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Application Update 159

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Determination of Volcanic Gases as Anions in Caustic Solutions Using AutoNeutralization, Automated Dilutions, and a Reagent-Free Ion Chromatography System

INTRODUCTION

Atmospheric, environmental, and geological scientists need analytical methods to determine the composition of volcanic gases. Volcanic gases alter the local environment and the atmosphere, and contaminate surface and drinking water.[1,2] They can pose severe health hazards, sometimes causing fatalities from asphyxiation by high concentrations of oxygen-displacing gases.[3] The type, amount, and ratios of volcanic gases characterize and predict impending volcanic activity and its intensity. Any change in carbon dioxide concentration, sulfur dioxide-carbon dioxide ratios, or halide gas composition may indicate impending volcanic eruptions.[4–7] An analytical technique for characterizing these gases could serve as an early warning of toxic or oxygen-displacing gas emissions and even help predict eruptions.

Carbon dioxide, water vapor, and sulfur dioxide are the main components of volcanic gases. Ammonia, hydrogen bromide, bromium oxide, hydrogen chloride, hydrogen fluoride, hydrogen iodide, nitrogen, helium, and arsine are also present at lower concentrations. Most of these gases can be determined by analyzing their corresponding anions in solution: carbon dioxide as carbonate, sulfur dioxide as sulfate, arsine as arsenate, and hydrogen bromide, hydrogen chloride, hydrogen fluoride, and hydrogen iodide as bromide, chloride, fluoride, and iodide, respectively. Most of these gases can be effectively trapped in a concentrated sodium hydroxide solution.

Volcanic gas condensate samples present multiple analytical challenges: a large disparity in analyte concentrations, a strong base matrix, difficulties in reliable carbonate determinations due to its inherent variability with pH and temperature, separation of neighboring anions from carbonate, and determination of early eluting anions. Analyte concentrations range from µg/L for halides to 105 g/L for carbonate. Due to the high concentration of the base anion, concentrated samples must be diluted prior to anion analysis. This dilution, however, sacrifices anion determinations at µg/L concentrations.

High carbonate concentrations pose multiple challenges. Carbonate is not typically determined and is often removed, especially when using hydroxide-based eluent systems. However, for volcanic samples, determining carbon dioxide as its ion carbonate is essential to monitor changes in gas composition and volcanic activity. It is difficult to determine accurate carbonate concentrations due to errors from the degassing or absorption of carbon dioxide over time, permeable sampling containers, and variable carbonate concentrations in both water and caustic diluents. Any sample dilution will be complicated by the variable carbonate concentration of the diluent. Determinations of sulfate and other anions eluting just after carbonate can also be difficult in samples with high concentrations of carbonate.

Currently, volcanic gas condensates are analyzed by labor-intensive wet chemistry (e.g. titration) and potentiometric (e.g. ion selective electrode) methods. Titration methods are usually not selective and ion selective electrode methods are sensitive to differences in the sample matrix. For anion and cation determinations, ion chromatography (IC) is the method of choice. It has been successfully used to determine fluoride, chloride, bromide, iodide, sulfate, and arsenate. A recent study showed that carbonate can also be determined accurately by suppressed conductivity detection in a limited range, 3 to 120 mg/L.[8]

To address the determination of anions in strong bases, Dionex developed AutoNeutralization™ technology (Dionex Application Note 93).[9] In this latest embodiment of AutoNeutralization, the sample is pumped into and trapped in the ASRN™ II Anion Self-Regenerating Neutralizer (a high capacity electrolytic ion exchange membrane device) for a set period, where the base is neutralized and the anions are converted to their acid forms. This technique is called Park and AutoNeutralize. An ICS-3000 Reagent-Free™ Ion Chromatography (RFIC™) system, with two pumps, two conductivity detectors, and an Automation Manager with a 10-port injection valve, executes the determination of trace anions in concentrated bases by automatically neutralizing the strong base with the ASRN II, concentrating the neutralized sample, and analyzing the concentrated anions by IC. Application Note 93 (AN 93) shows determinations of µg/L to mg/L concentrations of anions in concentrated bases but does not include iodide, thiosulfate, thiocyanate, and arsenate determinations.

Sample fluoride, chloride, bromide, iodide, thiosulfate, and arsenate concentrations in caustic base volcanic gas condensates were determined according to the AutoNeutralization procedure described in AN 93. AutoNeutralization was not used to determine carbonate and sulfate. To determine the high concentrations of carbonate and sulfate, the sample was diluted 1000-fold, a smaller amount of sample was injected, eluent conditions were optimized for separation of these two anions, and a column wash was added. To minimize both the loss of carbonate and the introduction of atmospheric carbonate, the samples were diluted by the autosampler with freshly degassed deionized water from a sealed glass sample vial.

EXPERIMENTAL

Equipment

Dionex ICS-3000 Reagent-Free Ion Chromatography system with:

- DC Detector/Chromatography module with single temperature zone, AM Automation Manager with 10-port valve, injection valve, temperature stabilizer (standard bore), and two CD Conductivity Detectors with integrated cells
- DP Dual Pump gradient or isocratic module with IonPac® Gradient Mixer GM-4 (P/N 049136) and ATC-HC trap columns (9 x 75 mm, P/N 059604)
- EG Eluent Generator module with EluGen® II potassium hydroxide cartridge (P/N 058900), degas modules, and Continuously Regenerating Anion Trap Columns (CR-ATC, P/N 060477)
- AS Autosampler with temperature control, sample syringe and sample prep towers, 500-µL sample syringe, 5-mL prep syringe, and 2-mL sample tray

Dionex Chromeleon® Chromatography Management Software, version 6.8 or higher

Dionex Virtual Column™ Separation Simulator, version 6.8 or higher

Filter unit, 0.2-µm nylon (Nalgene® Media-Plus with 90mm filter, Nalge Nunc International, P/N 164-0020) or equivalent nylon filter

Vacuum pump

Tubing:

- Black PEEK™ (0.25-mm or 0.01-in i.d., P/N 052306 for 5 ft) for liquid line connections for both systems and backpressure loops for the ASRS® ULTRA II suppressor
- Yellow PEEK (0.13-mm or 0.003-in i.d., P/N 052301 for 5 ft) for system backpressure loops
- Green PEEK (0.76-mm or 0.30-in i.d., P/N 044077 per inch) for eluent waste lines
- Low pressure Teflon® (E.I. du Pont de Nemours) tubing (1.6-mm or 0.063-in i.d., P/N 014157) for the CRD, external water regenerant lines for the ASRN II neutralizer, and ASRS Ultra II suppressor regenerant and degas waste lines
- 100 µL sample loop (P/N 42951)

Suppressor External Regenerant Installation Kit for external water mode (P/N 038018)
Polypropylene and glass sample vials, 1.5 mL with caps and slit septa (Dionex vial kit, P/N 061696 and P/N 055427, respectively)
Polystyrene sterile flasks, 225 mL, Corning or other brand of similar quality (Corning P/N 431081 or VWR P/N 29186-199)

Reagents and Standards

Use only ACS reagent grade chemicals for all reagents and standards.

