Dionex as your Continual Source for Water Analysis

As a leader in providing chromatography solutions for water analysis we understand the needs of providing the best solutions for water analysis. Not only does water analysis require good chromatorgraphy, but also an understanding of regulations. Finally, there are the practical implications for water analysis. These include workflow, cost, time, reducing complexity, reporting, system maintenance and upkeep, quality service, and many other factors. Learn how Dionex innovations like Reagent-Free Ion Chromatography, Eluent Generation, Eluent Regeneration, and Chromeleon Chromatography Data System software make IC Easy!

IMPORTANT LITERATURE	
Analyte	**Application or Poster**
Anions	AN 154: Determination of Inorganic Anions in Environmental Waters Using a Hydroxide-Selective Column
Anions	AN 140: Fast Analysis of Anions in Drinking Water by Ion Chromatography
Anions	AN 135: Determination of Inorganic Anions in Wastewater by Ion Chromatography
Cations	AN 141: Determination of Inorganic Cations and Ammonium in Environmental Waters by Ion Chromatography Using the IonPac CS1
Bromate	AN 187: Determination of Sub-µg/L Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection
Bromate	AN 208: Determination of Bromate in Bottled Mineral Water Using the CRD 300 Carbonate Removal Device
Bromate	AN 184: Determination of Trace Concentrations of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters
Iodine, Iodate	AN 236: Determination of Iodide and Iodate in Seawater and Iodized Table Salt by HPLC with UV Detection
Haloacetic Acids	AN 217: Determination of Haloacetic Acids in Water Using IC-ESI-MS/MS
Chromate	AU 144: Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography
Cyanide	AN 227: Determination of Total Cyanide in Municipal Wastewater and Drinking Water Using Ion-Exclusion Chromatography with Pulsed Amperometric Detection (ICE-PAD)
Carbamates	AN 96 Determination of N-Methylcarbamates by Reversed-Phase HPLC
CEC: Surfactants	Poster: High-Efficiency Separation of Anionic Surfactants Using Reversed-Phase HPLC and Suppressed Conductivity Detection
CEC: Surfactants	New Development in Surfactant Analysis by HPLC

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Passion. Power. Productivity.

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Water Analysis for a Global Market

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Water Quality
Global Supply, Local Concern

Currently, less than 1% of the planet's water is available for human consumption. Resources for potable water are under increased demand due to global population growth and global warming. With surface water contamination and groundwater resources overexploited, regulation and enforcement levels are increasing along with new regulatory and conservation policies. Coupled with the increased scrutiny of emerging contaminants, the need for effective water analysis and monitoring has never been higher.

Ground and surface water are a vital resource for a healthy environment. They are also the largest source of fresh water. These waters often represent complex matrices that interfere with detection for the analytes of interest. Dionex has overcome many of the challenges of surface and groundwater analysis through unique and innovative chromatography and sample preparation techniques.

Drinking water is analyzed for both primary and secondary contaminants. Primary contaminants are typically toxic compounds that cause health issues while secondary contaminants affect taste and overall water quality. Another major challenge for drinking water is the analysis of disinfection byproducts (DBP). During the drinking water treatment process, drinking water is treated with disinfectants to remove potentially harmful bacteria. These disinfectants also react with ions and residual organic matter resulting in the formation of DBPs. DBPs are highly toxic, are regulated, and require mitigation of their concentrations prior to distribution. Dionex has developed innovative techniques for the complete analysis of drinking water contaminants and DBPs.

Wastewaters discharged by industries and municipalities discharge a variety of pollutants, including heavy metals, toxins, oils, nutrients, and solids, all of which endanger ecosystems and pose a threat to human health. Contaminant analysis is complicated because waste waters contain a multitude of compounds that interfere with separation and detection of analytes, often resulting in low recoveries, false positives, or false negatives. To overcome these interference effects, wastewaters often require matrix elimination strategies, such as sample preparation, solid phase extraction, or other techniques in order to accurately determine the contaminant of interest.

Dionex offers the most comprehensive capabilities for inorganic and organic contaminant extraction and analysis for drinking, ground, surface, and even complex contaminated wastewaters. As your partner for water analysis, Dionex can provide you with the technology, experience, and support to help you monitor your water quality, provide safe drinking water, and protect the environment.

System Solutions

Ion Chromatography

Since the development of ion chromatography (IC) analysis over 30 years ago, Dionex has pioneered the development of IC systems, including Reagent-Free™ ion chromatography (RFIC™) systems. Whether you are running a few samples or high throughput, whether your analytical task is simple or complex, Dionex has the right system for you.

- Starter line and basic systems for straight forward and repetitive analyses of ions in water samples
- Reagent-Free systems reduce eluent and regenerant preparation
- Dual systems allow double throughput, simultaneous analysis, and complex methods
- Suppressed conductivity, pulsed amperometry, UV-vis, and MS detectors
- Ion-exchange, ion-exclusion, concentrator, and trap columns

Columns

The IonPac® column family offers a wide variety of ion exchange capabilities for hydroxide and carbonate based eluents.

Liquid Chromatography

The Dionex UltiMate® 3000 series of liquid chromatography systems allows you to choose from a variety of modules and configurations to adapt the instrument to your applications.

- Dual systems for multidimensional separations of organic compounds
- Rapid Separation LC (RSLC) systems for fast, high-flow-rate, ultrahigh-pressure applications
- Reversed-phase (mixed-mode HILIC and ion-exchange) and monolith columns for fast analysis
- Diode array, multi-wavelength, fluorescence, Corona® CAD®, and MS detectors

Columns

The Acclaim® column family meets the high standards set by modern HPLC, UHPLC, and LC/MS methods.

Solid-Phase Extraction

Liquid–liquid extractions for organic contaminant extraction that normally take hours can be automated using the AutoTrace® 280 SPE workstation. AutoTrace significantly reduces sampling handling compared to separatory funnel or vacuum manifold extraction. The tedious and time-consuming steps of liquid-liquid extraction can be greatly decreased by automating the SPE steps of condition, load, and rinse and elute. AutoTrace offers a lower sample preparation cost per sample by reducing solvent and labor costs by as much as 90%.

- Extractions for liquid sample sizes from 20 mL to 4 L
- Dramatic solvent reduction and reduced sample handling
- Wide range of applications
- Automation
- Handles acidic and alkaline matrices
- Approved for use by many government agencies

Columns

Dionex has several columns for offline SPE that are ideally suited for AutoTrace. These columns are designed for extraction based on EPA approved methods.

**ICS Series
IC/RFIC Analytical Systems**

**UltiMate Series
HPLC/RSLC Analytical Systems**

AutoTrace SPE workstation

The determination of common inorganic anions in drinking water is one of the most important applications for water analysis. Fluoride, nitrite, and nitrate are regulated as primary contaminants in many countries around the globe. In the United States, organic anions such as chloride and sulfate are regulated under the U.S. National Secondary Drinking Water Standards, which are guidelines regarding taste, color, and odor.

Anions

Dionex has a wide variety of carbonate- and hydroxide-selective columns for the determination of anions in a broad range of water matrices. The high capacity IonPac® AS22 is a carbonate-selective column that allows the separation of common inorganic anions in a variety of sample matrices, including drinking water, wastewater, process streams, and scrubber solutions. The AS22 selectivity provides retention of fluoride from the water dip and resolution of fluoride,

acetate, and formate, and is an excellent choice for EPA 300.0 and 300.1 for the determination of anions in drinking water.

The IonPac AS18 represents the culmination of over 20 years of column development, and is a key part of our RFIC system. The AS18 allows improved resolution between closely eluting peak pairs chloride:nitrite and sulfate:nitrate. It also elevates the ability to tolerate higher ionic strength matrices without column overloading. Hydroxide-selective stationary phases also give a better retention of weakly retained anions like fluoride and acetate, and only moderate retention of divalent anions such as sulfate. Additional advantages of hydroxide eluents are improved linearity, lower background conductivity, and improved MDLs compared to carbonate-based eluents.

