

ABSTRACT

A conventional ion chromatograph is equipped with a single injection valve and adding additional valves for various applications such as two dimensional separations and sample preparation applications is cumbersome. A recently introduced ICS-3000 instrument has an integrated automation manager (AM) supporting various valve configurations and reaction coil heater. In this paper we discuss the utility of the ICS-3000 system in conjunction with the AM module for various applications.

The first part of the poster will discuss the instrumentation details and configurations. The second part will discuss various applications such as two dimensional analyses of bromate and perchlorate in high ionic strength matrices. We will also present a new sample pretreatment concept and show results from trace enrichment of standard anion samples.

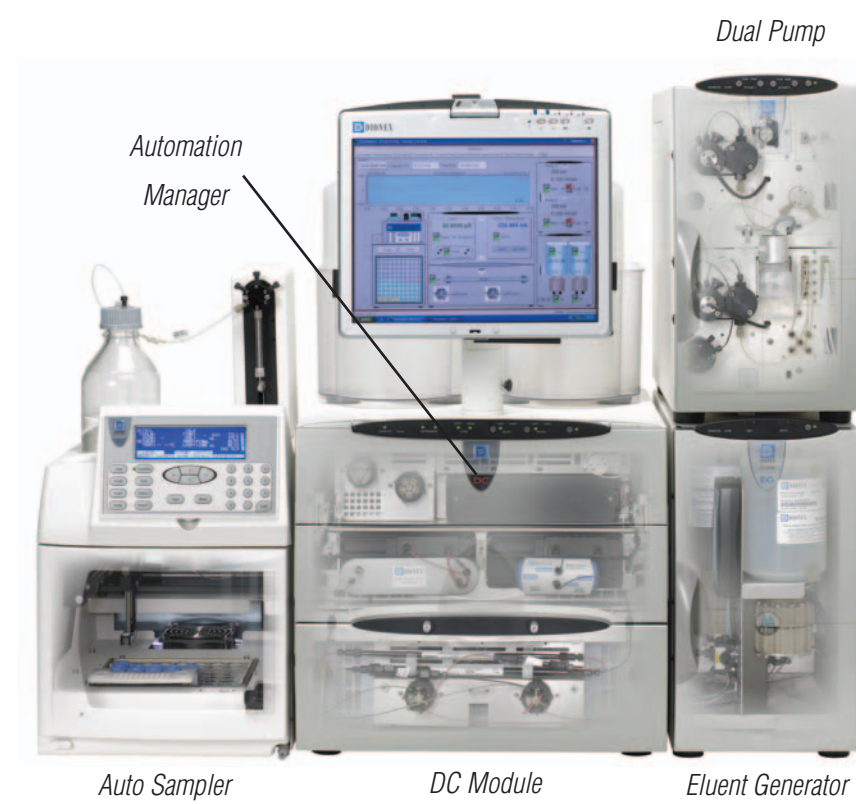


Figure 1. ICS-3000 system.

INSTRUMENTATION DETAILS AND CONFIGURATIONS

ICS-3000 Automation Manager Specifications

- High pressure valves—6 or 10 port, 2-way, PEEK
- Low pressure valves—2 or 3 port, PEEK
- Reaction coil heater
 - Reaction coil capacity = 2
 - Temperature range 5 °C above DC set temperature to 80 °C
 - Temperature accuracy +/- 1 °C
 - Temperature stability +/- 0.2 °C
 - Temperature settable in 1 °C increments



Figure 2. Automation Manager allows implementation of a variety of applications requiring switching valves and reaction coil heaters.

Analysis of Trace Ions in the Presence of Matrix Ions

- Trace analysis in a sample stream with low levels of matrix ions is typically done using
 - Pre concentration
 - Large loop injections
 - Example applications: analysis of ultra pure water (UPW)
- High concentration of matrix ions overload the column
 - Matrix ions may coelute with species of interest or may elute species of interest
 - Leading to recovery and integration issues due to band broadening
 - Example applications: analysis of drinking water, waste water
- These applications require an automated means of diverting the matrix prior to analyzing the trace ions

Bromate Analysis: Current Methods

Analysis done using AS9-HC chemistry with various detection modes

- EPA Method 300.1 part B with conductivity detection
 - Chloride removal required with some samples leading to added costs and time
- EPA Method 317 post column addition of o-dianisidine (ODA) followed by visible detection
 - Requires the hardware to implement the (PCR) post column reaction and detector
 - Requires frequent optimization of PCR reagent flow rate
 - Reagent purity was an issue
 - Handling of ODA a potential human carcinogen
- EPA Method 326 post column generation of hydroiodic acid in situ, by addition of potassium iodide to the eluent, that combines with bromate to form the triiodide anion that is detected by absorbance at 352 nm.
 - Requires the hardware to implement the PCR and a detector
 - Requires frequent optimization of PCR reagent flow rate