Deionized water, Type 1 reagent-grade, 18 MΩ-cm resistivity or better, freshly degassed by vacuum filtration
Potassium iodide (Sigma-Aldrich, P/N 221945)
Sodium arsenate, dibasic heptahydrate (VWR, Baker Analyzed P/N JT3486-4)
Sodium bicarbonate (Fisher, P/N S233-500)
Sodium bromide (Sigma-Aldrich, P/N 31,050-6)
Sodium chloride, crystalline (JT Baker ULTRAPURE BIOREAGENT, P/N JT3624-1)
Sodium fluoride (Fisher, P/N S299-100)
Sodium phosphate, monobasic (EMD Biosciences Inc., P/N 80058-650)
Sodium sulfate, granular (EM Science, P/N EM-SX0760-1)
Sodium thiocyanate (Sigma-Aldrich, P/N 251410)
Sodium thiosulfate (Sigma-Aldrich ReagentPlus™, P/N 217263)

Samples

Gas samples of volcano hot springs and fumaroles were collected at their respective locations by aspirating them into 6 M sodium hydroxide solutions. Samples, as their subsequent volcanic gas condensates, and controls for collecting the samples, were received from Dr. Bruce W. Christenson, Senior Geochemist of the National Isotope Centre (Lower Hutt, New Zealand) at GNS Science Limited.

CONDITIONS

Determination of µg/L Anions by AutoNeutralization

Sample Preparation:	***System 2*[a]**
Trap Column:	IonPac ATC-HC, 9 × 75 mm (P/N 059604)
Carrier:	Degassed deionized water
Flow Rate:	0.5 mL/min
Temperature:	30 ºC
AS Temperature:	10 ºC
Inj. Volume:	100 µL
Neutralization:	ASRN II Anion Self-Regenerating Neutralizer (P/N 063433), external water mode, 495 mA
Run Time:	9.2 min for AutoNeutralization and concentration
Typical System Backpressure:	~800 psi

Analytical:	***System 1***
Columns:	IonPac AG19, AS19, 4 mm (P/N 062887 and 062885)
Flow Rate:	1.0 mL/min
Eluent (EluGen KOH):[b]	10 mM Potassium hydroxide for 10 min after injection, 10–45 mM potassium hydroxide from 10–25 min after injection, 65 mM potassium hydroxide from 25–35 min
Column Temp.:	30 ºC
Concentrator:	IonPac UTAC-XLP1, 6 x 16 mm (P/N 063459)
Detection:	Suppressed conductivity, ASRS ULTRA II Anion Self-Regenerating Suppressor, recycle mode, 161 mA, with 4-mm carbonate removal device (CRD)
Typical Background:	<1 µS
Typical System Backpressure:	~2200 psi
Typical Noise:	<3 nS
Run Time:	35 min
Total Time:	45 min

[a] The AS Autosampler controls the AM_HP1 10-port valve and DC controls Inj. Valve 1. See the System Setup section for more information.

[b] Includes a 5 min equilibration at 10 mM potassium hydroxide during sample preparation time.

Determination of Carbonate and Sulfate by AutoNeutralization and Automated Dilutions with System 2 in the Configuration

The conditions above were also used for System 2 with the following exceptions:

Sample Preparation:	***System 2*[a]**
Inj. Volume:	25 µL (100 µL loop)
Dilution:	1000–fold by the AS Autosampler, using Pipet and Mix commands
Run Time:	9.2 min
Analytical:	***System 1***
Eluent (EluGen KOH):[b]	14 mM Potassium hydroxide for 25 min after injection, 100 mM potassium hydroxide column wash from 25–40 min
Detection:	Suppressed conductivity, ASRS ULTRA II Anion Self-Regenerating Suppressor, recycle mode, 248 mA, without 4-mm CRD
Typical Background:	<1 µS
Run Time:	40 min
Total Time:	50 min

[a] System 2 is not required for carbonate and sulfate determinations but it is left in place to minimize reconfiguration time. The AS Autosampler controls the AM_HP1 10-port valve and the DC controls Inj. Valve 1. See the System Setup section for more information.

[b] Includes a 5 min equilibration at 14 mM potassium hydroxide during sample preparation time.

Alternative: Determination of Carbonate and Sulfate by Automated Dilutions with System 2 Removed from the Configuration[a]

System 1

Columns:	IonPac AG19, AS19, 4 mm (P/N 062887 and 062885)
Flow Rate:	1.0 mL/min
Eluent (EluGen KOH):[b]	14 mM Potassium hydroxide from -5 to 25 min, 100 mM potassium hydroxide column wash from 25 to 40 min
Column Temperature:	30 ºC
AS Temperature:	10 ºC
Inj. Vol:	25 µL (100 µL loop)
Detection:	Suppressed conductivity, ASRS ULTRA II Anion Self-Regenerating Suppressor, recycle mode, 248 mA, without 4-mm CRD
Typical Background:	<1 µS
Typical System Backpressure:	~2200 psi
Typical Noise:	<3 nS
Run time:	45 min

[a] Conditions listed are for an alternative configuration using only System 1 for carbonate and sulfate determinations. The AS Autosampler controls Inj. Valve 1. See the System Setup section for more information.

[b] Includes a 5 min equilibration at 14 mM potassium hydroxide during sample preparation time.

PREPARATION OF SOLUTIONS AND REAGENTS

Preparation of Standards

Carbonate Standards

It is critical to use freshly degassed deionized water as the diluent for all carbonate standards and to minimize the introduction of atmospheric carbonate by immediately capping and sealing the standards during any preparation or handling steps. Use sodium bicarbonate to prepare carbonate standards. Sodium carbonate should not be used to prepare carbonate standards because atmospheric carbonate can dissolve more readily in basic pH solutions.

Stock Standards

To prepare individual 1000 mg/L stock solutions of fluoride, chloride, bromide, iodide, thiosulfate, phosphate, thiocyanate, and arsenate, weigh the amount of reagent grade compound (Table 1) into individual 125-mL HDPE sample bottles and dilute with deionized water to 100.00 g total weight. Cap the bottles and shake each stock solution to fully dissolve the reagent. Prepare separate 10,000 mg/L stock solutions of carbonate and sulfate in a similar way with freshly degassed deionized water. Swirl the solutions to fully dissolve the reagent. To minimize absorbing atmospheric carbonate, transfer the carbonate and sulfate standards into individual 50-mL HDPE sample bottles. Fill the bottles to the top to minimize the headspace. Discard the excess.

