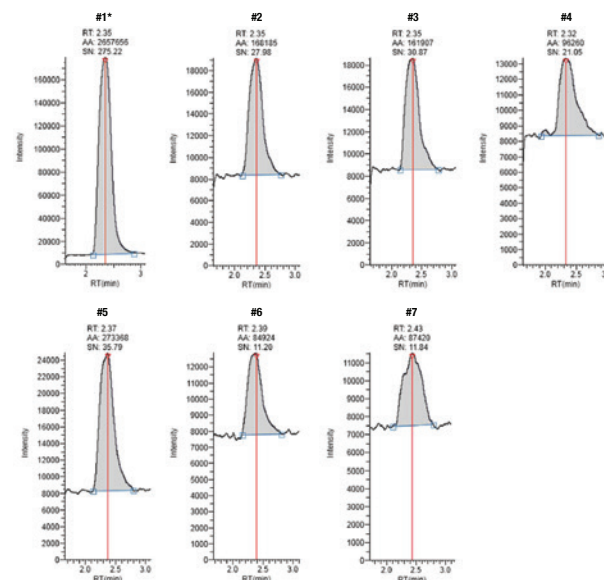
Sample chromatograms.

Sample analysis.

	Amount (µg/L)						
	#1*	#2	#3	#4	#5	#6	#7
Replicate 1	20.8	0.508	0.411	0.166	0.754	0.164	0.152
Replicate 2	19.5	0.481	0.456	0.172	0.815	0.150	0.162
Replicate 3	19.8	0.489	0.456	0.187	0.837	0.152	0.160
Average	20.1	0.493	0.411	0.175	0.802	0.155	0.158
RSD	3.28	2.81	5.89	6.18	5.36	4.88	3.35

*Required a 1:1 dilution with DI water.

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Oil and gas

Accurate and reliable analytical information at all stages of the oil and gas refining process is critical to meet performance and environmental standards. The presence of organic acids and halogens can result in costly corrosion, while precisely monitoring the amine scrubbing process ensures efficiency and product quality.

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Determination of formic and acetic acids in petroleum products by ion chromatography

Organic acids in crude oil, refined products, fuel, etc., are one of the biggest concerns of the oil, oil refining, and combustion engine manufacturers. As a result of their corrosive properties and the associated costs of corrosion, organic acids have become a topic of great industrial interest. To assess the acidity of petroleum products the 'total acid number' (TAN), defined by the ASTM as milligrams of KOH required to neutralize one gram of oil or petroleum product, is commonly used. Recently, it was determined that TAN is no longer a reliable indicator as a surrogate parameter. Low molecular weight organic acids are reported as the most aggressively corrosive in the refining process. Ion chromatography can be used for the selective and sensitive determination of low molecular weight organic acids in aqueous or water-miscible matrices.

This application note summarizes the use and evaluation of an automated analytical IC method using the Thermo Scientific™ Dionex™ IonPac™ AS11-HC column for the direct determination of acetic acid and formic acid in diesel, oil, and diesel/oil mixtures, to support research on corrosion processes of industrial production installations and car engines.

Diesel sample taken from a stressed diesel engine (TAN = 0.06).

For more information click here

Using ion chromatography with electrospray ionization mass spectrometry for the determination of cations and amines in alkanolamine scrubbing solutions

Sour crude and natural gas is very acidic, toxic, and highly corrosive, requiring treatment with amine-rich scrubber solutions to neutralize the CO_2 and remove the H_2S gas impurities. The scrubbing amine process typically uses alkanolamines to neutralize the sour gas impurities. When the neutralizing capacity is deemed inefficient, the amine solutions are regenerated and stripped of elemental sulfur. Dissolved salts (heat stable amine salts) remain, building up over time resulting in higher maintenance costs, and higher incidents of corrosion. Determinations of both the amine concentrations and the heat stable amine salts are needed to ensure a pure product and an efficient scrubbing process. These determinations can be challenging in the concentrated scrubbing amines solution.

In this application note, ion chromatography using the Thermo Scientific™ Dionex™ IonPac™ CS19-4μm column is combined with the Thermo Scientific™ ISQ™ EC Single Quadrupole Mass Spectrometer to confirm identities of μg/L to mg/L concentrations of ammonium, calcium, and alkylamines in high mg/L concentrations of alkanolamines.

Summary of calibration and MDL results.

Ion	Calibration Range (mg/L)	Type	Coefficient of Determination (r²)	MDL (μg/L)
Na·2H$_2$O	0.040–20	Quadratic fit, 2nd order	0.9995	8[++]
NH$_4$·H$_2$O	0.0025–25	Quadratic fit, 2nd order, weighted 1/×	0.9919	22[++]
EA	200–2000	Quadratic fit, 2nd order	0.9994	ND
DEA	200–3333	Quadratic fit, 2nd order	0.9971	ND
Potassium	0.005–50	Quadratic fit, 2nd order	0.9991	4[+++]
MDEA	200–3333	Quadratic fit, 2nd order	0.9984	ND
2Mg·H$_2$O	0.025–25	Quadratic fit, 2nd order	0.9989	15[++]
Ca·2H$_2$O	0.050–50	Quadratic fit, 2nd order	0.9962	64[++++]

MDL= 3 × S/N, n = 7. ND: not determined. MDL Standard, Dionex Combined Six Cation II standards:
[++]10,000-fold dilution, [+++]50,000-fold dilution, [++++]5,000-fold dilution.