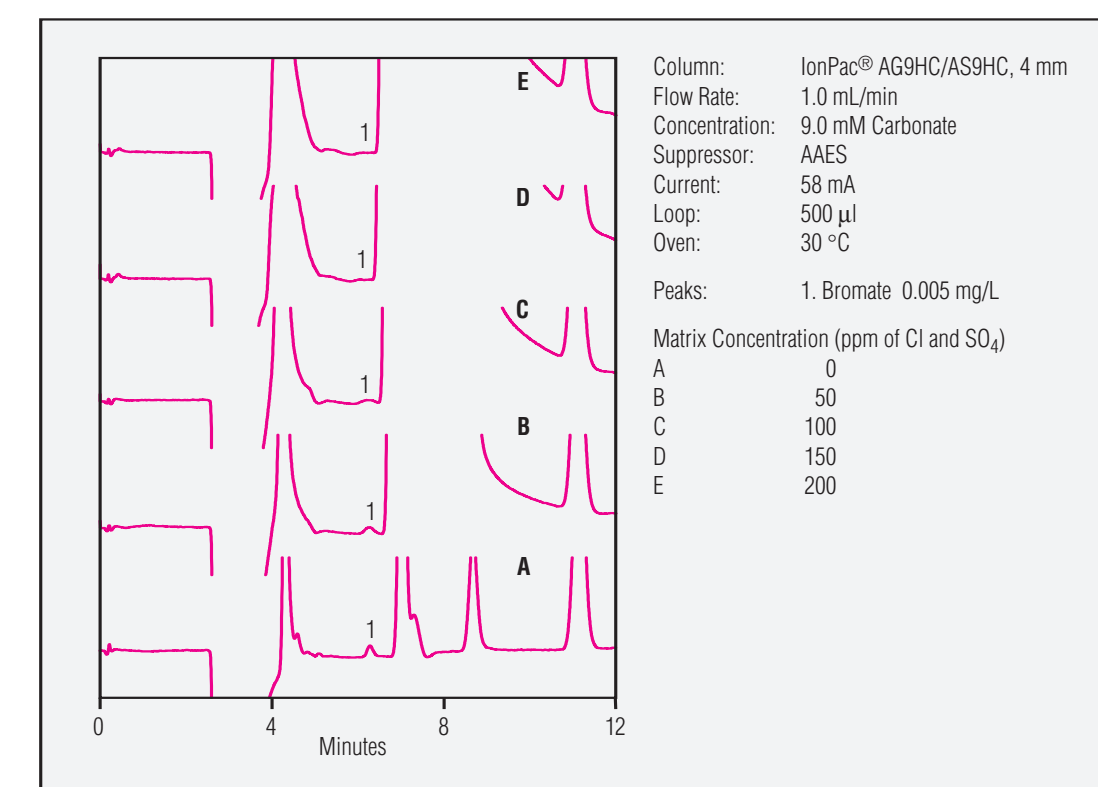


Figure 3. The effect of matrix concentration on bromate peak is shown using AS9-HC chemistry. For low-levels of matrix ions this method gave good peak area recovery and peak shapes. However, as the matrix concentration increased the bromate peak broadened and integration became difficult. In order to address the above issue a new matrix diversion method was developed.