Table 1: Amount of Compound Used to Prepare 100 mL of 1000 mg/L and 10,000 mg/L Individual Stock Solutions

Anion	Compound	Mass (g)
Fluoride	Sodium fluoride (NaF)	0.221
Chloride	Sodium chloride (NaCl)	0.165
Bromide	Sodium bromide (NaBr)	0.129
Carbonate[a]	Sodium bicarbonate ($NaHCO_3$)	1.400
Sulfate[a]	Sodium sulfate (Na_2SO_4)	1.479
Iodide	Potassium iodide (KI)	0.131
Thiosulfate	Sodium thiosulfate ($Na_2S_2O_3$)	0.141
Phosphate	Sodium phosphate, monobasic (NaH_2PO_4)	0.126
Thiocyanate	Sodium thiocyanate (NaSCN)	0.140
Arsenate	Sodium arsenate, dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$)	0.223

[a] Prepare with freshly degassed deionized water. The final concentrations for the carbonate and sulfate stock standards are 10,000 mg/L.

Intermediate, Working, and Method Detection Limit Standards

When determining µg/L concentrations, it is critical that the standards are stored in containers with low ionic contamination levels. Prepare 225-mL polystyrene flasks two or more days prior to using them by rinsing them five or more times with deionized water. Then fill the flasks to the top with fresh deionized water and let them soak overnight. Repeat the rinsing and soaking process on the second day. Use HDPE bottles for high mg/L concentration intermediate and working carbonate and sulfate standards.

Fluoride, Bromide, Chloride, Iodide, Thiosulfate, Phosphate, Thiocyanate, and Arsenate Standards

To prepare individual 10 mg/L intermediate standards of fluoride, bromide, chloride, iodide, thiosulfate, thiocyanate, arsenate, and phosphate, pipette 1000 µL of the respective 1000 mg/L stock solutions into separate pre-cleaned 225-mL polystyrene flasks. Dilute with degassed deionized water to a total weight of 100.0 g.

To prepare working standards of 10, 25, 50, 100, and 150 µg/L fluoride, chloride, bromide, iodide, thiosulfate, and thiocyanate, 20, 50, 100, 200, and 300 µg/L phosphate, and 30, 60, 150, 300, and 600 µg/L arsenate, pipette the amount of 10 mg/L intermediate standards listed in Table 2 into five separate 225-mL polystyrene flasks and dilute with degassed deionized water to a total weight of 100.0 g. Prepare separate 300 and 500 µg/L working standards of chloride in a similar way from the 10 mg/L chloride intermediate standard.

To prepare the standards for method detection limit (MDL) experiments, pipette 250, 500, 1250, and 2500 µL of each of the lowest concentration working standard (10 µg/L of fluoride, chloride, bromide, iodide, thiosulfate, and thiocyanate, 20 µg/L phosphate, and 30 µg/L arsenate) into 20-mL HDPE scintillation vials, and dilute to 5.0 g with degassed deionized water. The final concentrations are 0.5, 1.0, 2.5, and 5 µg/L fluoride, chloride, bromide, iodide, thiosulfate, and thiocyanate, 1.0, 2.0, 5.0 and 10 µg/L phosphate, and 1.5, 3.0, 7.5, and 15 µg/L of arsenate.

Carbonate and Sulfate Working Standards

Prepare carbonate and sulfate working standards in a 10:1 carbonate–sulfate ratio to simulate the sample concentrations. To prepare combined carbonate (5, 10, 20, 40, and 60 mg/L) and sulfate (0.5, 1.0, 2.0, 4.0, and 6.0 mg/L) working standards from 10,000 mg/L carbonate and sulfate stock solutions, pipette the amounts in Table 2 into 125 mL HDPE bottles. Dilute to 100.0 g total with freshly degassed deionized water. To minimize absorbing atmospheric carbonate, transfer the carbonate and sulfate standards into individual 50-mL HDPE sample bottles. Fill the bottles to the top to minimize the headspace. Discard the excess carbonate and sulfate standards. Prepare fresh working standard solutions within 2–3 days.

Table 2. Amount (µL) of 10 mg/L Intermediate Standards Used to Prepare 100 mL Working Standards

	Standard #											
10 mg/L Intermediate standards	**1[a]**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Fluoride, bromide, iodide, thiosulfate, and thiocyanate	100	250	500	1000	1500	—	—	—	—	—	—	—
Phosphate	200	500	1000	2000	3000							
Chloride	100	250	500	1000	1500	3000	5000	—	—	—	—	—
Arsenate	300	600	1500	3000	6000	—	—	—	—	—	—	—
Carbonate[b]	—	—	—	—	—	—	—	50	100	200	400	600
Sulfate[b]	—	—	—	—	—	—	—	5	10	20	40	60

[a] For example, Standard 1 is prepared with 100 µL each of 10 mg/L fluoride, bromide, iodide, thiosulfate, and thiocyanate, 200 µL of 10 mg/L phosphate, 100 µL of 10 mg/L chloride, and 300 µL of 10 mg/L arsenate intermediate standards.

[b] 10,000 mg/L stock solution

Sample Preparation

To minimize changes in carbonate concentration from degassing or absorption through permeable plastic containers, use glass sample bottles and vials for sampling and storing volcanic gas condensate samples and storing degassed deionized water diluent.

It is critical to use freshly degassed deionized water as the diluent for carbonate determinations. Seal freshly degassed deionized Type 1 water into 2-mL glass vials. The AS Autosampler will use the water in these vials as the diluent to minimize contamination of the samples by atmospheric carbonate. Immediately cap and seal diluent and samples during any preparation or handling steps. The collecting solutions for the volcanic gas condensates were used as controls and were treated in the same manner as the samples. The anion concentrations of the control are subtracted from the sample anion concentrations.

To determine the dilution accuracy of the AS Autosampler with these viscous volcanic condensate samples, the AS Autosampler was programmed to dispense, in triplicate, the same amount of sample and diluent used for the dilutions into separate pre-weighed vials. The vials were re-weighed within minutes after the samples were dispensed. The weighed amount agreed within 87.8 to 101.7% of the calculated weight of the dispensed volumes, with an RSD of <0.5 %. The data from this dispensing experiment were used to correct the analytical results with the actual dilution factors. For example, 100 µL of the sample and 900 µL of degassed deionized water were used to prepare a 10-fold dilution of the volcanic gas condensate. The average weights of the separate 100 µL of sample and 900 µL of degassed deionized water were 104.1 ± 0.1 µL and 888.8 ± 1.5 µL (n = 3), respectively. The measured dilution factor of 9.54 was used in place of 10 in the dilution corrections.

Preparation of Spike Recovery Samples in Volcanic Gas Condensates

Prepare spike recovery samples of 40 mg/L carbonate and sulfate in 1000-fold dilutions of the gas condensate samples using the AS Autosampler to first pipette 4 µL each of 10,000 mg/L carbonate and sulfate stock standards into a 1.5-mL sample vial. Pipette a 10 µL aliquot of a previously diluted 10-fold dilution of the volcanic gas condensate sample and 982 µL of freshly degassed deionized water into the sample vial. Mix the resulting solution by pipetting and dispensing 500 µL of the new solution back into the vial three times. The sample preparations and the program commands are discussed in the program section of this document.