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Sample: 1000-fold diluted
A: EA, B: DEA, and C: MDEA

Peaks:	A	B	C (mg/L)
1. Sodium·2H$_2$O	<0.003	0.27	0.003
2. Ammonium·H$_2$O	0.25	0.095	0.39
3. Ethanolamine (EA)	2100	< 10	--
4. Diethanolamine (DEA)	< 20	220	--
5. Methylaminoethanol	NQ	NQ	NQ
6. Methyldiethanolamine	--	<100	310
7. Triethanolamine (TEA)	--	~1	--
8. Magnesium	--*	--*	--*
9. Calcium	--*	--*	--*

* Not detected by MS
**NQ not quantified

Determinations of amines and cations in 1000-fold dilution of A) EA, B) DEA, and C) MDEA-based scrubbing amine samples.

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Fast separation of heat stable salts

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IC-MS determination of cations and amines in scrubbing solutions
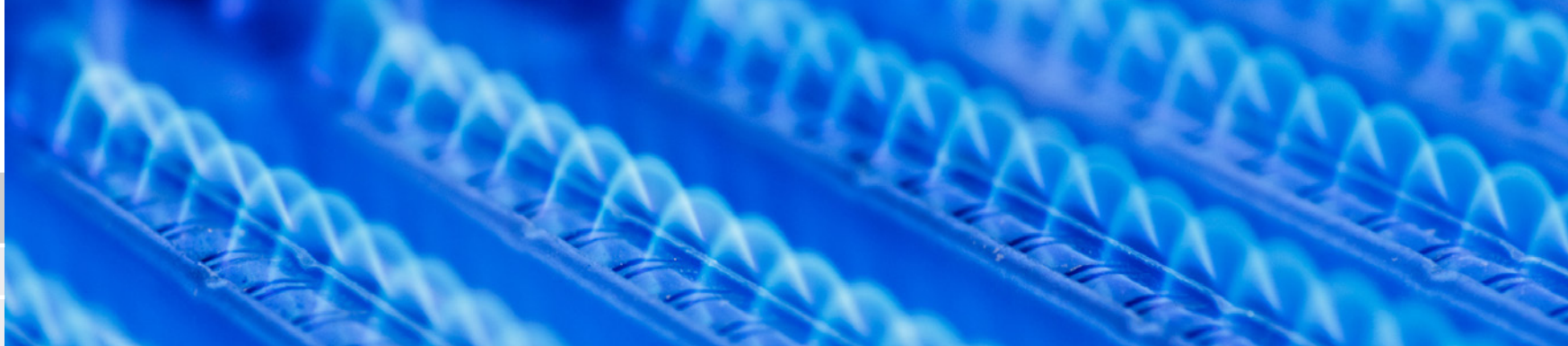
Fast separation of heat stable salts

Fluorine, chlorine and sulfur in aromatic hydrocarbons by CIC

Alkanolamine in neutralizing amines

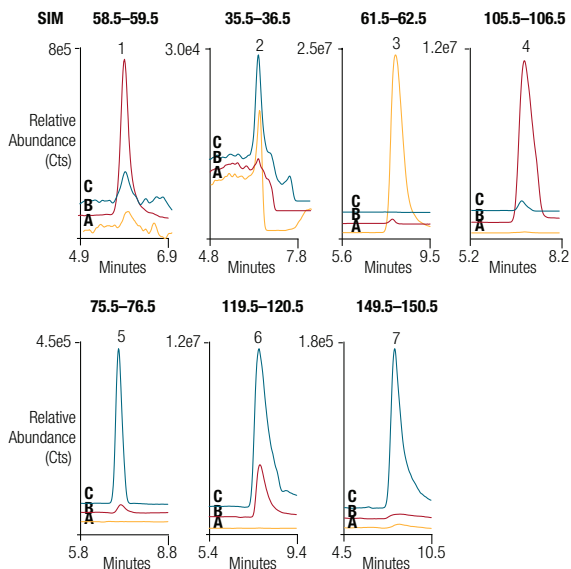Total fluorine, chlorine, bromine, and sulfur in LPG by CIC

Biofuels

Power

Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are often found in natural gas streams. These gases are removed using amine-rich solutions before they can be transported or used. However, amine solutions also extract other contaminants during this process, which is also known as the amine sweetening process. The contaminants in the acid gas removal processes are called heat stable salts (HSS). Increased HSS levels lead to corrosion and the resulting operation problems, resulting in unscheduled outages. Thus, it is important to monitor HSS in amine solutions so appropriate action can be taken to control them.

