

Automated Sample Pretreatment of Environmental Samples before Ion Chromatography

Bernard Sheldon,¹ Rosanne Slingsby,¹ and Rida Al-Horr²

¹Dionex Corporation, Sunnyvale, CA, USA; ²Dow Chemical, Houston, TX, USA

INTRODUCTION

Matrix elimination is a method of sample preparation that removes certain matrix species from a sample, typically by specifically binding matrix species to a solid phase. Interfering compounds can be removed before the analyte determination, thus improving the quality of results as well as lengthening the lifetime of consumables such as columns.

InGuard™ cartridges are designed for in-line matrix elimination and other sample pretreatment procedures. An autosampler or pump is used to pass the sample through the cartridge to remove matrix components. The InGuard chemistries are suitable for matrix elimination of a wide variety of sample types, and multiple cartridges can be used in series. The number of samples that can be treated with each InGuard cartridge depends on the matrix composition, concentration of compounds to be removed, and the sample injection volume. The cartridges generate such low backpressures that they can be operated at flow rates as high as 5 mL/min. The chemistries usually function optimally at flow rates between 0.5 and 2 mL/min. Since these pretreatment cartridges treat samples before chromatographic separation, they are suitable for both standard bore and microbore IC systems.

The InGuard line of sample pretreatment cartridges includes five chemistries in 9 × 24 mm PEEK™ cartridges. The cartridges have 10-32 end fittings and can be used with standard fittings in an ion chromatography (IC) system. The InGuard cartridges contain sorbents equivalent to the OnGuard® sorbents used for offline sample treatment, for example Ag, H, Na, and some newly developed phases, for example, HRP and Na/HRP. In this automated process, only the sample injection volume is treated for analysis. The cartridge size has been optimized for volume and capacity so that, depending on the application, one cartridge will treat from approximately 40 to more than 200 samples in an automated method. The limited sample volume of generally from 5 to 100 µL, which is treated and then trapped in a concentrator, is far less sample than that necessary in comparable off-line, e.g., OnGuard, methods.

Modern ion chromatographs such as the ICS-5000, ICS-3000, and ICS-1100/1600/2100 series instruments, with their multiple valve configurations, make automated application of InGuard cartridges simple.

CARTRIDGES AND USAGE

Table 1. Recommended Cartridge Applications

Cartridge	Functional Group(s)	Mode of Use	Example Applications
Ag	Ag ⁺ -form sulfonate	Ion exchange	Removal of halides
Na	Na ⁺ -form sulfonate	Ion exchange	Removal of cations
H	H ⁺ -form sulfonate	Ion exchange	Removal of cations, pH adjustment
HRP	Hydrophilic divinylbenzene	Adsorption, π-π bonding	Removal of hydrophobic species, azo- and cyano-containing species
Na/HRP	Dual Functionality	Ion exchange (Na) and adsorption	Removal of Ca ²⁺ (Na) and lipids (HRP) from dairy products

Table 2. InGuard Capacity

Cartridge Type, 9 x 24 mm PEEK	meq/cartridge
Ag	5-5.5
H	5-5.5
Na	5-5.5
HRP	2 g resin
Na/HRP	50% Na/ 50% HRP

Example Calculation of Resin Capacity

A 1% sodium chloride sample contains 10 g NaCl per liter. Of this 10 g NaCl, 35.45 g/mol divided by 58.45 g/mol is chloride, or 6.1 g. To convert to meq, 6.1 g chloride/ 35.45 g/mol is equal to 0.17 mol or 170 mmol. Thus there is 170 meq per liter or 0.17 meq/mL. A 100 µL injection of 1% NaCl contains 0.017 meq chloride. A cartridge containing 5 meq of Ag⁺ can treat a maximum of 5 meq/0.17 meq/sample, which is equal to 290 samples of 1% NaCl.

System Configurations

Optimum performance is achieved when the InGuard cartridges are used to treat the contents of an injection loop and the treated sample is then loaded onto a concentrator column. This configuration is shown in Figure 1 and can be accomplished on any IC with two 6-port, a 6-port and a 10-port, or two 10-port valves. By using a defined loop volume and a concentrator column, the need to time sample preparation in order to obtain an undiluted injection volume is avoided. In addition, smaller sample volumes can be treated thus extending the life of the InGuard cartridge.