Prepare spike recovery samples of 20 µg/L iodide, thiosulfate, and thiocyanate, and 100 µg/L of arsenate in 10-fold dilutions of the gas condensate samples by manually pipetting 40 µL each of 10 mg/L iodide, thiosulfate, and thiocyanate intermediate standards, and 200 µL of 10 mg/L arsenate intermediate standard into a 20-mL HDPE scintillation vial. Dilute to 20 g total weight with the 10-fold diluted volcanic gas condensate sample.

System Setup

The setups for the individual modules, components, and system are thoroughly described in the ICS-3000 Operator's and ICS-3000 Installation manuals,[10] and the Chromeleon Help menus.

This application update uses both systems of a dual ICS-3000 Chromatography system with two different configurations, although System 2 is not necessary for carbonate and sulfate determinations. Configure both systems for µg/L anion determinations by Park and AutoNeutralization. Later, System 1 will be reconfigured for carbonate and sulfate determinations.

Park and AutoNeutralization Setup and Configuration

To determine chloride, bromide, thiosulfate, iodide, phosphate, thiocyanate, and arsenate concentrations, configure both systems of the ICS-3000 system under one timebase and set up both systems according to AN 93. For more information on the columns, cartridge, neutralizer, suppressor, and Carbonate Removal Device (CRD) see the ICS-3000 Operator's manual,[10] the product manuals,[11–16] QuickStart instructions,[17] and Technical Note 62.[18] Under the High Pressure Valve tab in the DC module properties, assign control of the AM_HP1 valve to the AS Autosampler and control of the Inj. Valve 1 to the DC. Under the cartridge tab in the EG module properties, enter the serial number of the potassium hydroxide EGC II cartridge and link it to Pump_1. Under the AS Autosampler properties, verify that the box in front of Sample Overlap is checked. Sample Overlap reduces the total analysis time for each sample.

Set up the AS Autosampler in Normal mode with a cut volume of 15 µL and sample loop volume of 100 µL (or the calibrated volume) according to AN 93 and the AS Autosampler product manual.[19] Enter the correct volumes for the installed sample and prep syringes. Set the Flush and Prime volumes on the Chromeleon Default Panel. Enter 300 µL (or 3 to 10 times the sample loop) for the Flush volume and enter a large volume for the Prime volume (e.g. 5000 µL).

For full loop injections used in the µg/L to mg/L anion determinations, enter the same injection volume of 100 µL in the sequence. The volume removed from the vial is four times the injection volume plus the volume of the AS Autosampler transfer line.

Setup and Configuration for Carbonate and Sulfate Determinations

To set up System 1 for carbonate and sulfate determinations, the CRD must be removed from the eluent and regenerant flow to allow carbonate determinations. Disconnect the Eluent Out and Regen Out tubing from the suppressor and CRD. Reconnect the suppressor and cell in recycle mode, according to the suppressor product manual.[15] Use new black PEEK tubing from the Eluent Out on the suppressor to Eluent In on the cell. Connect the previous Regen Out tubing from the CRD to the Regen Out on the suppressor. Plug all of the fittings and tubing on the CRD. The CRD can be left in place for convenience.

Partial loop injections are used for the carbonate and sulfate determinations to reduce the injection volume. For the partial loop injection of 25 µL on the 100-µL loop, enter 25 as the injection volume in the sequence. The volume removed from the vial is the injection volume plus two times the cut volume (25 + (2 x 15) = 55 µL plus the volume of the AS Autosampler transfer line).

System 2 does not need any modifications nor is it essential to determine carbonate and sulfate concentrations. System 2 is left in the method to minimize the reconfiguration needed to change from trace anion determinations to carbonate and sulfate determinations.

To use only System 1 for sulfate and carbonate determinations, first remove System 2 from the Chromeleon server configuration. Close the Chromeleon program, open the Chromeleon Server Configuration program, and select the properties (right click) of the DC module. Click on the following marked boxes to uncheck them: AM_HP1 in the High Pressure Valve tab, ASRN (or Suppressor 2) in Suppressor tab, and Neutralizer (or CD 2) in Detector tab. Under the High Pressure Valve tab, re-assign control of Inj. Valve 1 to the AS Autosampler (from DC). The sample will not be injected if the control is not assigned to the AS Autosampler. As a further precaution, also re-assign control of AM_HP1 valve to the DC. Verify that the EGC II cartridge (potassium hydroxide) is linked to Pump_1 and listed on System 1. Save and close the server configuration program.

Table 3. Chromeleon Wizard Valve Commands to Control Inj. Valve and the AM_HP1 Valves[a]

Time (min)	Valve	Position	Action
0.2	AM_HP1	A	The sample is isolated onto ASRN II and neutralized.
8.1	Inj. Valve 1	Load	Inj. Valve 1 (System 1) is turned to Load.
8.2	AM_HP1	B	The neutralized sample is released from the neutralizer. Start concentrating the sample onto the UTAC-XLP1 concentrator column.
9.2	Inj. Valve 1	Inject	Inject neutralized, concentrated sample into analytical system.

[a] Table 4, AN 93[9]

After System 2 is removed in the server configuration, it must be disconnected from System 1 at two points. Remove the black PEEK tubing in Port 5 or "S" in Inj. Valve 1 and move the AS Autosampler transfer line tubing from the AM_HP1 valve to Port 5 or "S" in the Inj. Valve 1. Remove the IonPac UTAC-XLP1 concentrator column from System 1 Inj. Valve and 100-µL sample loop from the AM_HP1 10-port valve. Re-install the 100-µL sample loop into Ports 1 and 4 (L) in Inj. Valve 1. Plug the open ports in the 10-port valve and the disconnected PEEK tubing from Port 10 with 10-32 plug connectors (P/N 42772).

Creating Programs

Use the Chromeleon Program Wizard and the parameters from the Conditions sections in this document to create programs. Review the Creating the Program section in AN 93. Add the extra valve commands for the 10-port valve in the Relay & State Devices section (Table 3).

Use ASRS-MPIC as the suppressor type for the ASRN II neutralizer. Create separate methods (quantification files) for carbonate and sulfate, and trace anions. The valve commands from Table 3 are not used if System 2 is removed from the configuration for carbonate and sulfate determinations (System Setup section).

Pipet and Mix Commands for Automatic Dilutions

To automatically dilute and mix samples, use the Pipet and Mix commands from the AS Autosampler. Add these under Sampler Options. To direct the Autosampler to the sample, concentrate, diluent, or mix location, use the general location labels: *current, current+1, and current+2*, etc. *Current* is defined as the vial number listed in the sequence. *Current+1* and *current+2* are one or two incremental numbers from the *current* vial. For example, if vial #10 is to be injected in the sequence, *current* vial is 10, *current+1* is 11, and *current+2* is 12. Consistently follow the same order to prevent errors: place the empty vial in the *current* position, pipet the concentrate or mixed solution from the *current+1* into *current* vial, and pipet the degassed, deionized water diluent from the *current+2* into *current* vial. Mix the ingredients in the *current* vial (followed by load and inject from the current vial). Table 4 shows a serial dilution to prepare a 1000-fold dilution for carbonate and sulfate determinations. Include a Mix command for each dilution and specify the mix location for each dilution.