In this application note, a Thermo Scientific™ Dionex™ IonPac™ AS25A column was used to analyze various refinery samples for the presence of common inorganic anions as well as heat stable amine salt anions. The Dionex IonPac AS25A column is optimized to separate bromide and nitrate, which cannot be baseline resolved on a Thermo Scientific™ Dionex™ IonPac™ AS25 column. The Dionex IonPac AS25A column is a high-capacity, hydroxide-selective anion-exchange column ideally suited for determination of sulfur species in wastewater effluents from the chemical and petroleum industries.
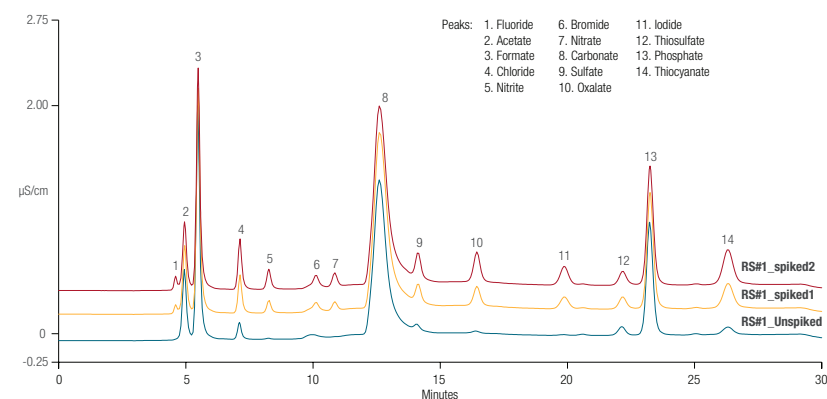
Chromatograms of unspiked and spiked refinery sample (RS) #1 at two levels.

Results for calibration, LOD, and LOQ for thiosulfate and thiocyanate.

Anion	Range (mg/L)	Calibration Type	Coefficient of Determination (r^2)	LOD (mg/L)	LOQ (mg/L)
Thiosulfate	0.10–10	Linear	0.99952	0.018	0.061
Thiocyanate	0.20–20	Linear	0.99932	0.016	0.053

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Determination of total fluorine, chlorine, and sulfur in aromatic hydrocarbons by oxidative pyrolytic combustion followed by ion chromatography

The total fluorine, chlorine, and sulfur contained in aromatic hydrocarbon matrices can contribute to emissions that cause pollution, be harmful to many catalytic processes, and lead to corrosion. Ion chromatography is a sensitive and versatile method for the determination of halides and sulfate. Application of combustion IC (CIC) has been demonstrated for many applications that determine the total amounts of these elements in samples. CIC has been used to determine potentially corrosive or environmentally damaging halogens and sulfur in complex sample matrices such as intractable solids, semisolids, liquids, and even gasses.

This application note describes determination of fluorine, chlorine, and sulfur in aromatic hydrocarbon samples based on ASTM method D7359-14a. A gasoline sample is used here as an example of an aromatic hydrocarbon sample to demonstrate method capabilities. The CIC system used for this method includes a
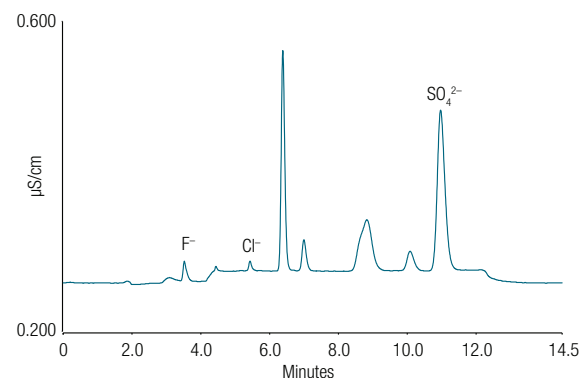
Combustion IC chromatogram of a gasoline sample.

Mitsubishi Automatic Combustion Unit Model AQF-2100H system and Dionex Integrion HPIC system equipped with the Dionex IonPac AS18-Fast-4μm column set.

Results for the spike recovery experiment (n=3).

Spike Conc. (mg/L)	F		Cl		SO$_4$	
	Average Amount (mg/L)	% Recovery	Average Amount	% Recovery	Average Amount (mg/L)	% Recovery
0 (Premium Gasoline)	0.24	–	0.22	–	4.37	–
0.5	0.75	102	0.71	96.5	4.82	91.0
1	1.22	98.0	1.08	85.9	5.30	93.0
2	2.11	93.7	2.03	90.5	6.30	96.3

For more information click here

Alkanolamine determinations in neutralizing amines samples with improved separation technology

Wet natural gas withdrawn from wells using hydraulic fracturing requires additional processing to remove the water, C_2 to C_5 hydrocarbons, and sometimes hydrogen sulfide (H_2S) and carbon dioxide (CO_2) before it can be sold. Sour crude natural gas is very acidic, toxic, and highly corrosive, requiring amine gas treatment with amine-rich scrubber solutions to neutralize the CO_2 and remove the H_2S gas impurities. Amine gas treatment typically uses percent concentrations of alkanolamines to neutralize the sour gas impurities. When the neutralizing capacity is deemed inefficient, the amine solutions are regenerated and stripped of elemental sulfur. Dissolved salts (heat stable amine salts) remain, building up over time and resulting in higher maintenance costs and higher incidents of corrosion. Determinations of both the amine concentrations and the heat stable amine salts are needed to ensure a pure product and an efficient amine gas treatment process. These determinations can be challenging in the concentrated alkanolamine solutions.

This application note demonstrates the separations of µg/L to 25 mg/L concentrations of inorganic cations and ammonium, and µg/L to 1250 mg/L concentrations of alkanolamines in 1000-fold diluted neutralizing amine solution sample on the Thermo Scientific™ Dionex™ IonPac™ CS20 cation-exchange column.