NEW TWO DIMENSIONAL MATRIX DIVERSION METHOD

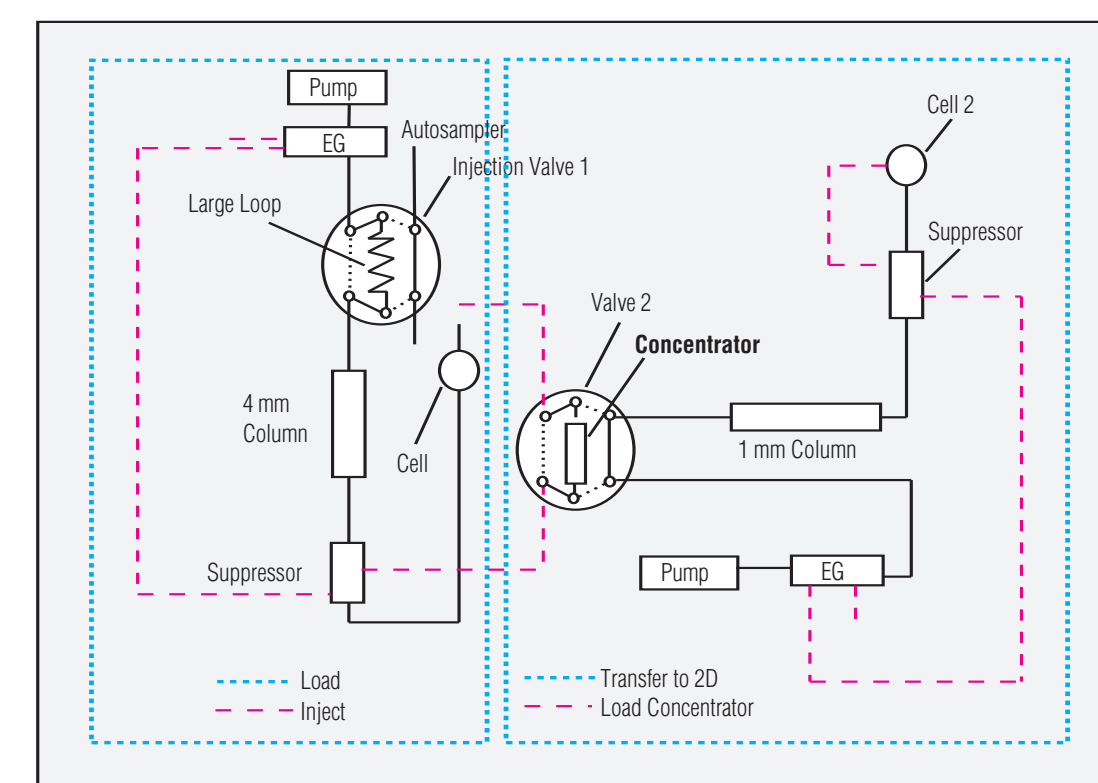


Figure 4. The experimental setup for a new two dimensional analysis method is shown above. The analysis in the first dimension is done using a 4 mm column chemistry and the analysis in the second dimension is done using a 1 mm or 2 mm column chemistry leading to improved sensitivity proportional to the flow rate ratio of the 1st dimension to the 2nd dimension.

New Two Dimensional Method: Features

- Allows for large loop injection in the first dimension (4 mm column)
 - Possible to inject a larger loop than the standard approach since the capacity and selectivity of the analytical column in the 1st dimension dictates the recovery and the analyte of interest is analysed in the 2nd dimension
- Focus the ions of interest in a concentrator column after suppression in the first dimension
 - Hydroxide eluent suppressed to DI water thus providing an ideal environment for focusing or concentrating the ions of interest
- Pursue analysis in the second dimension using a smaller column format operated at a lower flow rate leading to sensitivity enhancement that is proportional to the flow rate ratio of the 1st dimension to the 2nd dimension.
 - For a 4 mm column operated in the first dimension at 1 ml/min and a 1 mm column operated in the second dimension at 0.05 ml/min the enhancement factor is 20
- Easy implementation on the ICS-3000 system

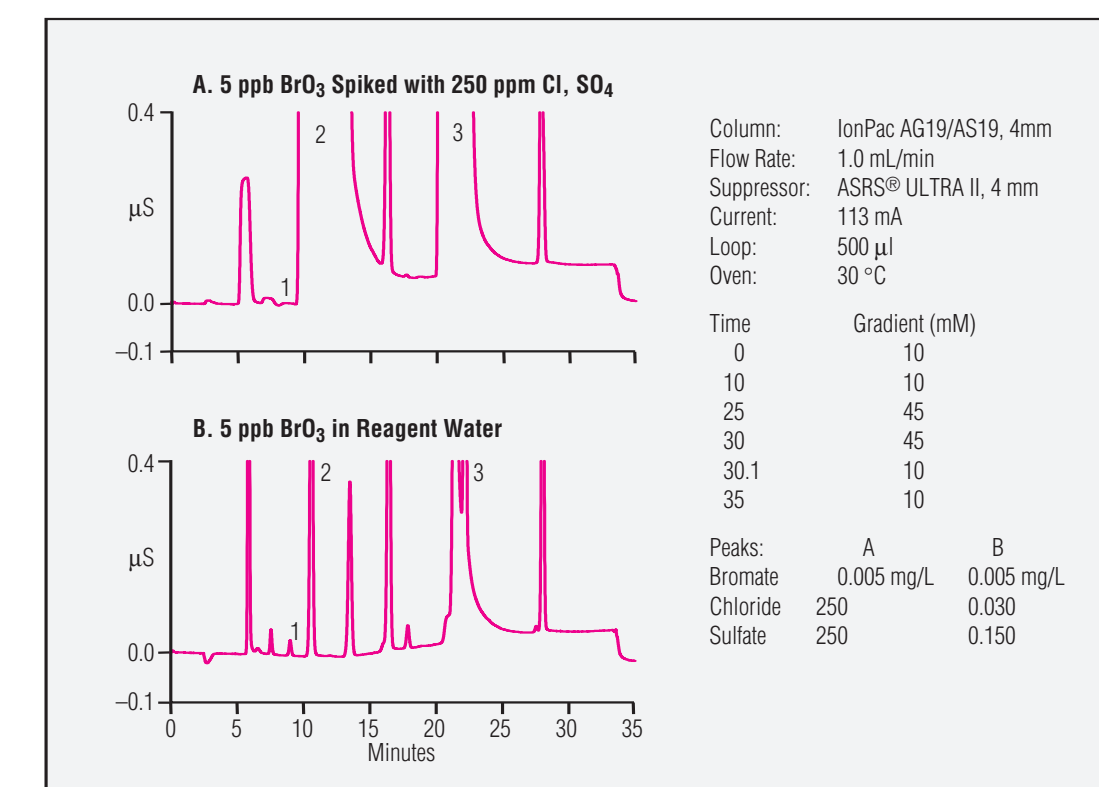


Figure 5. The bromate peak shape is completely lost in the case of the one dimensional approach with 250 ppm of matrix ions when compared to bromate standard in DI water.