Use the same Pipet command (Rows 1 and 4 in Table 4) to add concentrated standards as spiking solutions. For the source (location) of the concentrated standard, it is convenient to designate a position in the front row of the tray.

Table 4. AS Autosampler Commands for Automatic Dilutions (1000-fold Dilution Example)

Command	Amount (µL)	Source	Destination	Description
Pipet	100	current+2 vial	Current+1 vial	Pipet concentrated sample into empty vial for first dilution.
Pipet	900	current+4 vial	Current+1 vial	Pipet degassed deionized water into empty vial for first dilution.
Mix	500	3 times	Current+1 vial	Mixes new dilution 3 times by removing and dispensing half of the volume.
Pipet	10	current+1 vial	Current vial	Pipet 10-fold diluted sample into empty vial for second dilution.
Pipet	990	current+3 vial	Current vial	Pipet degassed deionized water into empty vial with 10 µL of diluted sample.
Mix	500	3 times	Current vial	Mixes new dilution 3 times by removing and dispensing half of the volume.

RESULTS AND DISCUSSION

Method Development and Calibration for Carbonate and Sulfate Determinations

In the previously cited method,[8] carbonate was separated on a Dionex IonPac AS17 column with 20 mM potassium hydroxide eluent and detected by suppressed conductivity. To determine whether carbonate could be separated from sulfate on the same column for anions determined by AutoNeutralization (IonPac AS19 4-mm column), the carbonate-sulfate separation was evaluated with the Dionex Virtual Column Separation Simulator. This simulator contains anion and cation separation data for IonPac columns used with their standard eluents and is used to predict the optimum separation conditions. To start the Virtual Column program, select Virtual Column under Tools in the Chromeleon browser. The following conditions were selected to develop the method used herein: anions for the analyte category, response by peak area, carbonate and sulfate analytes, hydroxide–isocratic methodologies, IonPac AS19 4-mm column, 30 °C, 1.0 mL/min flow rate, and the default condition for void volume. The Virtual Column program results showed the best isocratic separation conditions were in the range from 14 mM to 40 mM potassium hydroxide. As the eluent concentration increased, the resolution decreased. The simulator predicted that 14 mM potassium hydroxide is the optimum eluent to separate carbonate and sulfate.

The Virtual Column program results were experimentally verified with the highest concentration calibration standard (60 mg/L carbonate, 6 mg/L sulfate) using 10, 14, 15, and 20 mM potassium hydroxide eluent concentrations. The experimental results agreed with the Virtual Column data that the carbonate-sulfate peak resolution decreased with increasing eluent concentration and 14 mM potassium hydroxide was the best eluent for this application. Resolutions (USP) of carbonate from sulfate were measured as R = 1.7, 1.4, 0.8, and 0, using 10, 14, 15, and 20 mM potassium hydroxide, respectively.

$$R\ (\text{USP})^{a} = \frac{2 \times (\text{retention time}_{\text{sulfate}} - \text{retention time}_{\text{carbonate}})}{(\text{PW}_{\text{sulfate}} + \text{PW}_{\text{carbonate}})}$$

The peak widths (USP) of carbonate, measured at the baseline, were 2.8, 1.4, 1.4, and 1.3 min, and the peak responses (peak height) were 0.27, 0.35, 0.39, and 0.47 µS, respectively. Both values decreased with increasing eluent concentration (the same as above). The 10 mM potassium hydroxide eluent had the highest resolution (1.7) but poor peak shape (peak width of 2.8 min) and poor peak response (0.27 µS peak height), and therefore was not suitable. The 14 mM potassium hydroxide eluent had the best compromise between resolution (1.4), peak width (1.4 min), and peak response (0.35 µS). A 15-min 100 mM potassium hydroxide column wash was added after each injection to restore the column to its original state.

After optimizing the separation, the system was calibrated by measuring peak area responses at different concentrations. Triplicate injections of the five standards of carbonate with sulfate, with concentrations from 5–60 mg/L and 0.5–6 mg/L, respectively, were analyzed. Carbonate had a good peak shape, was well resolved from the sulfate peak, and had a quadratic peak response (r^2=0.994) to concentration in this range (Figure 1). The results were similar to those previously cited.[8] Sulfate peak area response with concentration was linear, r^2=0.999 (not shown), as reported in AN 93.

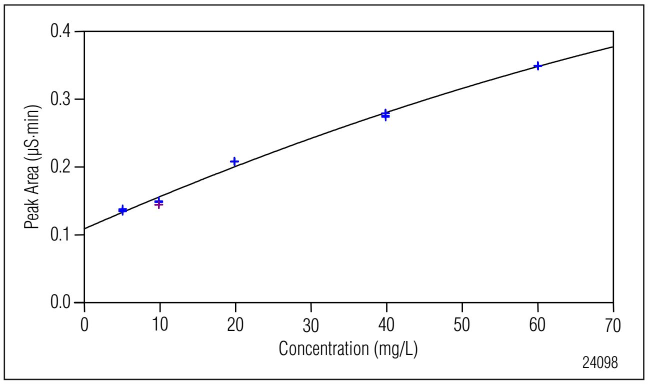

Figure 1: Calibration curve for carbonate without a CRD and using AutoNeutralization.

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[a] In the USP standard for determining resolution (R), peak width (PW) is measured at the baseline.

Calibration for µg/L Anion Determinations by AutoNeutralization

Bromide, chloride, sulfate, and phosphate were previously evaluated in AN 93, but iodide, thiosulfate, thiocyanate, and arsenate were not. The retention times of chloride, bromide, carbonate, and sulfate were verified, and the retention times of iodide, thiosulfate, thiocyanate, and arsenate were identified by injecting each single anion intermediate standard twice.

Bromide, iodide, thiosulfate, and thiocyanate were calibrated from 10 to 150 µg/L by triplicate injections of working standards 1 through 5 (Table 2). The linearities of phosphate and arsenate were evaluated in a similar manner, from 20 to 300 µg/L and 30 to 500 µg/L, respectively. The linearity of chloride was determined over a larger range, 10 to 500 µg/L, by triplicate injections of the five working standards plus two individual chloride working standards. The relationships of peak area responses of chloride, bromide, iodide, phosphate, thiosulfate, thiocyanate, and arsenate to concentration were linear, r^2=0.999 (not shown). The same relationship for fluoride was linear (r^2=0.994) with some instability at concentrations <20 µg/L (not shown).

The method detection limits (MDLs) were then determined for iodide, thiosulfate, thiocyanate, and arsenate (Table 5) with standards (0.5–15 µg/L) prepared from the lowest calibration standard (10 µg/L iodide, thiosulfate, and thiocyanate, and 30 µg/L arsenate). MDL is here defined as three times the signal to noise (1.1 ± 0.4 nS).