Peaks:		mg/L
1.	Sodium	186
2.	Ammonium	194
3.	EA	28.6
4.	DEA	28.2
5.	TEA	972
6.	Magnesium	20.7
7.	Calcium	30.7

1000-fold diluted TEA-based scrubbing amine sample.

For more information click here

Summary of calibration range and MDL results.

	Calibration Range (mg/L)	Type	Coefficient of Determination	MDL* (µg/L)
Sodium	0.5–25	Quadratic	0.9997	26
Ammonium	0.5–25	Quadratic	0.9994	160
EA	0.5–25	Quadratic	0.9991	49
	50–1250	Quadratic	0.9998	--
DEA	0.5–25	Quadratic	0.9997	100
	50–1250	Quadratic	0.9996	--
TEA	0.5–25	Quadratic	0.9989	100
	50–1250	Quadratic	0.9979	--
MDEA	0.5–25	Quadratic	0.9993	52
	0–1250	Quadratic	0.9992	--
Magnesium	0.5–25	Quadratic	0.9978	2
Calcium	0.5–25	Quadratic	0.9926	3

*n = 7, MDL = SD × 3.14.

For more information click here

Determination of total fluorine, chlorine, bromine, and sulfur in liquefied petroleum gas by pyrohydrolytic combustion ion chromatography
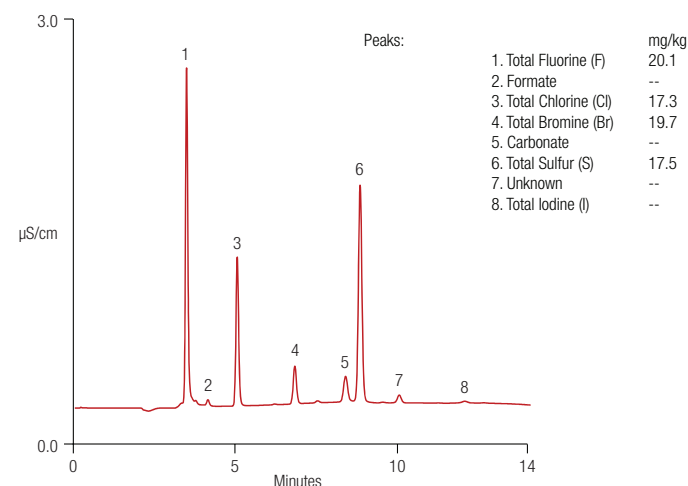
Heavier components of natural gas, C3-C5 can be compressed and is often pressurized to a liquid state to produce liquefied petroleum gas (LPG). Determinations of halogen and sulfur-containing compounds in LPG are needed because these contaminants can foul the catalysts during processing and cause corrosion. Analysis of LPG hydrocarbons is commonly done by GC-MS; however, the quantification of numerous halogen- and sulfur-containing compounds can be challenging. As with other challenging samples, pyrolytic combustion ion chromatography (CIC) is an ideal approach to eliminate the sample matrix and increase sample homogeneity.

This application note demonstrates the determinations of total halo-benzene compounds and total dimethylsulfide in n-butane LPG as fluoride, chloride, bromide, iodide, and sulfate using pyrohydrolytic combustion coupled with an IC system using a Thermo Scientific™ Dionex™ IonPac™ AS20 column.

Peaks:		mg/kg
1. Total Fluorine (F)		20.1
2. Formate		--
3. Total Chlorine (Cl)		17.3
4. Total Bromine (Br)		19.7
5. Carbonate		--
6. Total Sulfur (S)		17.5
7. Unknown		--
8. Total Iodine (I)		--

Nine incremental combustions of n-butane LPG standard with 2 mg/kg additives with results calculated using the 15–135 mg/kg calibration curve.

Method qualification results showing calibration ranges, linear response, and estimated MDL.

Compound*	Calibration Range (mg/kg)	Type	Coefficient of Determination (r²)	MDL using Small Loop Injections (µg/kg)	Calibration Range (mg/kg)	Type	Coefficient of Determination (r²)
Total Fluorine as Fluoride	2–18	Quadratic	0.9994	17	15–135	Quadratic	0.9992
Total Chlorine as Chloride	2–18	Linear	0.9990	280	15–135	linear	0.9988
Total Bromine as Bromide	2–18	Linear	0.9995	1000	15–135	linear	0.9996
Total Sulfur as Sulfate	2–18	Linear	0.9991	36	15–135	linear	0.9986
Total Iodine as Iodide*	--	--	--	4000	15–135	linear	0.9986*

*A calibration curve was obtained for total iodine using 50 mg/L peroxide, 1000 mg/L hydrazine absorption solution.

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For an overview of the Thermo Fisher Scientific portfolio of products for oil and gas, see Applications Notebook: Oil & Gas Application Notebook – Complete Workflow Solutions: Chromatography, Mass Spectrometry, Molecular Spectroscopy, Lab Data Management Software

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Biofuels

Reductions in the supplies of underground fossil fuels and increased production of greenhouse gases has led to a focus on alternative paths for energy generation from renewable resources, such as plants and algae (biomass).