For example, EPA 300.0 recommends diluting the sample if sulfate exceeds 95 mg/L. The IonPac AS18 column allows a large linear range from 0.2 to 200 mg/L, eliminating the need to dilute and re-analysis of high-ionic-strength samples.

Iodide and Iodate in Seawater

Iodine is an essential element naturally present in seawater and seafood. The most common forms of natural iodine in the diet are iodide and iodate. Dietary iodine deficiency affects thyroid function and leads to developmental diseases, neurological damage, goiter, and paralysis. Because iodine is found in high concentrations in seawater, it may be possible to generate iodated drinking water from seawater, thereby eliminating the need to iodize salt.
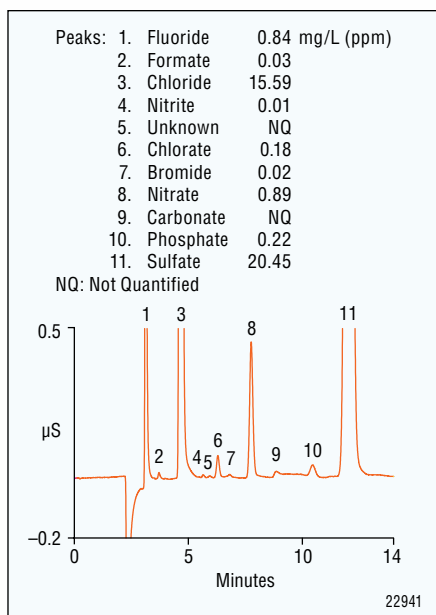
Peaks:		
1.	Fluoride	0.84 mg/L (ppm)
2.	Formate	0.03
3.	Chloride	15.59
4.	Nitrite	0.01
5.	Unknown	NQ
6.	Chlorate	0.18
7.	Bromide	0.02
8.	Nitrate	0.89
9.	Carbonate	NQ
10.	Phosphate	0.22
11.	Sulfate	20.45

NQ: Not Quantified

Figure 1. Determination of inorganic anions in a municipal drinking water sample on an IonPac AS22 column.

Peaks:		A	Amount Added
	1. Fluoride	0.14	1 mg/L
	2. Chloride	28.8	30
	3. Nitrite-N	—	2
	4. Carbonate	—	—
	5. Bromide	0.03	2
	6. Sulfate	99.5	80
	7. Nitrate-N	0.89	5
	8. Phosphate-P	—	0

Fortified Surface Water
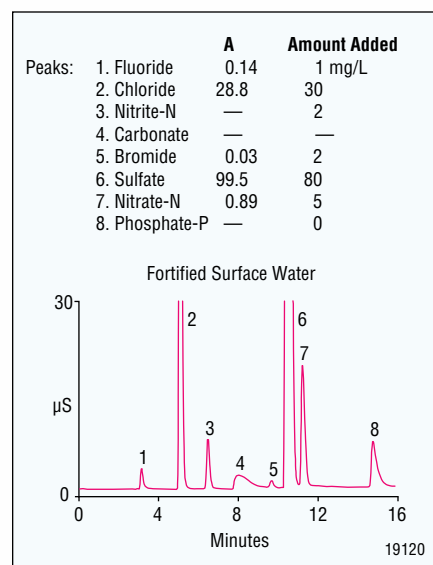
Figure 2. Determination of inorganic anions in fortified surface water using the IonPac AS18 column.

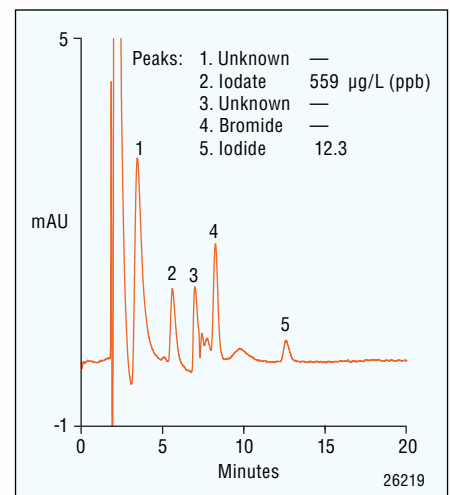| Peaks:		
1.	Unknown	—
2.	Iodate	559 µg/L (ppb)
3.	Unknown	—
4.	Bromide	—
5.	Iodide	12.3

Figure 3. HPLC using a mixed-mode column can determine iodide and iodate in seawater, synthetic sea salt, and table salt. This method is specific, sensitive, and rapid which minimizes the need for sample pretreatment or dilution.

Cations and Ammonia

The IonPac CS16 column is a high-capacity cation-exchange column that replaces the CS15 column for disparate concentration ratios of ammonium and sodium in diverse sample matrices. The CS16 is ideal for the determination of low concentrations of ammonium in environmental waters. It provides improved resolution of sodium from ammonium and alkanolamines, even for samples high in ionic strength.
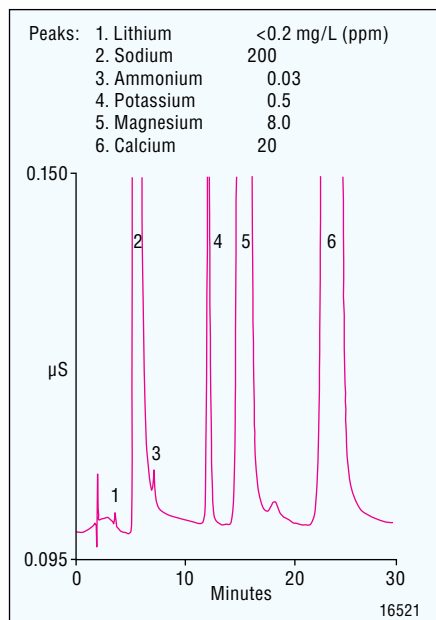

Peaks:
1. Lithium <0.2 mg/L (ppm)
2. Sodium 200
3. Ammonium 0.03
4. Potassium 0.5
5. Magnesium 8.0
6. Calcium 20

16521

Figure 4. Resolution of trace ammonium from high sodium with the IonPac CS16 column.

Fast IC for Anions and Cations

To meet increasing customer demands for productivity and higher throughput, faster analysis of anions and cations is becoming more and more important. The standard approach for achieving fast analysis times is simply to increase the flow rate. Limitations to this approach are high backpressure and increased waste. Another approach is to shorten the column length. However, this sacrifices resolution of critical peak pairs. To overcome these two limitations, IonPac ion-exchange resins with high capacity maintain resolution in a shorter column format.

The IonPac AS22 and IonPac CS12A columns have been specifically designed to have enough capacity to maintain resolution even in a short column format and for use on any Dionex system. This permits the determination of anions and cations with high resolution even in drinking, ground, surface, and wastewater matrices in under 5 min, allowing laboratories to achieve higher productivity and increased throughput to get faster results.

Peaks:
1. Fluoride 6. Bromide
2. Formate 7. Nitrate
3. Chloride 8. Carbonate
4. Nitrite 9. Phosphate
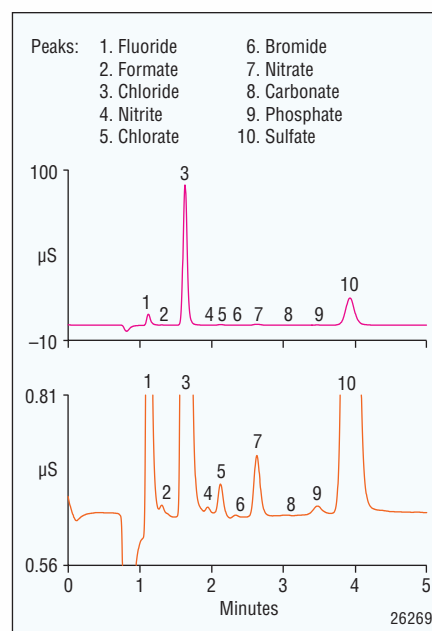5. Chlorate 10. Sulfate

26269

Figure 5. Analysis of municipal drinking water sample is shown using a new prototype Fast IonPac AS22 column (4 x 150 mm) at 2.0 mL/min. Run time is well under 5 min for this application. The bottom trace shows an enlarged image of the separation.