Table 5. Method Detection Limit (MDL)[a]

	MDL (µg/L)	RSD
Iodide	6.87	2.6
Thiosulfate	2.92	3.7
Thiocyanate	3.62	3.7
Arsenate	13.7	3.7
Bromide[b]	8	4
Chloride[b]	4	2
Phosphate[b]	24	12

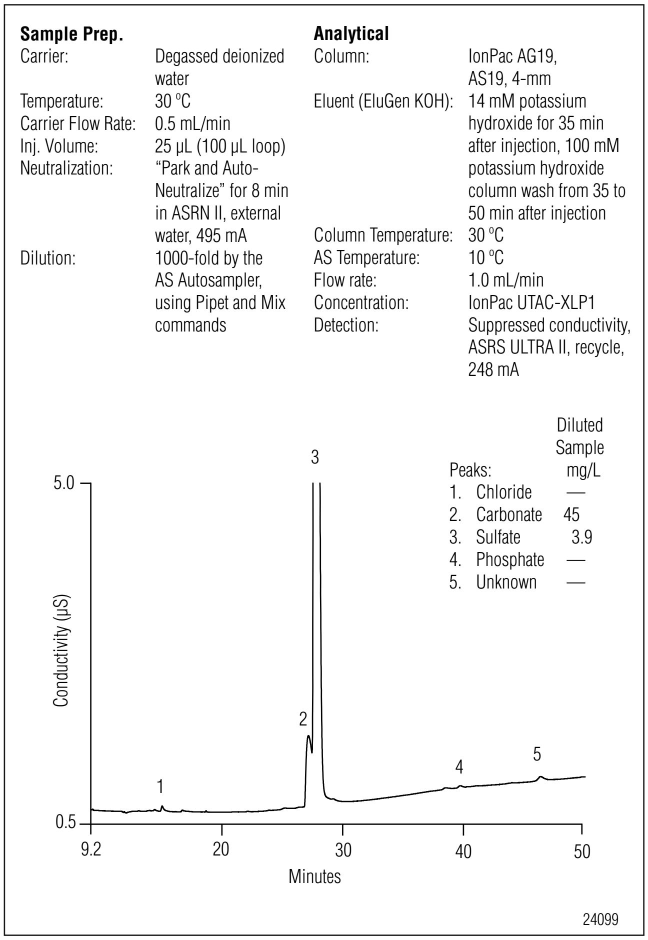
[a] Defined as 3 times Signal to Noise (1.1 ± 0.4 nS, n = 5).

[b] Values taken from Dionex AN 93.

Determinations of Carbonate and Sulfate in Volcanic Gas Condensate Samples

Using eluent conditions optimized for carbonate and sulfate resolution and automated dilutions, the volcanic gas condensate samples and control collecting solution were analyzed at 100 and 1000-fold dilutions with a 10:1 ratio of carbonate to sulfate. For most of the 100-fold diluted samples, the carbonate and sulfate peak areas were outside the calibration ranges and column overloading was evident. Most of the 1000-fold diluted samples had peak areas within the calibration ranges. For determination of high mg/L concentrations of carbonate and sulfate in these samples, a 1000-fold dilution reduced the carbonate concentration into the desired working range and minimized column overload. Some diluted samples needed further dilution.

Based on the dilution experiments, carbonate and sulfate concentrations in 1000-fold dilutions of the volcanic gas condensate samples and the control collecting solution were determined. The chromatogram of diluted volcanic gas condensate Sample 1 shows that carbonate and sulfate peaks were the dominant peaks and were well resolved (Figure 2). Carbonate and sulfate concentrations in the diluted sample, after subtracting the control collecting solution, were 45 mg/L and 3.9 mg/L, respectively. Fluoride, oxalate, and phosphate peaks were present but not quantified at this dilution with this method. In a 1000-fold dilution of the control collecting solution, chloride and oxalate were present, and carbonate was a significant peak in the chromatogram (Figure 3). The carbonate and sulfate concentrations were 7.2 mg/L and 0.3 mg/L in the diluted control collecting solution. Spike recoveries of 40 mg/L carbonate and sulfate in the 1000-fold dilution of volcanic gas sample were 111.8% and 99.3%, respectively (Table 6).

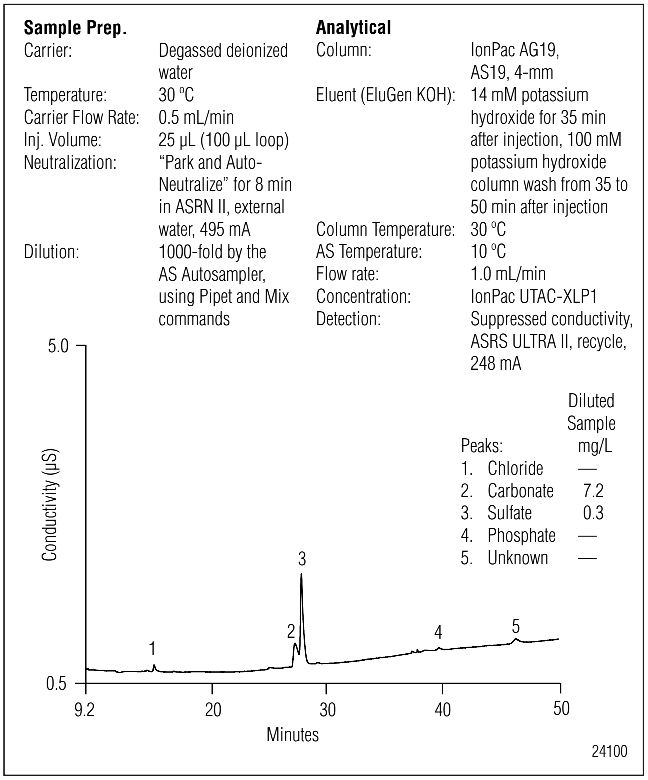


Sample Prep.
Carrier: Degassed deionized water
Temperature: 30 °C
Carrier Flow Rate: 0.5 mL/min
Inj. Volume: 25 µL (100 µL loop)
Neutralization: "Park and Auto-Neutralize" for 8 min in ASRN II, external water, 495 mA
Dilution: 1000-fold by the AS Autosampler, using Pipet and Mix commands

Analytical
Column: IonPac AG19, AS19, 4-mm
Eluent (EluGen KOH): 14 mM potassium hydroxide for 35 min after injection, 100 mM potassium hydroxide column wash from 35 to 50 min after injection
Column Temperature: 30 °C
AS Temperature: 10 °C
Flow rate: 1.0 mL/min
Concentration: IonPac UTAC-XLP1
Detection: Suppressed conductivity, ASRS ULTRA II, recycle, 248 mA

Peaks:	Diluted Sample mg/L
1. Chloride	—
2. Carbonate	45
3. Sulfate	3.9
4. Phosphate	—
5. Unknown	—

Figure 2. Carbonate and sulfate determinations in a 1000-fold dilution of volcanic gas condensate Sample 1 using AutoNeutralization.