For biomass-derived fuel (biofuels) monitoring the efficiency of biomass-to-biofuel conversion ensures that required yields and process economics are achieved. As with petroleum-derived fuels, determination of the presence of potential corrosives is essential to minimize any associated damage.
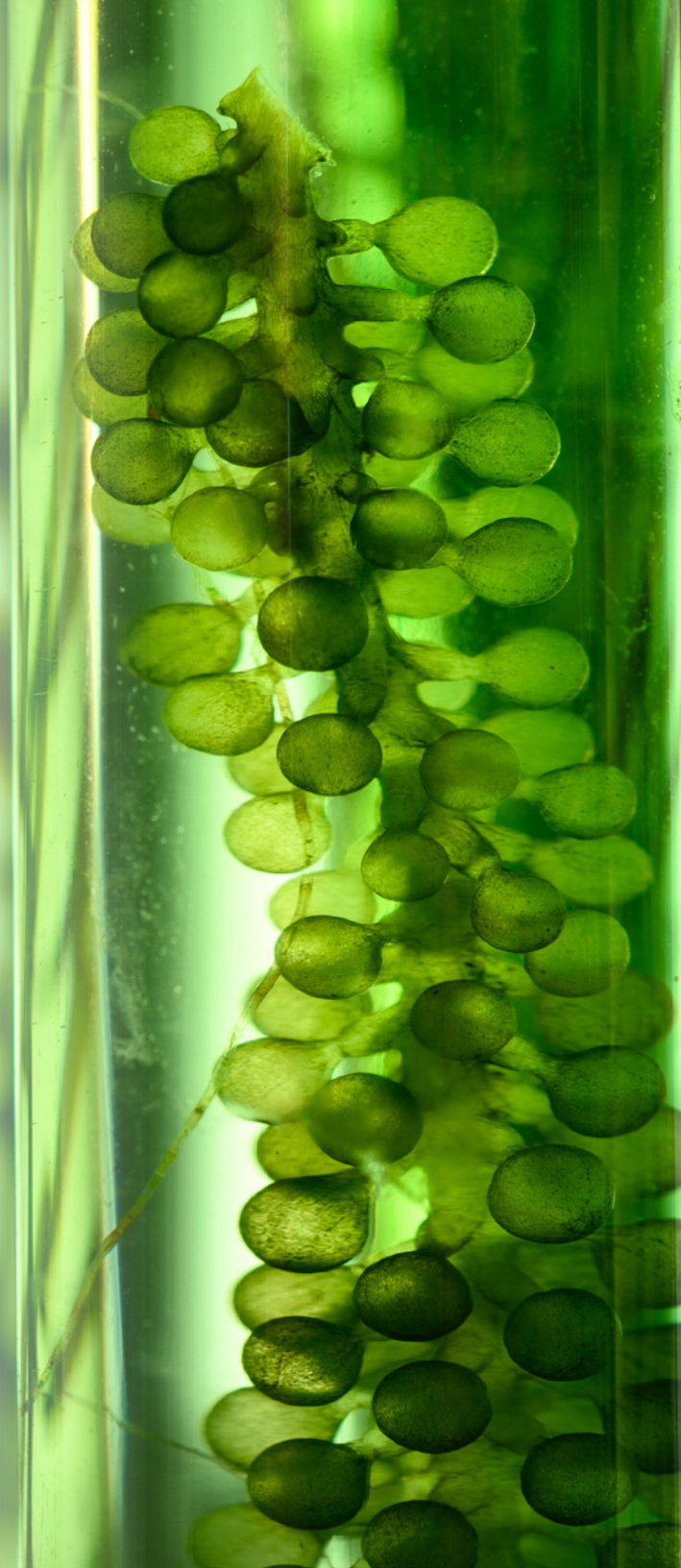
Fast determination of biofuel sugars by HPAE-PAD
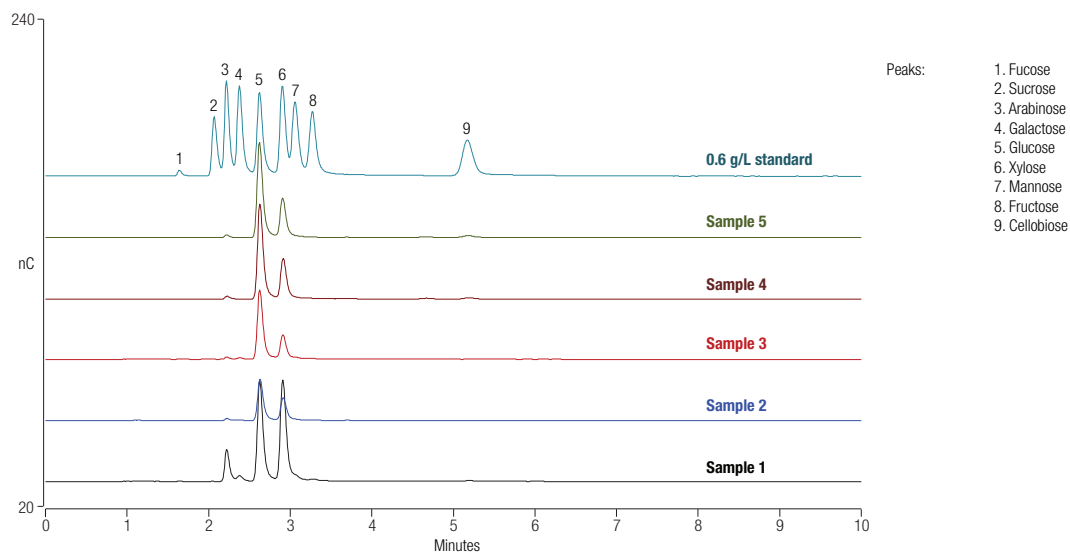
Monitoring the release of 5- and 6-carbon sugars, which can be fermented into biofuels like ethanol and biodiesel, is required for evaluating the overall efficiency of biomass-to-biofuel conversion and is directly related to target biofuel yield and process economics. Hence, the determination of carbohydrates in hydrolysates derived from lignocellulosic biomass is a crucial step in biofuel production, although development of robust analytical methods still remains a challenge. Currently used methods suffer from several drawbacks such as low throughput, poor analyte resolution, and

nonapplicability to a wider set of biomass samples. High-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD) can be used to determine sugars from biomass hydrolysate samples.