Disinfection of drinking water is considered to be one of the major public health advances of the 20th century. Water is often disinfected before it enters the distribution system to ensure that dangerous microbial contaminants are killed. Chlorine, chlorates, chlorites, chloramines, or chlorine dioxides are most often used because they are very effective disinfectants, and residual concentrations can be maintained in the water system. Drinking and bottled waters are commonly disinfected with ozone. These processes can leave behind dangerous byproducts that must be monitored for safety.

Oxyhalides and Bromate

Over the last two decades, Dionex has led the effort in developing sensitive and robust ion chromatography (IC) methods for the determination of bromate and other oxyhalides (e.g., chlorite and chlorate). Determination of bromate in natural mineral waters has been demonstrated using IonPac AS19 column with a hydroxide eluent, or the IonPac AS23 column and a carbonate/bicarbonate eluent using direct injection and suppressed conductivity detection.

Determining low concentrations of bromate in high-ionic-strength matrices using suppressed conductivity detection is subject to potential interferences and loss of sensitivity. Dionex products were instrumental in the development of the postcolumn derivation techniques in U.S. EPA Methods 317.0 and 326.0, and ISO-1428. Although postcolumn reaction methods do not generally suffer from interferences by common anions, column overloading with high-ionic-strength samples can still cause peak broadening and loss of response. Natural mineral waters typically contain elevated levels of common anions that can significantly exceed the concentrations

present in most municipal drinking water samples. Finally, postcolumn methods using visible detection either generate carcinogenic by products and/or have not been shown to be robust enough under normal use. The high-capacity IonPac AS19 and IonPac AS23 columns allow conductivity detection to be used for bromate determination in many drinking waters
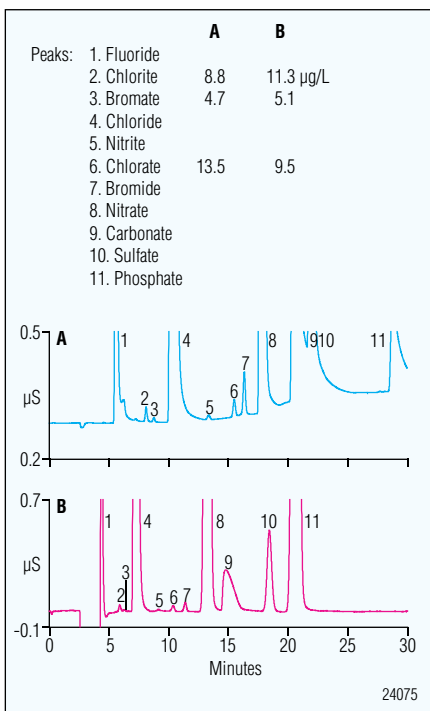

Figure 6. Comparison of the A) IonPac AS19 and B) IonPac AS23 columns for the separation of trace concentrations of common anions and DPB anions spiked in mineral water A.

Another strategy for bromate determination in high-ionic-strength drinking waters is the use of a two-dimensional (2-D) IC system. Figure 7 shows the results of a 2-D IC separation of bromate in a high-ionic-strength matrix. The bromate that was undetectable in the first dimension is fully resolved in the second. Using this 2-D IC technique, an MDL of 0.036 µg/L can be achieved in high-ionic-strength matrices without the need for postcolumn derivatization. This method is approved for compliance monitoring as EPA 302.
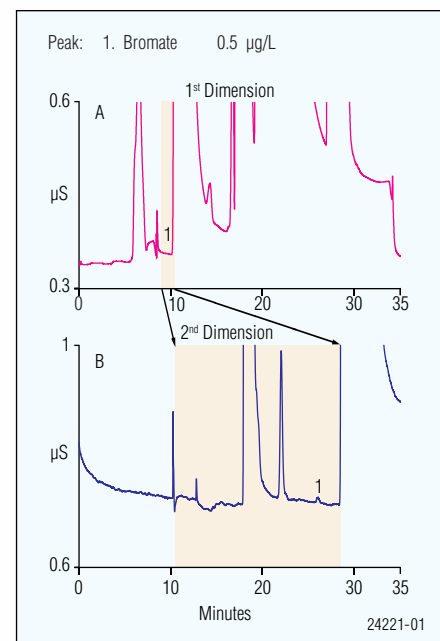

Figure 7. Results of a 2-D IC separation of bromate in a high-ionic-strength matrix.

Haloacetic Acids, Bromate, and Dalapon

Haloacetic acids (HAAs) are disinfection byproducts produced during chlorination of water containing natural organic matter and bromide. The current EPA Methods 552.1, 552.2, and 552.3 require derivatization and multiple extraction steps followed by gas chromatography (GC) with electron capture detection (ECD). Ion chromatography-mass spectrometry (IC-MS/MS) offers a sensitive and selective direct injection technique that does not require sample pretreatment. The separation of all nine HAAs and bromate is achieved using the IonPac AS24 anion-exchange column with a hydroxide gradient. The unique selectivity of this column allows separation of these analytes from common inorganic matrix ions so that the chloride, sulfate, nitrate, and bicarbonate are diverted to waste during the analytical run, thereby avoiding signal suppression of the ESI-MS/MS instrument. Using RFIC technology along with the IonPac AS24 column, all nine haloacetic acids, bromate, and Dalapon can be separated and quantified in low ppb levels using IC-MS/MS detection. Dionex developed this technique specifically for the U.S. EPA for compliance monitoring of disinfection by products in drinking water. This IC-MS/MS based method has been approved by the U.S. EPA Office of Ground Water and Drinking Water as EPA 557. This strategy is also used in Japan and the United Kingdom.

Nitrosamines

Nitrosamines represent a nitrogen based class of DBPs that are formed from natural organic matter present in water. Their presence is heavily monitored through the U.S. EPA Contaminant Candidate List and Unregulated Contaminant Monitoring Rule. The analysis of nitrosamines by GC, as in U.S. EPA Method 8270, is problematic due to the thermal instability and reactivity of these substances.

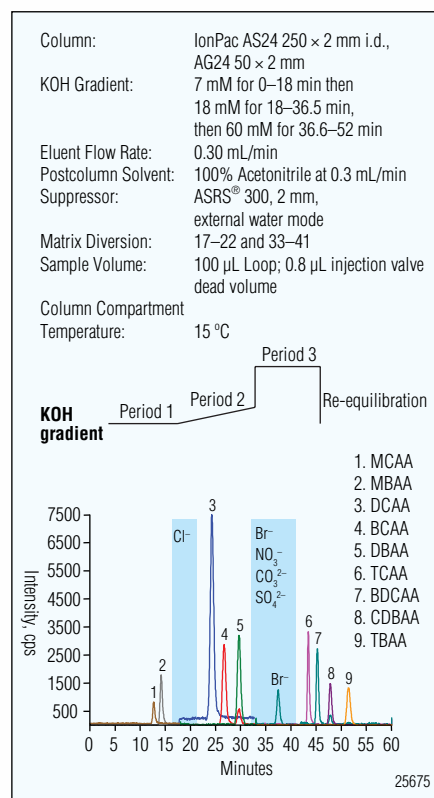|	
Column:	IonPac AS24 250 × 2 mm i.d., AG24 50 × 2 mm
KOH Gradient:	7 mM for 0–18 min then 18 mM for 18–36.5 min, then 60 mM for 36.6–52 min
Eluent Flow Rate:	0.30 mL/min
Postcolumn Solvent:	100% Acetonitrile at 0.3 mL/min
Suppressor:	ASRS® 300, 2 mm, external water mode
Matrix Diversion:	17–22 and 33–41
Sample Volume:	100 µL Loop; 0.8 µL injection valve dead volume
Column Compartment Temperature:	15 ºC

Figure 8. Complete chromatographic resolution of HAA9 in high high-ionic-strength matrix waters using an IonPac AS24 column.