Sample Prep.
Carrier: Degassed deionized water
Temperature: 30 °C
Carrier Flow Rate: 0.5 mL/min
Inj. Volume: 25 µL (100 µL loop)
Neutralization: "Park and Auto-Neutralize" for 8 min in ASRN II, external water, 495 mA
Dilution: 1000-fold by the AS Autosampler, using Pipet and Mix commands

Analytical
Column: IonPac AG19, AS19, 4-mm
Eluent (EluGen KOH): 14 mM potassium hydroxide for 35 min after injection, 100 mM potassium hydroxide column wash from 35 to 50 min after injection
Column Temperature: 30 °C
AS Temperature: 10 °C
Flow rate: 1.0 mL/min
Concentration: IonPac UTAC-XLP1
Detection: Suppressed conductivity, ASRS ULTRA II, recycle, 248 mA

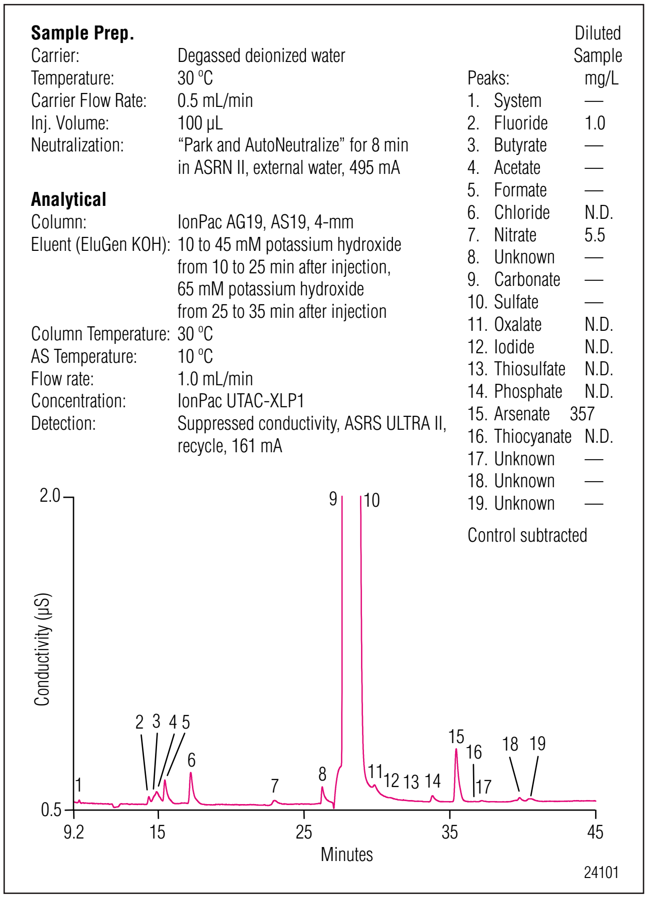
Peaks:	Diluted Sample mg/L
1. Chloride	—
2. Carbonate	7.2
3. Sulfate	0.3
4. Phosphate	—
5. Unknown	—

Figure 3. Carbonate and sulfate determinations in a 1000-fold dilution of control collecting solution using AutoNeutralization.

Table 6. Spike Recovery of Anions in Diluted Volcanic Gas Condensate Sample

	Amount Present (mg/L)	RSD	Amount Added (mg/L)	Recovery (%)	RSD
Carbonate[a]	35.2	0.7	4.0	111.8	7.1
Sulfate[a]	1.0	0.7	4.0	99.3	0.3
Iodide[b]	N.D.[c]		0.019	96.7	5.4
Thiosulfate[b]	N.D.		0.019	88.8	3.2
Thiocyanate[b]	N.D.		0.019	93.4	0.3
Arsenate[b]	0.34	0.7	0.095	91.8	0.4

[a] Spike recovery in 1000-fold dilution of volcanic gas condensate sample with the 4-mm CRD removed (n = 3).
[b] Spike recovery in 10-fold dilution of volcanic gas condensate sample with the 4-mm CRD in place.



Sample Prep.

Carrier: Degassed deionized water
Temperature: 30 °C
Carrier Flow Rate: 0.5 mL/min
Inj. Volume: 100 µL
Neutralization: "Park and AutoNeutralize" for 8 min in ASRN II, external water, 495 mA

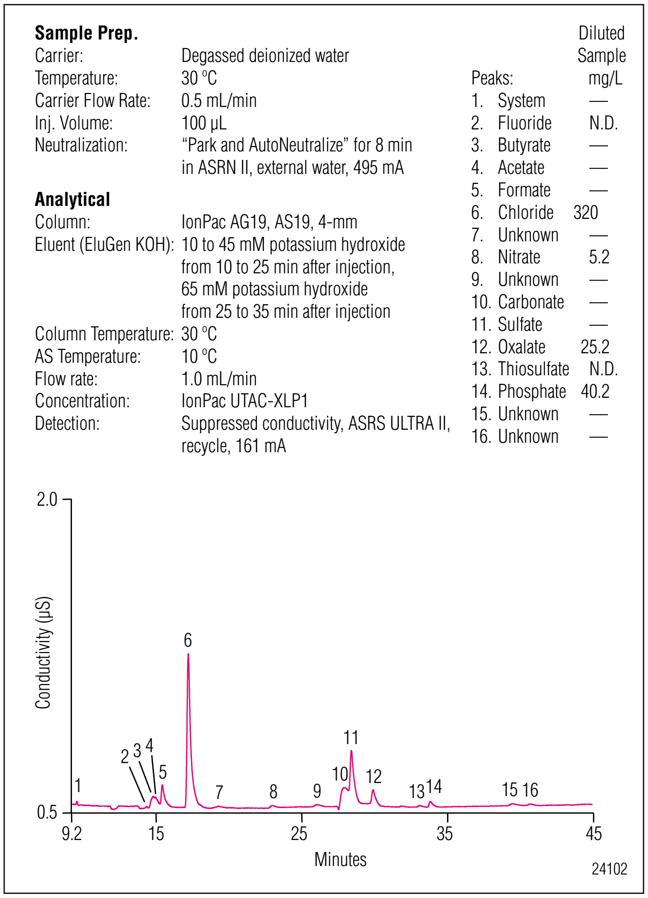
Analytical

Column: IonPac AG19, AS19, 4-mm
Eluent (EluGen KOH): 10 to 45 mM potassium hydroxide from 10 to 25 min after injection, 65 mM potassium hydroxide from 25 to 35 min after injection
Column Temperature: 30 °C
AS Temperature: 10 °C
Flow rate: 1.0 mL/min
Concentration: IonPac UTAC-XLP1
Detection: Suppressed conductivity, ASRS ULTRA II, recycle, 161 mA

Peaks:	Diluted Sample mg/L
1. System	—
2. Fluoride	1.0
3. Butyrate	—
4. Acetate	—
5. Formate	—
6. Chloride	N.D.
7. Nitrate	5.5
8. Unknown	—
9. Carbonate	—
10. Sulfate	—
11. Oxalate	N.D.
12. Iodide	N.D.
13. Thiosulfate	N.D.
14. Phosphate	N.D.
15. Arsenate	357
16. Thiocyanate	N.D.
17. Unknown	—
18. Unknown	—
19. Unknown	—

Control subtracted

Figure 4. Trace anion determinations in a 10-fold dilution of volcanic gas condensate Sample 2 using AutoNeutralization.