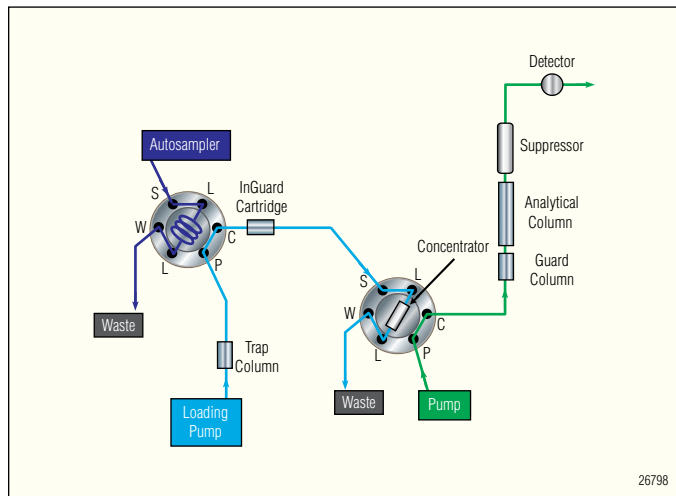


Figure 1. Configuration 1: two 6-port valves and two pumps.

The key aspects of the system shown in Figure 1 include:

1. Two independently controlled valves such as 2 injection valves or 2 high-pressure auxiliary valves from an ICS-3000 DC module; or an injection valve and auxiliary valve in an ICS-1100/1600/2100 instrument.
2. Two pumps such as from an ICS-3000 DP dual-pump system, or an AXP auxiliary pump combined with an ICS-3000 SP single pump system or ICS-1100/1600/2100 instrument. The first, analytical, pump provides eluent to the separator columns. The second pump is used to load the loop contents through the InGuard column and onto the concentrator. The backpressure of the InGuard and concentrator columns together is typically below 120 psi.
3. An ATC-3 column (for anion analysis) or an Electrolytic Water Purifier (EWP, P/N 072629) to clean the water used to load the concentrator. If an EWP is used, the loading pump is not required.

Note that flow across the concentrator column to the analytical column should be in the reverse direction to the flow across the concentrator when it is being loaded. This results in narrower peaks and better chromatographic resolution.

Figure 2 shows a plumbing configuration where the cell effluent is recycled for sample preparation. The Electrolytic Water Purifier (EWP) is used to clean the cell effluent water for trace level analysis.

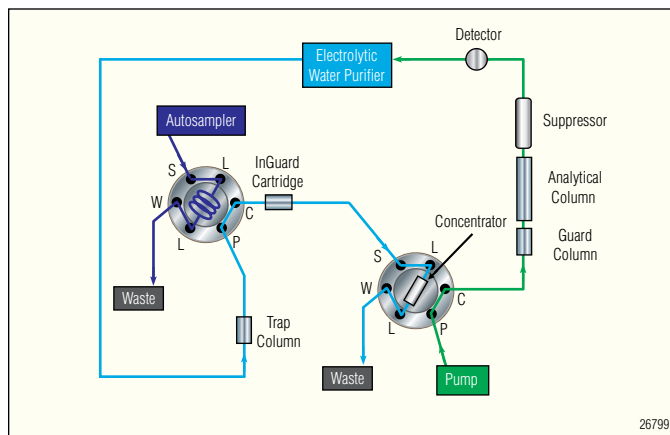


Figure 2. Configuration 2: two 6-port valves, one pump, and EWP.

Figure 3 shows a plumbing configuration where a 10-port valve replaces the second of the 6-port valves in Figure 1. In this arrangement, water does not flow over the InGuard cartridges between runs, so the re-dissolution of silver halide precipitates (formed during the removal of halides in the matrix) is significantly reduced.

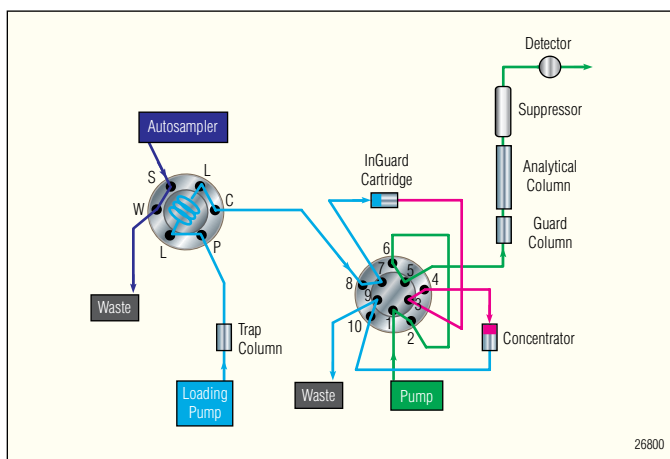


Figure 3. Configuration 3: one 6-port and one 10-port valve and two pumps with stopped flow.