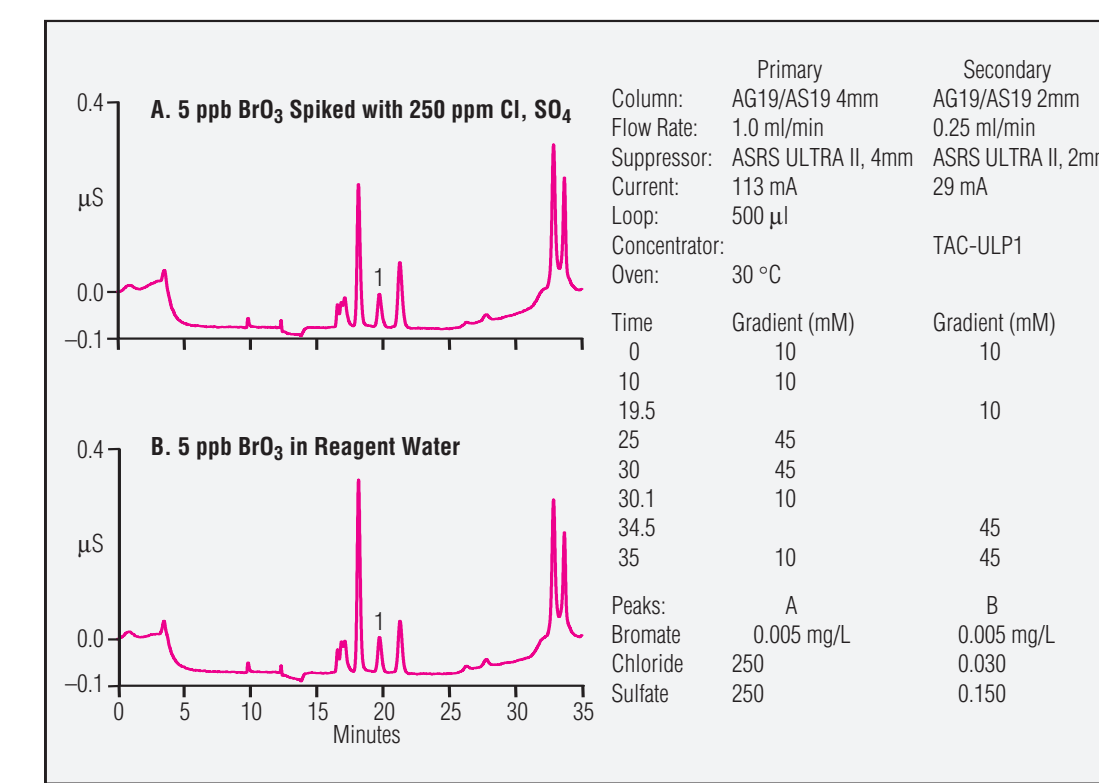


Figure 6. In the new two dimensional analysis approach the bromate peak shape is retained even in the presence of high levels of matrix ions.

Matrix Concentration* (ppm)	Bromate Peak Area	Recovery
0	0.0248	100%
50	0.0245	98.8%
100	0.0250	100.8%
150	0.0244	98.4%
200	0.0249	100.4%
250	0.0249	100.4%

*Matrix concentrations are for individual ions (chloride and sulfate)

Table 1. The above table summarizes excellent recovery for bromate in the presence of matrix ions with the new two dimensional analysis method.

Dimension	Peak Area Response	Flow Rate (mL/min)	Sensitivity
First (4 mm)	0.0063	1	1
Second (2 mm)	0.0248	0.25	3.936

MDL based on n = 7 runs (students t test) 0.2 ppb for a 500 µL Injection with 200 ppm of chloride and sulfate using suppressed conductivity detection

Table 2. The above table shows the observed sensitivity enhancement with the new two dimensional method.

Columns	EPA Method 314.0	EPA Method 314.1
	IonPac AG16/AS16 (4 mm)	IonPac AG16/AS16 (2 mm), (primary method) IonPac AG20/AS20 (2 mm), (confirmatory method)
Eluent	50 mM NaOH	0.5 mM NaOH 0-12 min, 65 mM 12.1-28 min, 100 mM 28.1-30 min
Temperature	30 °C	35 °C
Flow rate	1.5 mL/min	0.25 mL/min
Sample Volume	1000 µL	2 mL
Rinse Volume	—	1 mL (10 mM NaOH)
Concentrator	—	IonPac Cryptand C1 (4 x 35 mm)
Detection	Suppressed conductivity, ASRS-ULTRA II (4 mm), Autosuppression external water mode	Suppressed conductivity, ASRS-ULTRA II (2 mm), Autosuppression external water mode

Table 3. Perchlorate analysis: U. S. EPA Methods 314.0 and 314.1.