Sample Prep.

Carrier: Degassed deionized water
Temperature: 30 °C
Carrier Flow Rate: 0.5 mL/min
Inj. Volume: 100 µL
Neutralization: "Park and AutoNeutralize" for 8 min in ASRN II, external water, 495 mA

Analytical

Column: IonPac AG19, AS19, 4-mm
Eluent (EluGen KOH): 10 to 45 mM potassium hydroxide from 10 to 25 min after injection, 65 mM potassium hydroxide from 25 to 35 min after injection
Column Temperature: 30 °C
AS Temperature: 10 °C
Flow rate: 1.0 mL/min
Concentration: IonPac UTAC-XLP1
Detection: Suppressed conductivity, ASRS ULTRA II, recycle, 161 mA

Peaks:	Diluted Sample mg/L
1. System	—
2. Fluoride	N.D.
3. Butyrate	—
4. Acetate	—
5. Formate	—
6. Chloride	320
7. Unknown	—
8. Nitrate	5.2
9. Unknown	—
10. Carbonate	—
11. Sulfate	—
12. Oxalate	25.2
13. Thiosulfate	N.D.
14. Phosphate	40.2
15. Unknown	—
16. Unknown	—

Figure 5: Trace anion determinations in a 10-fold dilution of the control sample using AutoNeutralization.

Determinations of µg/L Concentrations of Anions in Volcanic Gas Condensate Samples

Using the AutoNeutralization application, the volcanic gas condensate samples and control collecting solution were analyzed at 100-fold dilutions, and then the dilution experiments were expanded to include neat (no dilution), 10, and 100-fold dilutions. In most of the neat samples, the bromide peak was hidden by the carbonate peak and column overloading was evident. In most of the 100-fold dilutions, the peak responses were too low or absent. For determination of µg/L concentrations of anions in these samples, a 10-fold dilution gave the most sensitivity to the anions of interest without overloading the column with carbonate and sulfate.

Based on the dilution experiments, the concentrations of fluoride, chloride, bromide, iodide, thiosulfate, thiocyanate, phosphate, and arsenate were determined in 10-fold dilutions of the volcanic gas condensate samples and the control collecting solution. In the 10-fold dilution of volcanic gas condensate Sample 2, fluoride, chloride, oxalate, arsenate, and phosphate peaks were well-resolved small peaks; thiosulfate and iodide peaks were present; and carbonate and sulfate peaks were too large to quantify (Figure 4). Fluoride, iodide, and thiosulfate were less than 5 µg/L in the diluted sample. Chloride, phosphate, and arsenate were 50.8, 32.1, and 356.5 µg/L, respectively. Oxalate was variable, from concentrations less than the concentration found in the control collecting solution to 30 µg/L. In a 10-fold dilution of the control collecting solution, fluoride and thiosulfate were present; carbonate, sulfate, and oxalate were significant peaks; and chloride (320 µg/L) was the dominant peak in the chromatogram (Figure 5). The large chloride concentration is believed to be contamination from the glass sampling bottle or from the tape used to seal the glass bottle. Spike recoveries of 19 µg/L iodide, thiosulfate, thiocyanate, and 95 µg/L of arsenate in the volcanic gas sample ranged from 88.8 to 96.7% (Table 6).

The results for all anions in two of the volcanic gas condensate samples are tabulated in Table 7. The results are presented in mg/L units for clarity. Fluoride, bromide, and iodide are typically present in µg/L concentrations. Arsenate was found at concentrations ranging from 3.6 to 4.1 mg/L. The chloride concentrations were variable and may reflect contamination from the sealing tape and glass sample containers rather than actual sample results. The carbonate and sulfate concentrations were very high, from 45,000 to 77,000 mg/L, and from 3900 to 5200 mg/L, respectively.

CONCLUSION

Complex and challenging samples such as volcanic gas condensate samples can be analyzed with multiple applications and pretreatments on one analytical system, an ICS-3000 RFIC system using two valves (one six-port and one 10-port), two pumps, two detectors, and two eluent generators. This saves operators the time and labor involved in reconfiguring systems or using two different systems. Automated dilutions by the AS Autosampler reduce errors when determining ions whose concentrations can change with additional exposure to the atmosphere, such as carbonate. This application illustrates the advantages of the AutoNeutralization pretreatment method for analyzing samples important to volcanology.

Performing automated dilutions with the AS Autosampler minimizes the errors from introduced and lost carbonate, by using degassed deionized water from a sealed vial and minimizing exposure to the atmosphere during dilution. However, the sample carbonate concentration can still change at any time from the beginning of sampling until the end of sample analysis. Carbonate can still be introduced from atmospheric carbonate dissolved in diluents or eluents, gas bubbles in the system, or changes in pH or temperature changing the solubility of CO_2. Carbonate determinations should thus be considered estimations only.

Precautions

Always handle concentrated bases with extreme caution. Consult the Material Safety Data Sheets (MSDS) for protective clothing, storage, disposal, and health effects. Use only low pressure concentrator columns, such as the IonPac UTAC-XLP1, with the ASRN II neutralizer. Follow precautions stated in Application Note 93, especially those concerning the ASRN II neutralizer, pressure limits for any of the components, the use of external water regenerant, and baseline sulfate concentrations.

Carbonate concentrations are expected to be unstable because solutions can gain or lose carbonate with exposure to the atmosphere, changes in pH, and/or changes in temperature. For carbonate determinations use glass sample and storage bottles, and glass autosampler vials to minimize atmospheric carbonate contamination. Prepare carbonate standards quickly with freshly degassed deionized water diluent and keep sample and standard containers capped until use. Flush and prime the AS Autosampler prep and sample syringes and syringe lines until all gas bubbles are removed. This is critical for accurate and precise injections and dilutions.

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We would like to thank Dr. Bruce W. Christenson for his generosity and expertise and for providing these interesting and challenging samples.

Table 7. Summary of Anion Determinations of Volcanic Gas Condensate Samples[a]

	Fluoride (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Bromide (mg/L)	Carbonate (mg/L)	Sulfate (mg/L)	Oxalate (mg/L)	Iodide (mg/L)	Thiosulfate (mg/L)	Phosphate (mg/L)	Arsenate (mg/L)	Thiocyanate (mg/L)
#1	0.05 ± 0.00[b]	N.D.[c]	0.35 ± 0.01	N.D.	77,000 ± 1100	5,200 ± 35	0.28 ± 0.00[b]	N.D.	N.D.	N.D.	4.12 ± 0.01	N.D.
#2	0.01 ± 0.00[b]	N.D.	0.06 ± 0.00[b]	N.D.	45,000 ± 540	3,900 ± 39	N.D.	N.D.	N.D.	N.D.	3.57 ± 0.07	N.D.

[a] Controls subtracted (n = 3).

[b] The standard deviation was less than the last significant figure for the experiment.

[c] N.D. = Not detected or less than control concentration.

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