Here, eight common sugars are separated in less than six minutes using HPAE-PAD that utilizes the 4 μm resin particle size and 150 mm length of the Thermo Scientific™ Dionex™ CarboPac™ SA10-Fast-4μm column.

Peaks:
1. Fucose
2. Sucrose
3. Arabinose
4. Galactose
5. Glucose
6. Xylose
7. Mannose
8. Fructose
9. Cellobiose

Representative chromatograms of five lignocellulosic biomass-based biofuel samples 1–5.

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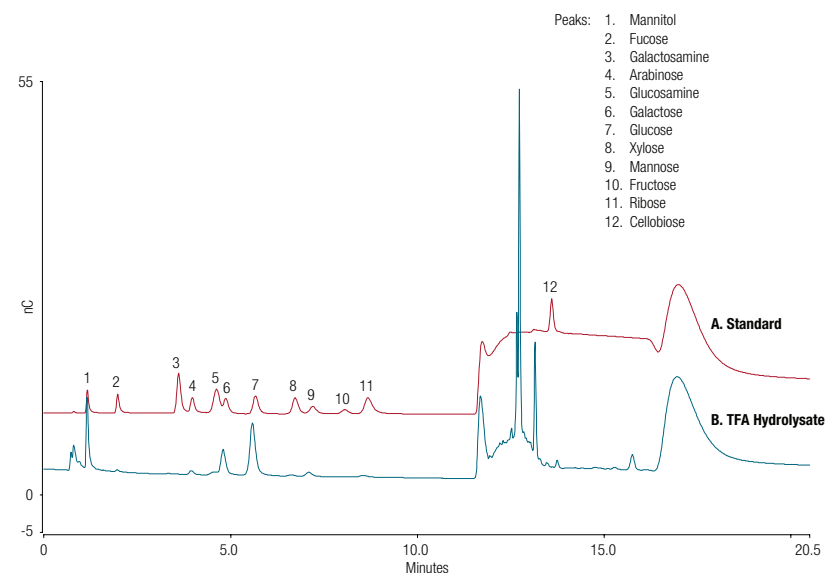# Determination of carbohydrates in algal biofuel samples

Microalgae have received significant attention not only because of their potential to be a viable feedstock for bio-based production of transportation fuel, but also because of the nutritional value and health benefits of algae-based foods. The breakdown of fermentable carbohydrates present in algal biomass is used for monitoring the efficiency of biomass-to-biofuel conversion and is directly related to target biofuel yield and process economics. In addition, a complete characterization of the carbohydrate breakdown products in the algae is essential for efficient nutrient recycling to determine which sugars are best absorbed by the algae. Determination of carbohydrates in algal biomass is a crucial step in designing a production process, although the development of robust analytical methods remains a challenge.

High-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD) can be used to determine carbohydrates in these samples and the current work describes two methods that use a Thermo Scientific™ Dionex™ CarboPac™ PA20-Fast-4μm column for the determination of key sugars present in acid-hydrolyzed algal biomass.

Peaks: 1. Mannitol
2. Fucose
3. Galactosamine
4. Arabinose
5. Glucosamine
6. Galactose
7. Glucose
8. Xylose
9. Mannose
10. Fructose
11. Ribose
12. Cellobiose

A. Standard
B. TFA Hydrolysate

Short method for determination of sugars in TFA hydrolysed algae samples.

Recovery of algae sugar spiked into the algae acid hydrolysates using the short method (n=3).

Spike Level (mg/L)	Glucose		Xylose		Mannose		Ribose	
	Avg Amount (mg/L)	%Recovery	Avg Amount (mg/L)	%Recovery	Avg Amount (mg/L)	%Recovery	Avg Amount (mg/L)	%Recovery
0.5	1.13	91	0.01	100	0.18	95	0.03	100
0.2	1.11	95	0.01	110	0.18	110	0.04	100

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Determination of potential sulfate in denatured ethanol using modified ASTM D7328 method

Ethanol, a renewable alternative energy source made from grain and other biomass resources, can be used as a fuel either by itself or blended with gasoline. Contamination of fuel ethanol with nonvolatile ions, such as chloride and sulfate, can cause corrosion problems and affect engine performance.

This application update describes a simple ion chromatography (IC) method to determine potential sulfate in denatured ethanol. This method is consistent with the modified procedure described in ASTM D7328-17, which covers an IC procedure for the determination of the total and potential inorganic sulfate and total inorganic chloride content in hydrous and anhydrous denatured ethanol to be used in motor fuel applications. Our IC method allows for the analysis of denatured ethanol samples using a Thermo Scientific™ Dionex™ IonPac™ AS22 column set on a compact IC system (Dionex Integrion HPIC System).