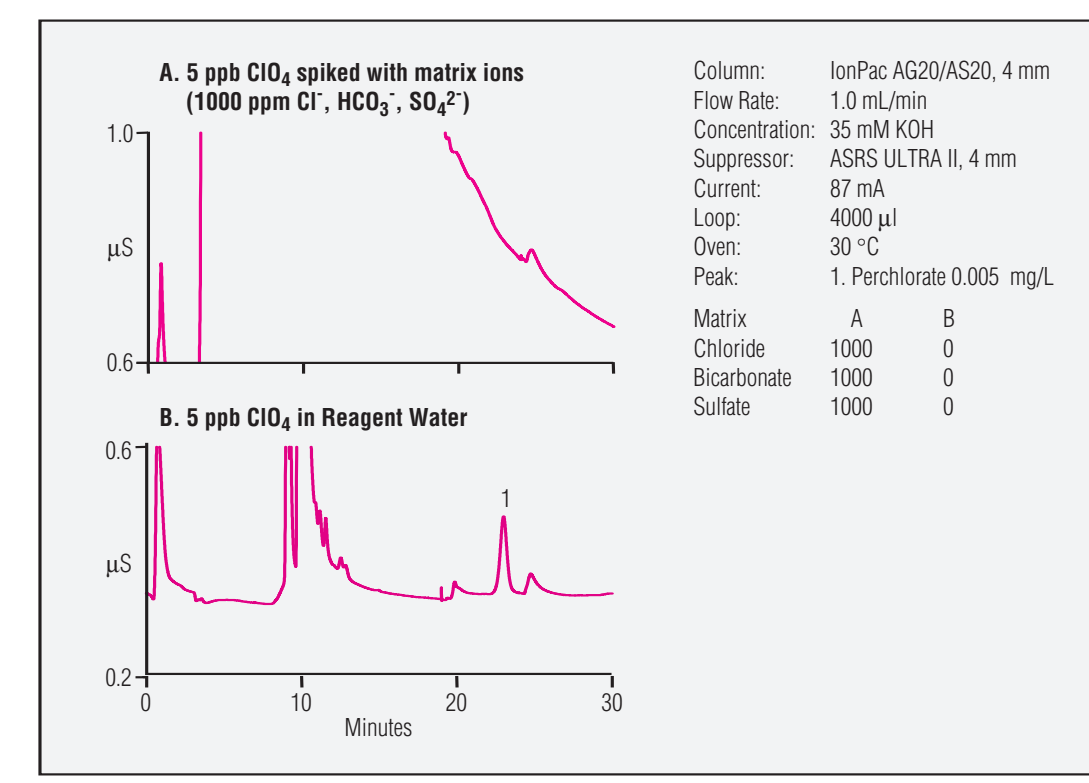


Figure 7. The perchlorate peak shape and response is poor in the presence of matrix ions and when compared to analysis done with perchlorate standard in DI water.