We present an alternative using HPLC. The substances in this list differ greatly in hydrophobicity, and a very wide gradient program is needed to resolve them all. The Acclaim® PA column, unlike most C18 columns, can be used reliably with highly aqueous mobile phases without risk of dewetting.
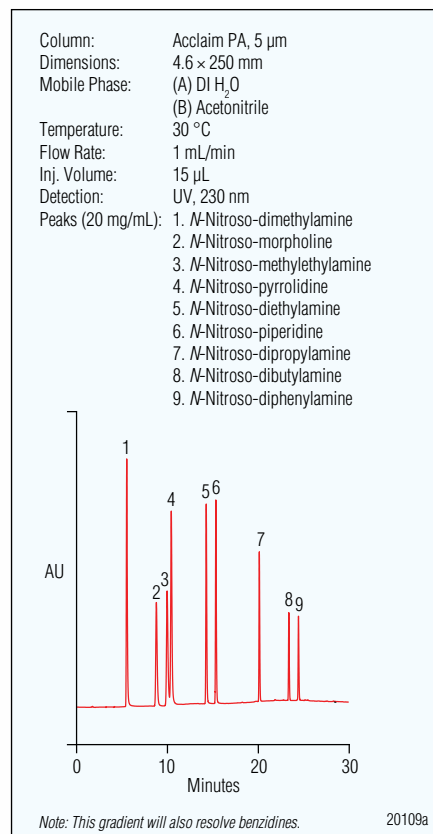
Column:	Acclaim PA, 5 µm
Dimensions:	4.6 × 250 mm
Mobile Phase:	(A) DI H_2O (B) Acetonitrile
Temperature:	30 °C
Flow Rate:	1 mL/min
Inj. Volume:	15 µL
Detection:	UV, 230 nm
Peaks (20 mg/mL):	1. N-Nitroso-dimethylamine
	2. N-Nitroso-morpholine
	3. N-Nitroso-methylethylamine
	4. N-Nitroso-pyrrolidine
	5. N-Nitroso-diethylamine
	6. N-Nitroso-piperidine
	7. N-Nitroso-dipropylamine
	8. N-Nitroso-dibutylamine
	9. N-Nitroso-diphenylamine

Note: This gradient will also resolve benzidines. 20109a

Figure 9. Separation of nitrosamines using an Acclaim PA column.

Pesticides play a large role in agriculture, industry, home/garden maintenance, and public health by supporting the ability to produce many crops, commodities, and services around the world.

Carbamates

N-methylcarbamates and *N*-methylcarbamoyloximes are among the most widely used pesticides in the world, and due to their toxicity are regulated in water and soil. HPLC is the preferred method for separating carbamates. Gas chromatographic analysis has proven unsuccessful due to degradation of the analyte compounds during vaporization. HPLC with UV detection does not offer the sensitivity or specificity required for the sample matrices of interest. HPLC with postcolumn derivatization using fluorescence detection or positive mode electrospray ionization mass spectrometry have been shown to be effective for optimal detection.
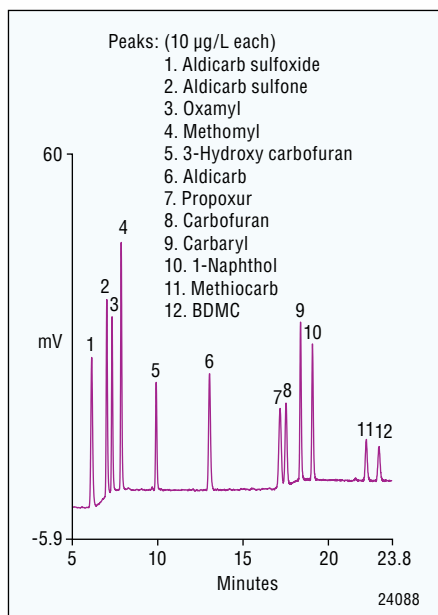

Peaks: (10 µg/L each)
1. Aldicarb sulfoxide
2. Aldicarb sulfone
3. Oxamyl
4. Methomyl
5. 3-Hydroxy carbofuran
6. Aldicarb
7. Propoxur
8. Carbofuran
9. Carbaryl
10. 1-Naphthol
11. Methiocarb
12. BDMC

Figure 10. The Acclaim 120 C8 column provides the ideal chromatographic resolution of most carbamates in a single injection.

Atrazine

Atrazine is the most widely used herbicide in conservation tillage systems, which are designed to prevent soil erosion. As a result of widespread and long-term usage, Atrazine and other triazine herbicide metabolites can be found in the environment and groundwater at low levels. Monitoring of atrazine, its metabolites desethyl-atrazine and desisopropylazine, as well as the other triazine herbicides, is important for environmental protection and food safety control since it has been linked to endocrine and possible carcinogenic effects.

Peaks:
1. Atrazine-desisopropyl   SIM1: 173.9–174.3 (0–5 min)
2. Atrazine-desethyl   SIM2: 187.9–188.3 (2–8 min)
3. Simazine   SIM3: 202.0–202.4 (8–15 min)
4. Atrazine   SIM4: 216.1-216.5 (12–18 min)
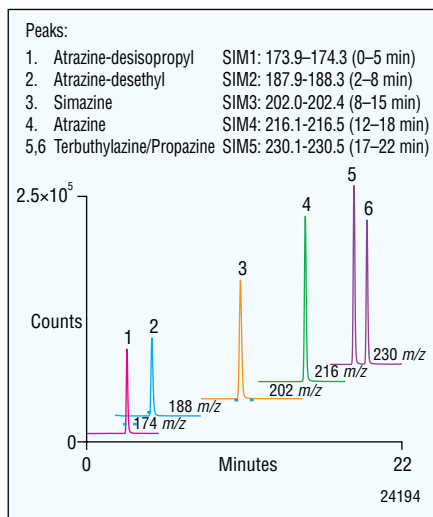5,6 Terbuthylazine/Propazine SIM5: 230.1-230.5 (17–22 min)

Figure 11. Triazine pesticides can be separated by HPLC using an Acclaim 120 C18 column and an acetonitrile/water gradient. Triazine herbicides are detected using ESI in positive mode.