The configuration shown in Figure 4 is used to minimize sulfate background.

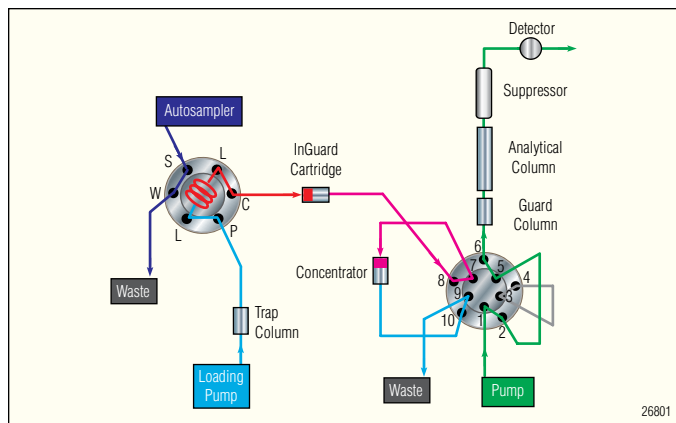


Figure 4. Configuration 4: one 6-port and one 10-port valve and two pumps with continuous wash.

Use of Concentrator Columns

The use of concentrator columns in a system configured for automated matrix elimination or preconcentration allows the collection of all treated sample ions for analysis using injection volumes of the same size as used in direct injection methods. Additionally, it eliminates the necessity to determine delay volumes and removes any concern regarding sample band broadening. InGuard cartridges have sufficiently low backpressure to be directly loaded by an autosampler's syringe drive.

Standard InGuard Use Conditions

The volume necessary for complete sample loading through the InGuard cartridges and onto the concentrator column can be determined experimentally as shown in Table 3. Enough volume needs to be pumped through the InGuard cartridge to displace the entire sample, while at the same time displacing the minimum possible amount of the trapped matrix.

This is particularly noticeable when using an Ag cartridge to remove halides. Silver halides will redissolve in excess loading water, so only enough transfer water should be used to fully transfer the sample. For halide removal with tandem Ag and Na cartridges in series with a 100 μL sample loop, a loading volume of 2–4 mL is sufficient.

Table 3. Optimizing Sample Prep Time Using Two InGuard Cartridges		
InGuard Ag and Na Cartridges with 100 μL Sample Loop		
Loading Volume (flow rate 0.5 mL/min)	Percent Recovery of 50 ppb Nitrate in 16,000 ppm Chloride	Peak Area ($\mu\text{S} \cdot \text{min}$) Chloride Residual from 16,000 ppm Chloride
1	0	3
1.5	76	7
2.0	96	19
4.0	86	36

Table 4. General Use Parameters for InGuard Cartridges				
Type	Pump 2 Loading Solvent	Pump 2 Maximum Flow Rate (mL/min)*	Void Volume (μL)	Typical Backpressure (psi)
Ag	DI water	2	850	50
H	DI water	2	850	50
Na	DI water	2	850	50
HRP	100% DI water to 100% solvent	2	850	50
Na/HRP	DI Water	2	850	50

* If using an AS autosampler to load the cartridge, a Syringe Speed setting of 2, 3 or 4 is recommended.

InGuard Ag, Na, and H

InGuard Ag cartridges contain 40 μm diameter Ag^+ form sulfonated styrene-divinylbenzene (S-DVB) resin beads, the same material used in OnGuard II Ag cartridges. Matrix elimination using this cartridge is based on the very low solubility of silver salts of halides (except for fluoride). Since the salts are not infinitely insoluble, the precipitate can redissolve to some extent. The chemical process for this matrix elimination requires the displacement of Ag^+ from the resin by sample cations and the subsequent precipitation in the ion-exchange bed. The small amount of silver ion that redissolves should be trapped using a Na^+ or H^+ InGuard cartridge placed after the InGuard Ag cartridge. This will avoid fouling of downstream cation exchangers including the suppressor. The use of the Na or H cartridge after the Ag cartridge should be standard practice.

InGuard Ag cartridges have a fixed capacity and cartridge lifetime which depends on sample matrix, injection volume, etc. Due to the consumption of silver as discussed above, the halide matrix peak will gradually increase over the lifetime of the cartridge.