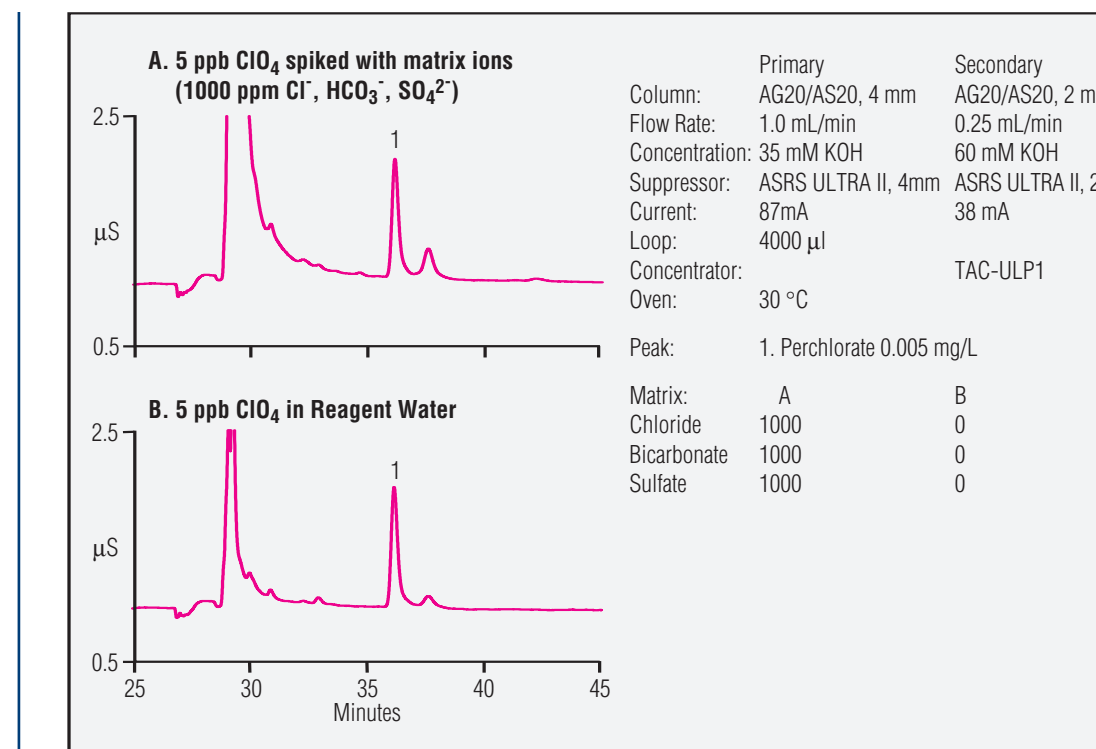


Figure 8. The perchlorate peak shape and response is preserved in the presence of matrix ions in the new two dimensional analysis method.

Matrix* (ppm)	Perchlorate Peak Area	Recovery
0	0.3522	100%
50	0.3560	101.1%
100	0.3567	101.3%
200	0.3509	99.6%
500	0.3505	99.5%
800	0.3468	98.5%
1000	0.3438	97.6%

*Matrix concentrations are for individual ions (chloride, bicarbonate, and sulfate)

Table 4 shows excellent recovery for perchlorate under a variety of matrix concentrations with the new two dimensional method.

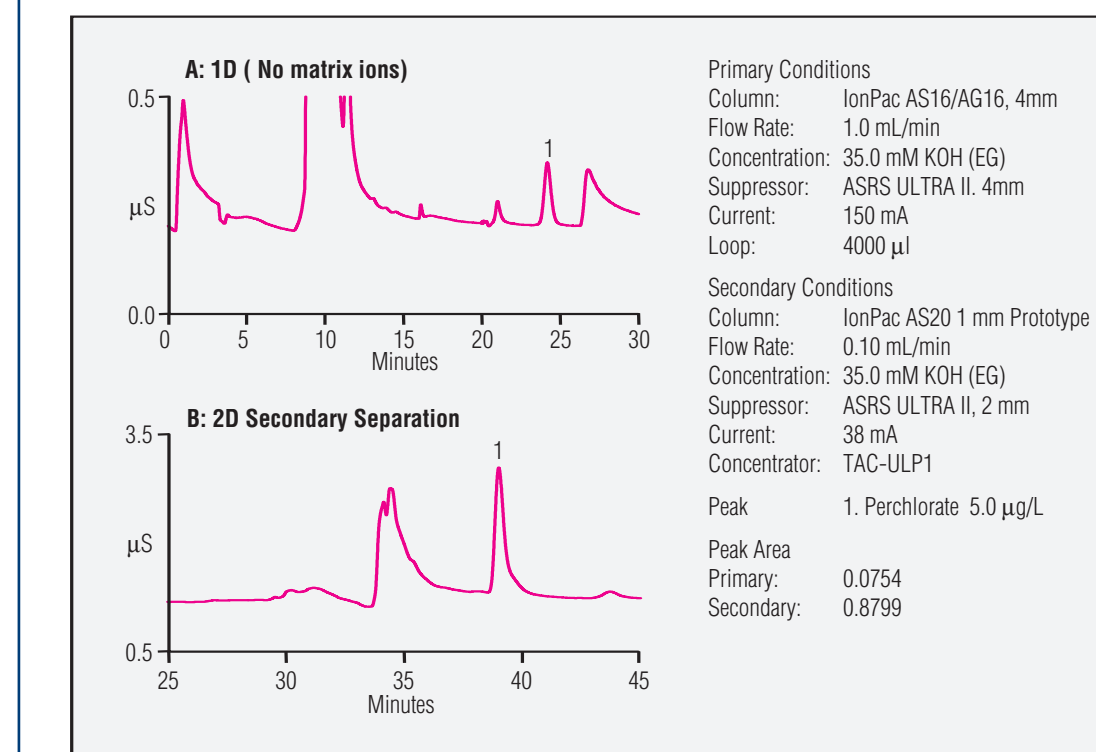


Figure 9. This figure shows the benefit of pursuing the analysis using a 1 mm column operated at 0.1 mL/min flow rate. The sensitivity gain for the two dimensional analysis method from the observed peak response is roughly 10x greater than the one dimensional approach as predicted from theory.