Glyphosate

Glyphosate is the most commonly used agricultural herbicide and second most commonly used herbicide around homes and gardens. Although the bacteria in soil break down glyphosate into the aminomethyl phosphonic acid (AMPA), wastewater discharge samples and drinking water samples in United States and Europe have tested positive for glyphosate. Typical methods for glyphosate use precolumn derivatization or solid-phase extraction (SPE) followed by postcolumn derivatization. Silica-based C18 columns which use cation-exchange mechanisms experience difficulty with the retention of such polar compounds. Using IonPac AS24 direct injection RFIC systems, along with MS Detection, it is possible achieve chromatographic resolution with ppt level detection.
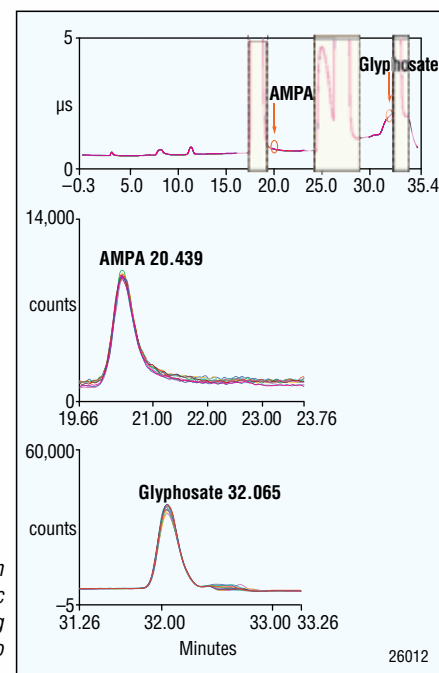

Figure 12. Anion-exchange separation using an IonPac AS24 column and IC-MS/MS detection. IonPac AS24 is a high-capacity column created for dealing with high-ionic-strength samples which are known to contribute to signal suppression within MS/MS detectors.

Dionex has developed a wide variety of analytical techniques for the quantitative determination of toxic ions and metals. These applications involve a thorough understanding of analytical separation as well as matrix interferences that can result in poor recoveries, false negatives and false positives, and affect overall method robustness.

Cyanide

Cyanide is regulated as an environmental contaminant in drinking water, surface water, and wastewater. The typical sources of cyanide contamination are industrial waste from plating and mining industries, burning coal, plastics, and effluent from publicly owned treatment works (POTW). Total cyanide can be determined spectrophotometrically, amperometrically, or by titration. These methods are complicated, often requiring multiple distillation apparatuses, and are subject to interference from high-pH solutions, oxidizers, and sulfur-containing compounds. Chromatographic methods, such as ion-exchange (IE) and ion-exclu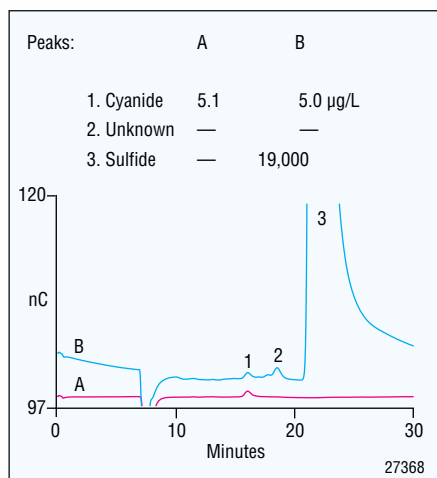sion chromatography (ICE) can eliminate some of these interferences during analytical separation. ICE is preferred because strong acid anions such as chloride and sulfate are excluded from the column, and cyanide is resolved from sulfide.

Perchlorate

Perchlorate inhibits the normal uptake of iodide by the thyroid gland which results in reduced thyroid hormone production. Ammonium perchlorate is manufactured for use as the primary component in solid propellant for rockets, missiles, and fireworks. Perchlorate has been detected in nearly 400 sites across the United States, where most of the contamination appears to be confined to the western and southwestern regions. It is estimated that over 11 million people have perchlorate in their drinking water supplies. Recent evidence suggests that perchlorate is also becoming a global problem. EPA Methods 314.0 and 314.1 were developed to determine trace concentrations of perchlorate in drinking water. The determination of trace perchlorate in high-ionic-strength matrices is still a challenging problem. Alternatively, a two-dimensional ion chromatographic approach can be used to resolve perchlorate from high concentrations of common matrix ions. This 2-D strategy has resulted in a new method, EPA 314.2, which provides an MRL of 0.06 ppb.

Figure 13. Low-level CN⁻ determinations in the presence of high sulfide. Using ICE, interfering anions, such as Cl⁻ and SO₄²⁻, are quickly eluted from the column, while sulfide is well resolved downstream of CN⁻. The detection step has also been improved with the development of platinum electrodes.
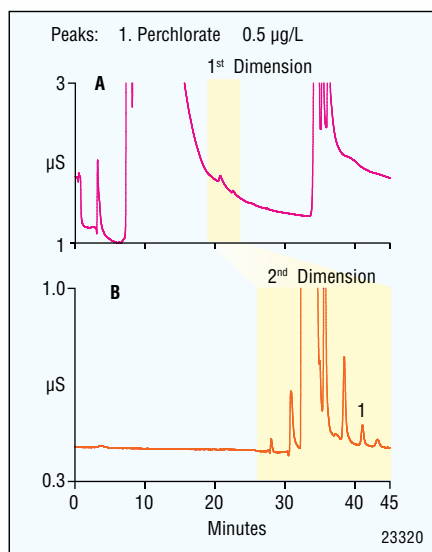

Figure 14. 2-D IC provides several advantages: injection of large sample volumes, the ability to trap perchlorate that is partially resolved in the first dimension onto a concentrator column and separating it in the second dimension, and the ability to combine two different column chemistries to enhance selectivity and reduce the possibility of a false positive.

Naturally occurring and man-made contaminants are prevalent in environmental waters. Metal and chemical precursors often contaminate groundwater sources to impact drinking water supplies. Recent toxicological information indicates that contaminant groundwater species and/or breakdown products must also be considered when making regulatory decisions.

Metals

Metals, amalgams, and alloys play an instrumental role in almost every facet of our lives. Yet when used or disposed of incorrectly, metals can become serious contaminants in soil and water. Dionex has developed columns that can accurately assay groups of metals at very low levels in a variety of matrices, as well as speciate certain elements such as Fe^{2+} and Fe^{3+}. Chelation ion chromatography facilitates the determination of low concentrations (µg/L and lower) of transition metals in samples including seawater, brines, estuarine waters, and a variety of biological samples. Chelation ion chromatography removes alkali and alkaline earth metals while concentrating the sample, then determining the analytes of interest.

Selenium and Chromium

Hexavalent chromium, Cr(VI), is the most toxic form of the metal chromium and frequently requires regulatory monitoring as a primary drinking water contaminant at levels as low as 0.2 µg/L. Ion chromatography can determine dissolved Cr(VI) in drinking water, groundwater, industrial wastewater, and solid waste extracts. U.S. EPA Method 218.6 specifies the use of the IonPac AS7 anion-exchange column, postcolumn reaction with diphenlycarbazide, and UV detection at 530 nm.

Arsenic

Arsenic is ubiquitous in the environment and speciates into toxic and nontoxic forms. In general, methylated and other organoarsenicals are less toxic than inorganic arsenic, and pentavalent arsenic is considerably less toxic than the trivalent state. The inorganic forms of arsenic—arsenite and arsenate—are the usual forms found in drinking water, and the U.S. EPA has set a maximum contamination level (MCL) for total arsenic at 10 µg/L. Some foods, such as fish and seaweed, can contain organic forms of arsenic resulting from contamination and biological processes.