Peaks:		A (mg/L)
	1. Fluoride	2
	2. Chloride	10
	3. Nitrite	10
	4. Bromide	10
	5. Nitrate	10
	6. Phosphate	20
	7. Sulfate	10
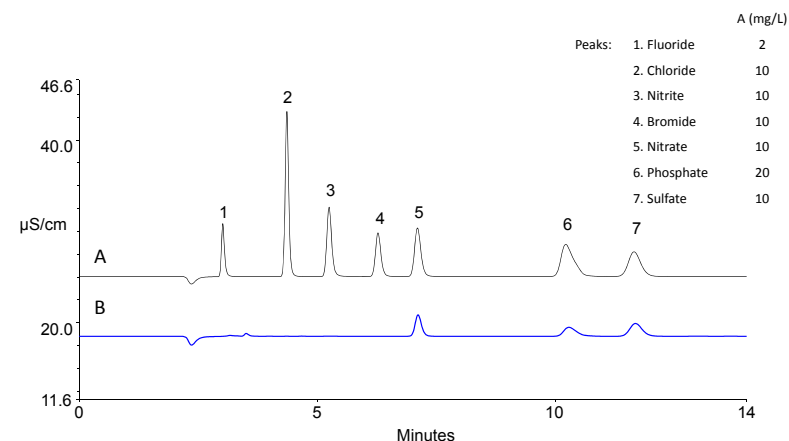
Separation of (A) seven common anions and (B) a denatured ethanol sample.

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Power

The ionic purity of boiler water, feedwater, borated water, and steam is important to maintain component reliability, safety, and the overall economic viability of nuclear power plant (NPP) and fossil fuel power plant (FFPP) operation. Failure mechanisms in the boiler, turbine, heaters, and condensers of power plants can be directly related to water and steam ionic purity. By understanding the ionic contamination levels for water and steam contaminants that are determined by IC, utilities and operators can eliminate or reduce damage from corrosion, scaling, and deposition. For additional corrosion protection, organic amines are commonly added to plant waters and monitoring their presence in wastewater, along with degradation products, is critical to ensure compliance with regulatory discharge limits.

Determination of trace sodium and transition metals in power industry samples by ion chromatography with nonsuppressed conductivity detection

It is critical for power plants to continuously monitor corrosive ionic impurities in various plant water streams. Corrosive contaminants—particularly sodium, chloride, and sulfate—have been implicated as a major source of corrosion and deposition-related plant shutdowns in nuclear and fossil-fueled plants. Ion chromatography (IC) can measure these contaminants and has been implemented in several U.S. power plant water chemistry monitoring programs. The measurement of ultratrace levels of sodium in boiler waters treated with amine additives, such as ethanolamine, is a particularly challenging analytical problem. Nuclear and fossil-fueled power plants also require the monitoring of various metals that can also play a role in corrosion. Although suppressed and nonsuppressed conductivity can be used for the detection of alkali and alkaline earth metals, only nonsuppressed conductivity is suitable for the detection of transition metals.

This application note compares suppressed to nonsuppressed conductivity detection for the determination of sub-ppb concentrations of sodium in simulated power plant matrices using the Thermo Scientific™ Dionex™ IonPac™ SCS 1 column. In addition, this application note describes the determination of transition metals by nonsuppressed conductivity detection.

Peaks:	A	1. Ammonium	— µg/L (ppb)
		2. Ethanolamine	3000
	B	1. Sodium	0.25 µg/L (ppb)
		2. Ammonium	—
		3. Ethanolamine	3000
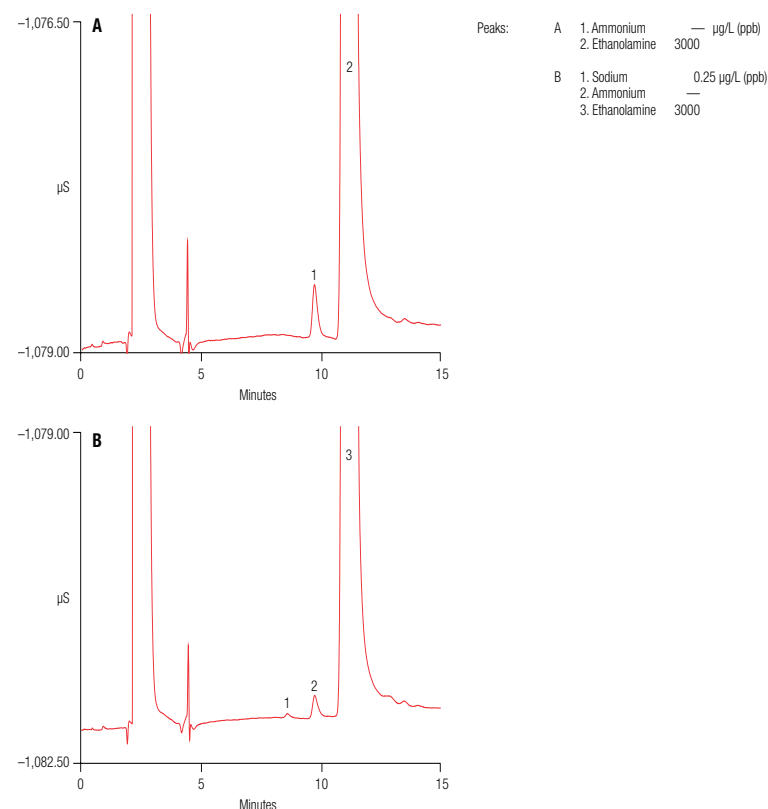
A representative chromatogram of 3000 µg/L ethanolamine spiked with (A) no sodium, and (B) 0.25 µg/L sodium.