NEW SAMPLE PRETREATMENT WITH RFIC™ SYSTEMS

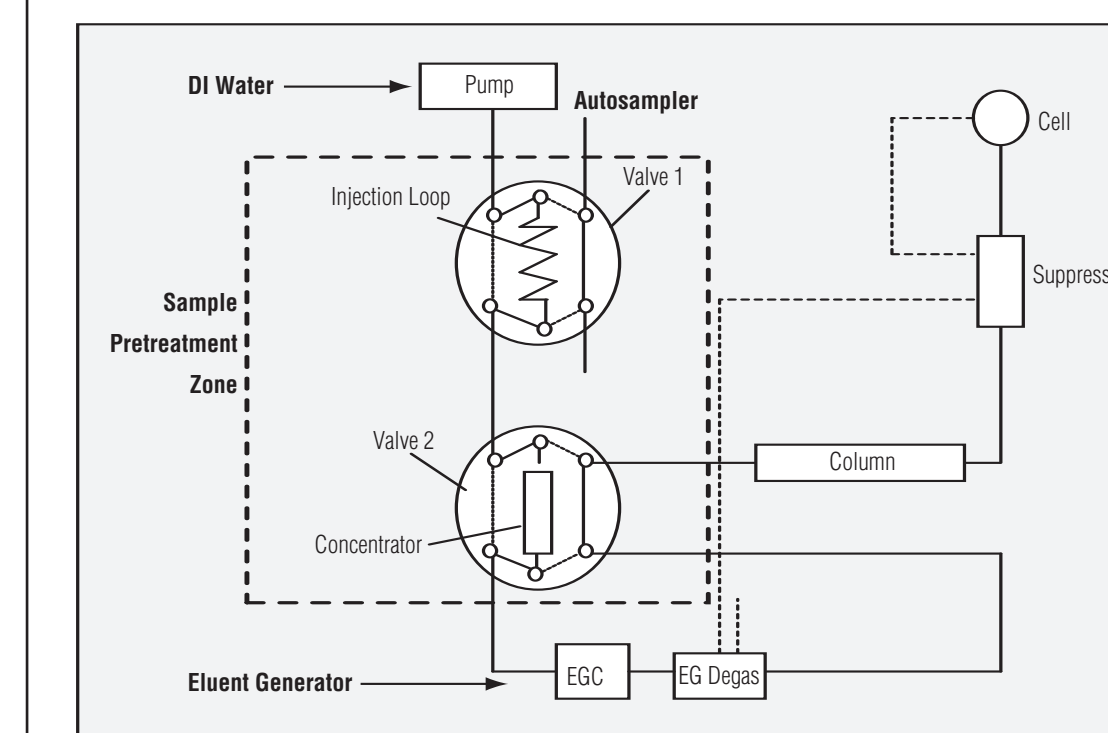


Figure 10. The experimental setup for implementing the new sample pretreatment approach in conjunction with RFIC is shown above. In this example the trace enrichment of ions is possible with this setup.

New Sample Pretreatment with RFIC

- Utilizes the "Just Add Water" pump for sample prep applications followed by eluent generation
 - Trace Enrichment
 - Multiple loop injections
 - Sample overlap
 - Neutralization with acid or base samples
 - Matrix ion removal
 - Automation and ease of use of RFIC
 - Low cost sample prep applications
 - Improved analysis and detection of trace components
- CONCLUSIONS**
- ICS-3000 system equipped with an Automation Manager allowed implementation of applications with multiple valving schemes
 - The new two dimensional method showed
 - Enhanced sensitivity for selected analytes (Bromate, Perchlorate) using suppressed conductivity detection
 - Minimal interference from matrix ions
 - Overall a simpler analytical method when compared to post column reactions
 - The new two dimensional methods are preferably operated with RFIC providing
 - Automation and ease of use
 - Requires only DI water
 - No issues with reagent preparation
 - No health issues
 - No stability and shelf life issues
 - No reagent purity issues
 - No need to optimize post column reagent flow rate or mixing
 - The new sample pretreatment with the RFIC system
 - Eliminates the need for an extra pump
 - Allows for improved preconcentration and sensitive detection of trace components
 - Is suitable for other applications such as neutralization and matrix removal