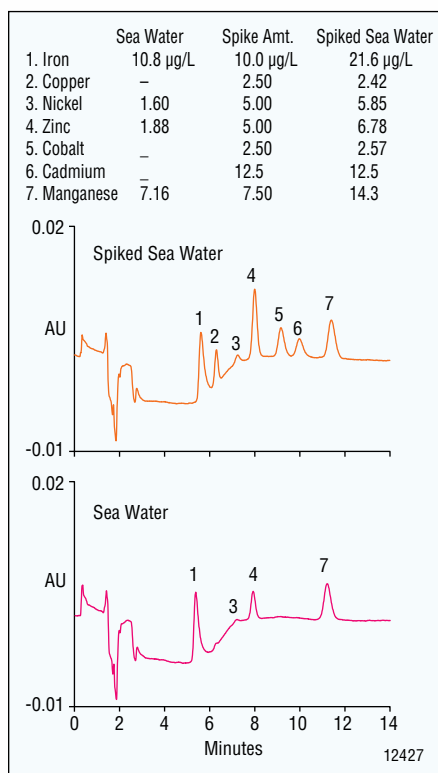|	Sea Water	Spike Amt.	Spiked Sea Water
1. Iron	10.8 µg/L	10.0 µg/L	21.6 µg/L
2. Copper	–	2.50	2.42
3. Nickel	1.60	5.00	5.85
4. Zinc	1.88	5.00	6.78
5. Cobalt	_	2.50	2.57
6. Cadmium	_	12.5	12.5
7. Manganese	7.16	7.50	14.3

Figure 15. Demonstrates the trace level detection of metals in high-matrix-strength samples such as seawater. The spiked sample shows the potential to find additional metals resulting from pollution runoff into seawater.
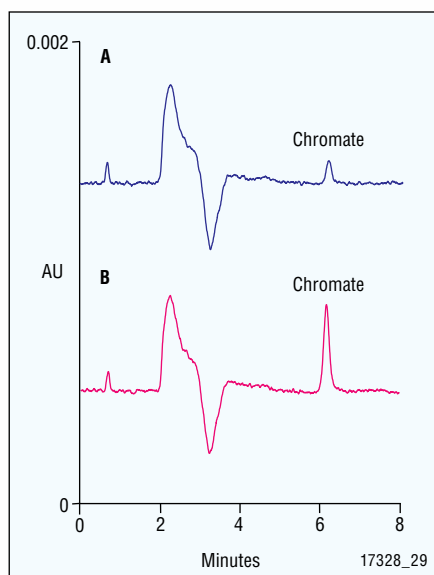

Figure 16. Determination of chromate in drinking water (A) and drinking water spiked with 0.2 µg/L chromate (B); peaks, (A) chromate (0.055 µg/L) and (B) chromate (0.245 µg/L).
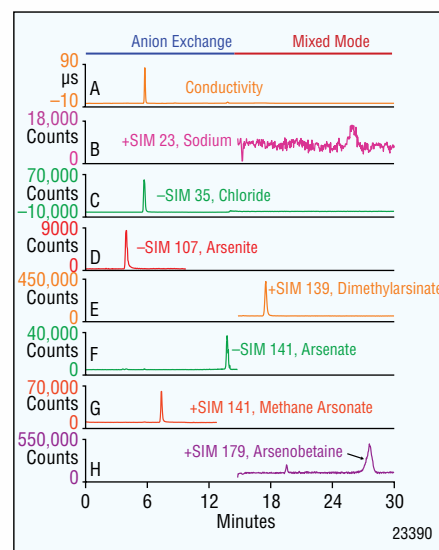

Figure 17. The above shows dual analysis of the anionic and cationic forms of arsenic and an example of a complex speciation experiment. Using IC coupled with MS detection, structural forms of each species are also obtained.

Acrylamide

Acrylamide has been found in certain prepared foods, and has recently been included among the substances to be monitored in drinking water according to the last European Community Directive on potable water. A new method for determination of this compound based on the combination of ion-exclusion chromatographic separation and MS detection has been developed accordingly. A sample of drinking water can be directly injected onto the IonPac ICE-AS1 column and detected in SIM mode by a single quadrupole system with electrospray ionization. This method was evaluated for analysis of drinking water samples.
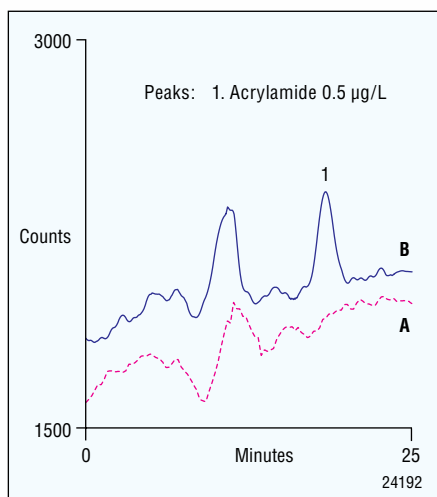

Figure 18. Chromatogram of a water sample spiked with 0.5 µg/L acrylamide using IonPac ICE-AS1 and MS (SIM) Detection.

Aldehydes and Ketones as DNPH Derivatives

Large quantities of carbonyl compounds are used worldwide, primarily in the chemical and plastics industries. Potentially carcinogenic, these compounds have been found in industrial waste which can contaminate groundwater and drinking waters. Aldehydes and ketones in air or vehicle exhaust are converted to their dinitrophenylhydrazine derivatives before analysis.

Peaks:
1. Formaldehyde-DNPH
2. Acetaldehyde-DNPH
3. Acetone-DNPH
4. Acrolein-DNPH
5. Propionaldehyde-DNPH
6. Crotonaldehyde-DNPH
7. Butanone-DNPH
8. Methacrolein-DNPH
9. Butyraldehyde-DNPH
10. Benzaldehyde-DNPH
11. Valeraldehyde-DNPH
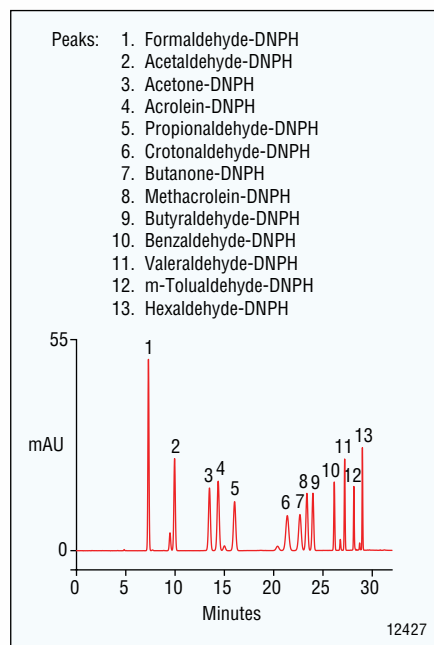12. m-Tolualdehyde-DNPH
13. Hexaldehyde-DNPH

Figure 19. Conventional C18 columns do not have favorable selectivity, but the unique selectivity of the Acclaim Explosives E2 column for nitroaromatic molecules makes it the superior choice for this application.

Explosives

Gas chromatography has traditionally been used to detect and quantify explosive compounds. Because some are thermally unstable or nonvolatile, using this method can result in inexact determinations. HPLC with UV detection, however, is ideally suited for low-level determination because it is not subject to these limitations. U.S. EPA Method 8330 describes an HPLC method with UV detection for determination of 14 priority explosives and related substances. The method recommends the use of a C18 reversed-phase column as the primary column for separation, and a CN⁻ secondary column for confirmation. Acclaim Explosives E1 and E2 columns have equivalent selectivities to these phases, respectively, with improved resolution.

A. EPA 8330 standards mix
B. ISO22478 additions
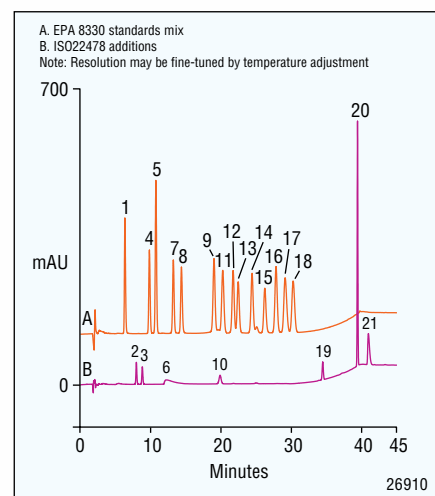Note: Resolution may be fine-tuned by temperature adjustment

Figure 20. Acclaim Explosives E1 and E2 columns can provide baseline resolution for 14 compounds with complementary selectivity under identical chromatographic conditions while reducing analysis time.