InGuard Na and H cartridges contain 40 μm Na^+ form or H^+ form S-DVB resin beads, the same as that used in OnGuard II cartridges. They remove cations including metals by cation exchange governed by the standard selectivity of sulfonated resins for cations. A partial selectivity series for these resins is $\text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Ca}^{2+} < \text{transition metals (as cations)}$. Multiply charged cations are more highly retained than monovalent ions. Relative concentration also affects selectivity; ions present in higher concentration can elute ions present in relatively lower concentration.

Determination of Nitrite in Brine

The most common application for the InGuard Ag cartridge is the removal of chloride from high chloride samples for the determination of ppm concentrations of other anions. As noted above the Ag cartridge must be used in tandem with an InGuard Na or H cartridge. The Na cartridge will not acidify the sample as does InGuard H. It should be chosen for applications where the sample is pH sensitive, for example, in the determination of nitrite. Nitrite is readily oxidized to nitrate at low pH.

The system can be configured as shown in Figure 1, Figure 2, or Figure 3.

Figure 1 shows a system configured with two 6-port valves, two pumps and features a continuous wash of the InGuard cartridges throughout the run. The Figure 2 configuration is very similar except that the system uses only one pump and the detector cell outlet fluid is used in a recycle arrangement with an Electrolytic Water Purifier. The Figure 3 system uses one 6-port valve and one 10-port valve with two pumps. In this arrangement the flow of the pump supplying DI water for the sample preparation is diverted during the run so that no water flows over the InGuard cartridge stack during a run. This helps minimize dissolution of the silver halide precipitates.

The cartridges can be used with standard bore or microbore columns since they are used for sample pretreatment during loading of a concentrator column. The sulfate blank will be approximately 50 ppb, depending on flow rate and the age of the cartridge.

Figure 5 shows an overlay of an untreated 1.6% NaCl blank (Chromatogram 1), a 1.6% NaCl blank after InGuard Ag and Na treatment (Chromatogram 2), a water blank (Chromatogram 3), and a standard containing 2 ppm nitrite, sulfate, and nitrate in 1.6% NaCl (Chromatogram 4).

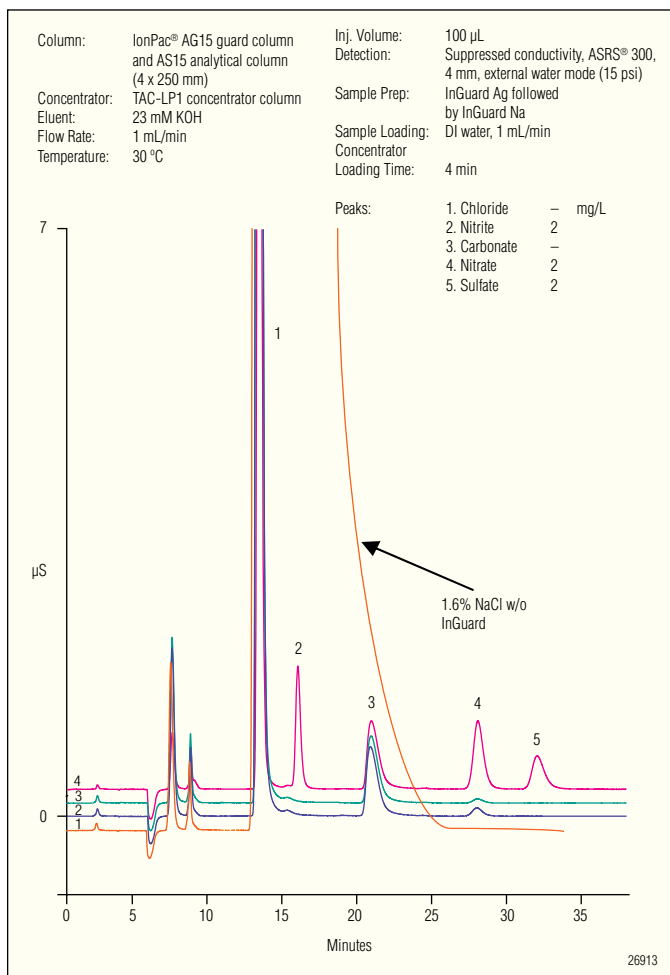


Figure 5. Analysis of nitrite, nitrate, and sulfate in brine.

InGuard HRP and Na/HRP

The InGuard HRP cartridge contains a 35 µm hydrophilic reversed phase resin based on divinylbenzene. The material has a surface area of about 300 m²/g. Since this material is water-wettable, 100% aqueous samples can be applied without disruption of the column bed. This material can be used to remove organic matrix material over a wide range of hydrophobicity.