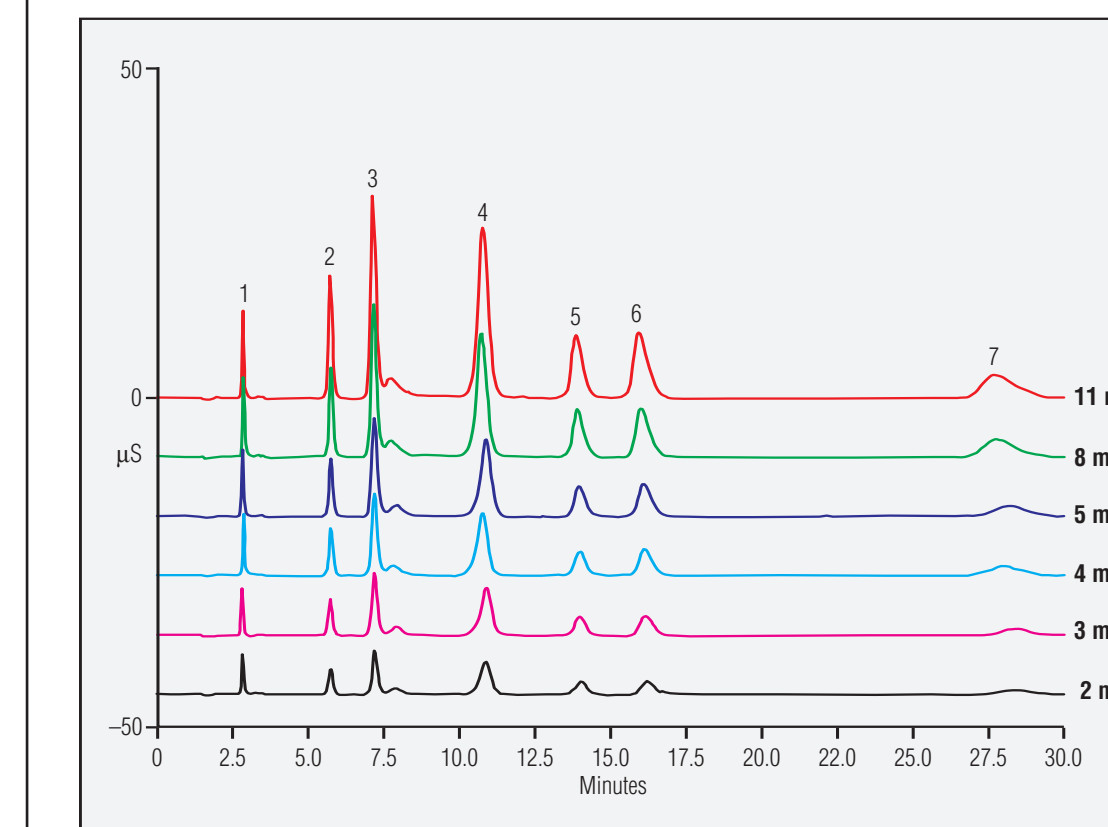


Figure 11. The analysis of trace levels (ppb levels) of a standard anion mixture is shown at different enrichment volumes using AS15 chemistry and a TAC-LP1 concentrator column.

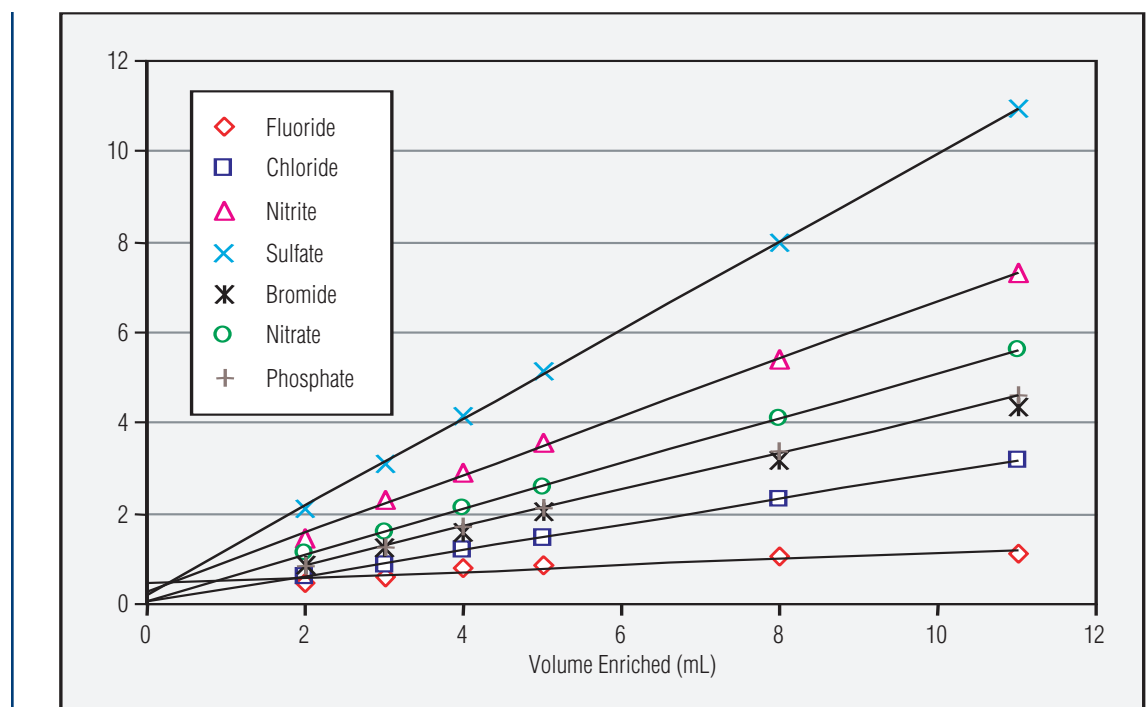


Figure 12. The response versus the volume enriched plot showed excellent linearity of the enrichment method and correlation coefficients were in the 0.9999 regime.

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