Chemicals from the manufacturing industry often contaminate the environment. The very aspects that make chemicals viable for manufacturing, such as reactivity, solubility and persistence, make them potentially toxic to living things. Chemical toxicity and release into the environment leads to problems for future generations.

Benzidine

Benzidine (4,4'-diaminobiphenyl) is an aromatic amine. A mutagen and a proven human carcinogen, its primary site of tumor induction is the bladder. Water can be contaminated with benzidine, its derivatives, and dyes if plant water is discharged into water supplies serving a residential community. As with some other aromatic amines such as 2-aminonaphthalene, benzidine has been significantly withdrawn from use in most industries because it is so carcinogenic.
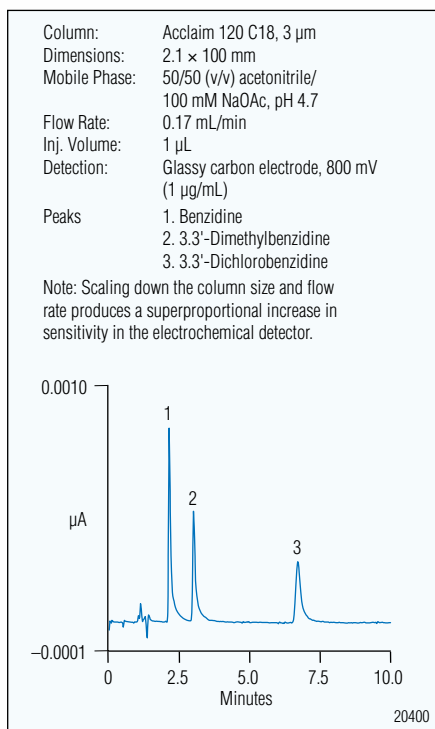
Column:	Acclaim 120 C18, 3 µm
Dimensions:	2.1 × 100 mm
Mobile Phase:	50/50 (v/v) acetonitrile/ 100 mM NaOAc, pH 4.7
Flow Rate:	0.17 mL/min
Inj. Volume:	1 µL
Detection:	Glassy carbon electrode, 800 mV (1 µg/mL)
Peaks	1. Benzidine
	2. 3.3'-Dimethylbenzidine
	3. 3.3'-Dichlorobenzidine

Note: Scaling down the column size and flow rate produces a superproportional increase in sensitivity in the electrochemical detector.

Figure 21. The Acclaim 120 C18 column is used with electrochemical detection for the determination of benzidines.

Phenols

Phenolic compounds are subject to regulation as water pollutants due to their toxicity. The European Community (EC) Directive specifies a legal tolerance level of 0.5 µg/L for each phenol in water intended for human consumption and Japan's Ministry of Health, Labor, and Welfare specifies a maximum contaminant level (MCL) of 5 µg/L for phenols in drinking water. The U.S. EPA specifies a MCL of 1 µg/L for pentachlorophenol and eleven common phenols are on the U.S. EPA priority

Peaks: 1. Phenol
2. 2,4-Dinitrophenol
3. 4-Nitrophenol
4. 2-Chlorophenol
5. 2-Nitrophenol
6. 2,4-Dimethylphenol
7. 4,6-Dinitro-2-methylphenol
8. 4-Chloro-3-methylphenol
9. 2,4-Dichlorophenol
10. 2,4,6-Trichlorophenol
11. Pentachlorophenol

Figure 22. The Acclaim RSLC PolarAdvantage column shows fast separation of phenolic compounds.

pollutants list. The method typically used for determining phenols is gas chromatography (GC) combined with flame ionization detection (FID) or mass spectrometric detection (GC-MS). However, liquid chromatography (LC) methods combined with UV/DAD electrochemical, and fluorescence detection are finding increased application, particularly due to nonvolatiles in many samples that can poison GC columns. Method detection limits (MDLs) of LC techniques employing direct injection of samples are too high for the detection of the low levels allowed in natural waters. Therefore, water samples require preconcentration before analysis. The new Acclaim RSLC PA column shows fast separation of a wide variety of phenols.
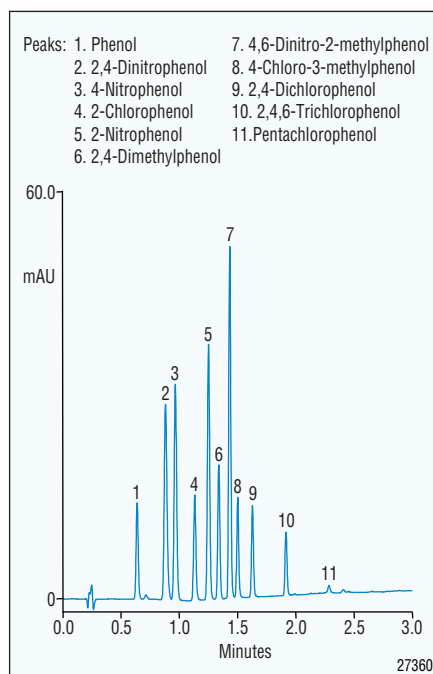
Pthalate

Phthalates, or phthalate esters, are esters of phthalic acid and are mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity). They are primarily used to soften polyvinyl chloride (PVC) plastic. Most plastic shoes are made from softened PVC. Phthalates are being phased out of many products in the United States and European Union over health concerns. The phthalate DEPH (diethyl-hexyl phthalate) is classified as harmful to the reproductive system.
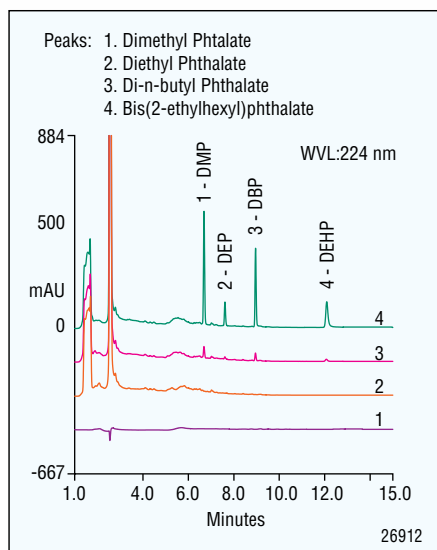
Figure 23. Using the NG1 trap column with the Acclaim C18 120A in combination with the dual UltiMate HPLC system, you can easily determine trace analysis with direct injection. Online SPE takes the labor out of sample preconcentration.

Because phthalates do not chemically bind to the PVC, they can easily leach into ground water, evaporate into the air, or be absorbed through direct contact. Phthalates can be analyzed by GC-MS. However, online SPE using HPLC with UV detection is a cost-effective alternative for trace analysis of these environmental contaminants.

Perflourinated Organic Compounds

Perflourinated organic compounds have been used for decades. The chemical structure of the alkyl fluorine bond imparts unique and useful properties for both consumer and industrial applications. Some of these properties result in these compounds being widely dispersed in the environment and bioaccumulating, yielding highly persistent and potentially toxic degradation products. Perfluorochemicals (PFCs) have been used extensively since the 1950s in multiple commercial applications including surfactants, paper and textile coatings, lubricants, paints, polishes, food packaging, and fire-retarding foams. Several PFCs are persistent in the environment and humans, and are ubiquitous contaminants in wildlife. Human exposure to PFCs is also widespread

although the ranges of concentrations and frequencies of detection of PFCs among countries and even within the same region may vary. No clear association between human exposure to PFCs and adverse health effects has been established. However, based on results from animal studies, a potential risk exists for developmental and other adverse effects associated with exposures to PFCs in humans. For this reason PFOS and PFOA are placed on the EU priority pollutant list and the US Contaminant Candidate List 3.
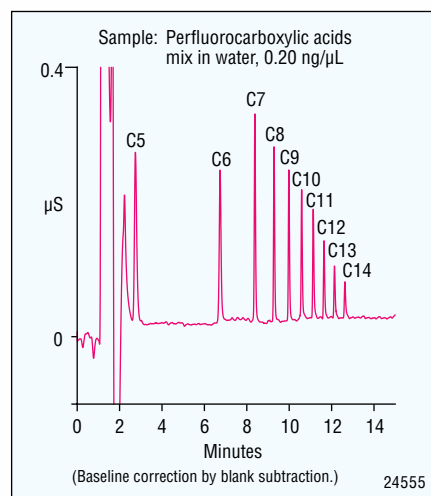

Figure 24. The Acclaim PA 2 column shows excellent resolution of PFC's from C5 to C14 for both the acidic and sulfonated forms

Contaminants of Emerging Concern (CEC) is a general term that attempts to describe a broad group of compounds including pesticides, pharmaceuticals, personal care products (PCPs), and surfactants that have adverse effects on the environment. Although present in low levels, the long term exposure effects are not well known.