The InGuard Na/HRP cartridge contains a blend of Na⁺-form sulfonated resin and HRP resin to provide the dual functionality of removing both cations including metals and organic contaminants from a sample. This cartridge is designed to provide general purpose cleanup of samples for anion analysis.

Removal of Organics from Whole Milk

Figure 6 shows the determination of nitrite in whole milk after the removal of organic materials, such as lipids and proteins, using an InGuard HRP cartridge. The goal of sample preparation in this application is to achieve a stable retention time for the analytes. This is achieved by removal of organic material that fouls the analytical column. The InGuard Na/HRP cartridge can also be used for this application to remove both Ca^{2+} and organic components from the milk.

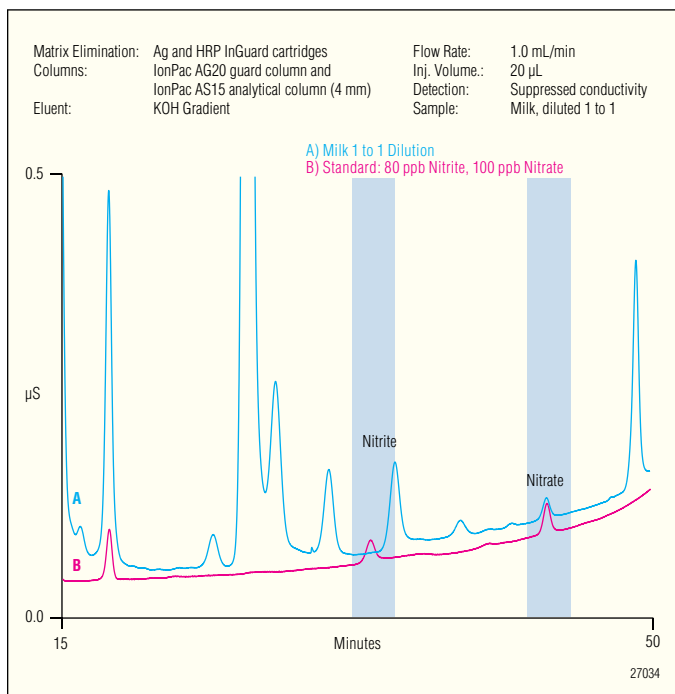


Figure 6. Analysis of nitrite and nitrate in whole milk.

Table 5: Summarized Results from 180 Injections of Whole Milk

Injection no.	% Retention time reduction (nitrate) from Injection 1
1–60	<0.4%
61–180	<1.25%

Table 5 provides results from 180 injections of whole milk on one HRP cartridge. Samples were prepared by dilution with an equal volume of 100% acetonitrile. Samples were allowed to stand for 30 min. The supernatant was sampled and this fraction analyzed by IC (10 μL injection volume) using IonPac AG15 and AS20 columns. The fouling rate was measured by calculating the retention time reduction of nitrate detected by the IC. Based on this data, the capacity limit using this method was determined to be approximately 60 samples/cartridge. Nitrite and nitrate can easily be detected at levels below 100 ppb using this technique.

CONCLUSION

A new series of inline cartridges for automated sample preparation have been introduced. These cartridges are designed to perform matrix elimination procedures on samples. Automated sample preparation of this type is enabled by the availability of ion chromatography instruments with a second high pressure valve. Instruments with dual valves provide a great deal of flexibility of configuration, yet integration of the instrument with high performance chromatography data system software makes instrument operation easy.

PEEK is a trademark of Victrex PLC.

InGuard is a trademark and ASRS, IonPac, and OnGuard are registered trademarks of Dionex Corporation.

Passion. Power. Productivity.



Dionex Corporation

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

North America

U.S./Canada (847) 295-7500

South America

Brazil (55) 11 3731 5140

Europe

Austria (43) 1 616 51 25 Benelux (31) 20 683 9768 (32) 3 353 4294
Denmark (45) 36 36 90 90 France (33) 1 39 30 01 10 Germany (49) 6126 991 0
Ireland (353) 1 644 0064 Italy (39) 02 51 62 1267 Sweden (46) 8 473 3380
Switzerland (41) 62 205 9966 United Kingdom (44) 1276 691722

Asia Pacific

Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 2764 2735
Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190
Taiwan (886) 2 8751 6655

www.dionex.com



LPN 2422-01 3/10
©2010 Dionex Corporation