Calibration and MDL for sodium using nonsuppressed conductivity detection with a 3 mL sample volume.

Analyte	Range[a] (ng/L)	Linearity (r²)	Calculated MDL[b] (ng/L)	MDL Standard (ng/L)
Sodium	100–500	0.9998	68	200

[a] Calibration levels were 100, 250, and 500 ng/L (each standard injected in duplicate).

[b] MDL = t × S where t = Student's t value for a 99% confidence level and a standard deviation estimate with n – 1 degrees of freedom (t = 3.14 for seven replicates of the MDL standard), and S = standard deviation of the replicate analysis.

Calibration and MDL for copper and zinc using nonsuppressed conductivity detection.

Analyte	Range[a] (ng/L)	Linearity (r²)	Calculated MDL[b] (ng/L)	MDL Standard (ng/L)
Copper	0.125–1.00	0.9998	33	125
Zinc	0.025–0.50	0.9999	6.7	25

[a] 25 µL injection volume.

[b] MDL = t × S where t = Student's t value for a 99% confidence level and a standard deviation estimate with n – 1 degrees of freedom (t = 3.14 for seven replicates of the MDL standard), and S = standard deviation of the replicate analysis.

Determination of morpholine, ethanolamine, and hydrazine in simulated nuclear power plant wastewater

Nuclear power plant (NPP) wastewater can contain high salt content from periodic flushes of the boiler (blowout) to remove salt buildup (i.e., scale). The determination of morpholine, ethanolamine (ETA), and hydrazine in the presence of mg/L concentrations of ammonium is an analytical challenge due to their similar selectivity on cation-exchange phases and the presence of higher concentrations of ammonium and other common cations. These challenges were met by optimizing one method to determine both hydrazine and morpholine and a second method to determine ETA.

This application note describes two methods to determine µg/L concentrations of hydrazine, morpholine, and ETA in disparately larger concentrations of ammonium and other cations in a simulated NPP wastewater sample. Hydrazine and morpholine were determined in the simulated NPP wastewater matrix on the Thermo Scientific™ Dionex™ IonPac CS16 column by suppressed conductivity detection and integrated pulsed amperometric detection (IPAD). Ethanolamine is separated by cation-exchange chromatography on the Thermo Scientific™ Dionex™ IonPac CS15 column with suppressed conductivity detection using the column's selectivity to elute ethanolamine before ammonium.

Peaks:
1. Lithium   1000 µg/L
2. Sodium   50,000
3. Ammonium   50,000
4. Ethanolamine   150
5. Hydrazine   20
6. Potassium   10,000
7. Morpholine   200
8. Magnesium   50,000
9. Calcium   50,000
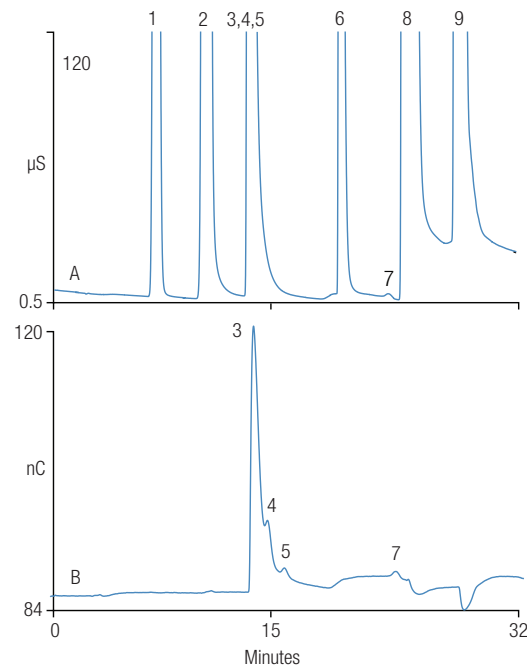
Comparison of hydrazine and morpholine in a simulated NPP wastewater matrix by A) suppressed conductivity detection and B) IPAD.

Precisions and accuracies of amine determinations in a simulated NPP wastewater matrix[a].

Analyte	Retention Time RSD	Peak Area RSD	Amount Added (µg/L)	Average Recovery (%)
Hydrazine[b]	0.05	1.9	20	109.0
Morpholine[b]	0.08	2.9	200	97.2
Ethanolamine[c]	0.43	1.8	200	101.7

[a] The simulated NPP wastewater matrix contains 1 mg/L lithium, 10 mg/L potassium, and 50 mg/L each of sodium, ammonium, calcium, and magnesium.

[b] The precision and recoveries of hydrazine and morpholine are determined in 100% of the simulated NPP wastewater matrix.

[c] The precision and recovery of ethanolamine are determined in 80% of the simulated NPP wastewater matrix.

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For more a more comprehensive collection of power application notes see:
Power Plant Water Applications Summary Notebook

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