Online Sample Preparation for Pharmaceuticals and Personal Care Products

Due to the large number of man-made chemicals manufactured and their environmental persistence, there is a growing need for multi-target screening techniques. The figure below shows an example of pesticide screening of 100 pesticides and PPCP's using the UltiMate® 3000 Rapid Separation LC (RSLC) system optimized for

fast chromatography up to 10 peaks in 10 seconds. Using online SPE, the separation and quantitation of over 100 pesticides and PCPs from a single injection is possible from complex water samples with reproducibility equivalent to EPA 1694.

This table shows the recoveries from an online SPE method using a dual UltiMate HPLC system with MS/MS detection from drinking, raw, surface, and wastewaters. Note the wide variety of compounds classes that can be readily determined from these matrices.

Surfactants

Alkylphenol polyethoxylates (APEO), one of the most commonly used classes of nonionic surfactants, are known endocrine disruptors that affect estrogenic function. APEO breakdown products are also important for understanding the overall environmental impact in surface waters, sediments, and sludge, and are regulated by the U.S. EPA and EU commission. Determination and quantification of the breakdown profile of APEOs is hindered by the inability to chromatographically resolve the numerous breakdown products, resulting in ion suppression from co-eluting species. The Dionex Acclaim Surfactant column solves this problem by chromatographically separating the majority to APEOs.
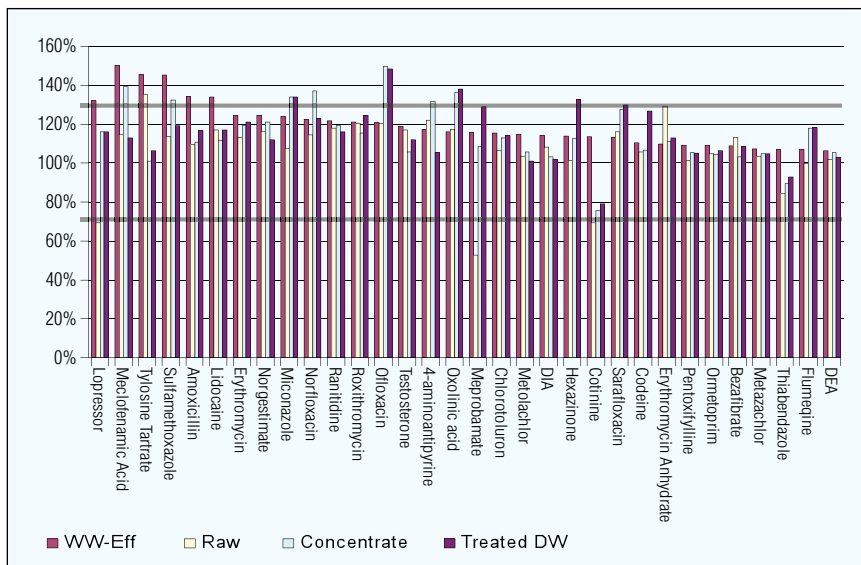

Figure 25. Online SPE of surface water samples spiked with over 100 pharmaceuticals, pesticides, and personal care products shows excellent recovers from a wastewater effluent, drinking, and surface waters.
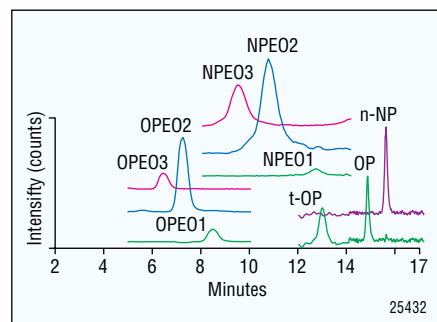

Figure 26. Chromatographic resolution minimizes signal suppression and in turn lower detection limits are achieved when using the Dionex Acclaim Surfactant column.

Dionex also offers the AutoTrace® instrument as an alternative to labor intensive, solvent wasting liquid-liquid extraction for a variety of regulated methods. The AutoTrace instrument is an automated solid-phase extraction (SPE) system designed for use with SPE adsorbents (cartridge or disk format).. Strong solvents are then used to generate an extract ready for analysis.

Offline Sample Preparation

Dionex also offers the AutoTrace instrument as an alternative to labor intensive, solvent wasting liquid-liquid extraction for a variety of regulated methods. SPE requirements vary depending on the amount of sample required and correspondingly SPE systems are separated into large and small volumes. The AutoTrace 280 workstation automates cartridge or disk conditioning, sample loading, rinsing, drying, and eluting steps for large volume liquid extractions (20 to 4000 mL).

Matrix often interferes with analysis when present in disparate amounts from the analyte of interest. For example, seawater or brine samples typically contain very high concentrations of chloride that interfere with determination of nitrite. To overcome this, one strategy may be to use an analytical column with a higher capacity. When this still does not solve the problem, matrix elimination can be a more viable choice. The OnGuard® and InGuard™ line of disposable sample pretreatment cartridges remove matrix interferences such as phenols, metals, cations, anions, and hydrophobic substances such as humic acids commonly found in surface waters.
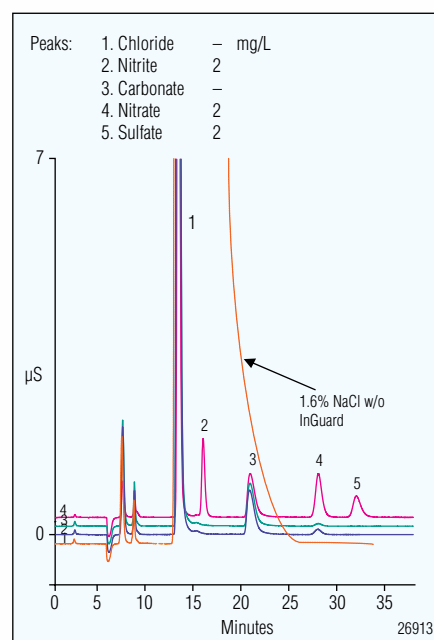

Figure 27. The most common application for this cartridge is the removal of chloride from high chloride samples for the determination of ppm concentrations of other anions. In this application, a 1.6% NaCl solution results in a very large chloride peak that obscures nitrate. Using the InGuard or OnGuard Ag in tandem with an InGuard Na or H cartridge, the chloride is effectively removed for quantitation of low levels of nitrate.

Performance				
Pesticide Recovery Study N=6	AutoTrace 280 SPE		Vacuum Manifold SPE	
Compound	Recovery %	%RSD	Recovery %	%RSD
Atrazine	88	1.8	54	12.2
Propazine	91	1.5	80	7.3
Alachlor	99	3.4	96	4.1
Metachlor	99	4.3	96	2.9

Table 1 shows a pesticide recovery study comparing the AutoTrace 280 SPE with a vacuum manifold technique. The improvements in recovery and reproducibility are attributed to the microprocessor control of all the liquid flow rates—both sample and SPE reagents.