

# Determination of Anions and Cations in Process Water from Steam Assisted Gravity Drainage Oil Sands Extraction

Carl Fisher, Thermo Fisher Scientific, Sunnyvale, CA, USA

## Key Words

Dionex ICS-5000+, Dionex IonPac CS16, Dionex IonPac AS18-4 $\mu$ m, Capillary IC, SAGD

## Goal

Use ion chromatography to quantify anions and cations in process water resulting from extraction of hydrocarbons in oil sands recovered using steam assisted gravity drainage.

## Introduction

Oil sands are petroleum deposits that are estimated to contain over two trillion barrels of oil with the majority of these deposits being located in Canada (~70%), primarily in the province of Alberta.<sup>1</sup> These oil reserves are considered unconventional because the method used for extraction differs from that of a conventional oil well (i.e., one from which oil can be extracted after drilling just by the natural pressure of the well and the pumping operation). Oil sand is composed of sand, water, clay, and oil, the latter component being in the form bitumen, which is a highly viscous liquid or semi-solid that is too thick to flow unless diluted or heated. To recover the oil contained within these deposits, the two most commonly used methods are surface mining and drilling using steam assisted gravity drainage (SAGD).<sup>1</sup> In surface mining of material that is within 200 feet of the surface, deposits are transported to a crusher that breaks the material into smaller pieces that are then mixed with hot water and pumped to a nearby processing facility where the bitumen is separated from the other components. The wastewater that results from this process contains dissolved solids in addition to sand, clay, and residual oil. This mixture (the tailings) is pumped into dammed basins where the fine particles are precipitated and the water is prepared for use in subsequent rounds of oil sands processing.



However, approximately 80% of oil sand reserves are not accessible from the surface and require alternative methods to recover them. The primary technique used to extract these buried deposits is SAGD, an in situ method in which steam (created from a mix of fresh and brine waters) is pumped through a well drilled into the oil sand layer (Figure 1) causing the bitumen to flow and allowing it to be pumped through a parallel pipe, positioned below the first, to the surface for processing.

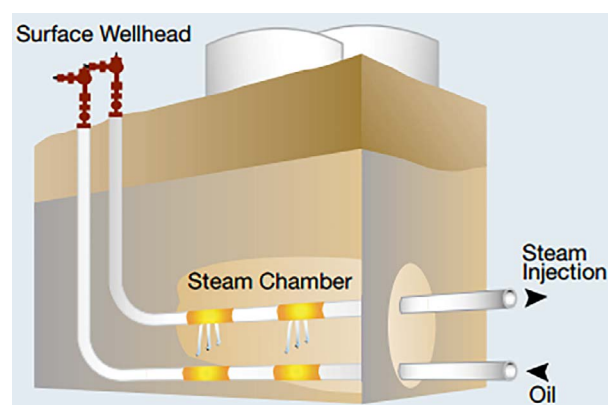


Figure 1. Diagram of steam assisted gravity drainage.<sup>1</sup>

At the processing plant, the injected and formation (occurring naturally within the pores of rock) waters are treated for reuse as boiler feedwater. In the most commonly used treatment process, the water is de-oiled, softened to remove silica and hardness, filtered, and, finally, treated by weak acid cation-exchange to remove calcium and magnesium to prevent fouling.<sup>2</sup> Once treated, it can be continuously recirculated between the well and the processing plant. Determinations of the ionic constituents of SAGD process water can be used to optimize and monitor the treatment plan.

In this Application Note, water samples obtained from SAGD oil sands processing were analyzed using a Thermo Scientific™ Dionex™ ICS-5000+ Reagent-Free™ High-Pressure™ Ion Chromatography (HPIC™) system for anion and cation determinations using Thermo Scientific™ Dionex™ IonPac™ AS18-4µm and Dionex IonPac CS16 capillary columns, respectively.

## Equipment

- Dionex ICS-5000+ Reagent-Free HPIC capillary system including:
  - SP Single Pump or DP Dual Pump
  - EG Eluent Generator module
  - DC Detector/Chromatography module with Thermo Scientific™ Dionex™ IC Cube™ and CD Conductivity Detector

## Autosampler

- Thermo Scientific Dionex AS-AP Autosampler
- Vial kit, 1.5 mL, Polypropylene with caps and blue septa (P/N 079812)

## Software

- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2

## Reagents and Standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ-cm resistivity or better

## Anions

- Thermo Scientific Dionex
  - 1000 mg/L Chloride Standard (P/N 037159)
  - 1000 mg/L Fluoride Standard (P/N 037158)
  - 1000 mg/L Sulfate Standard (P/N 037160)
  - 1000 mg/L Bromide Standard (Ultra Scientific P/N ICC-001)
- Fisher Scientific, ACS Grade
  - Sodium Acetate, anhydrous (P/N S210)
  - Sodium Formate (P/N S648)
  - Sodium Nitrate (P/N S343)

## Cations

- Ultra Scientific
  - 1000 mg/L Lithium Standard (P/N ICC-104)
  - 1000 mg/L Sodium Standard (P/N ICC-107)
  - 1000 mg/L Ammonium Standard (P/N ICC-101)
  - 1000 mg/L Potassium Standard (P/N ICC-106)
  - 1000 mg/L Magnesium Standard (P/N ICC-105)
  - 1000 mg/L Calcium Standard (P/N ICC-103)
- Fisher Scientific, ACS Grade
  - Barium chloride, dihydrate (P/N B34)
  - Strontium chloride, hexahydrate (P/N S541)

## Samples

Process water samples were obtained from SAGD operations in Northern Alberta, Canada and were stored at 4 °C prior to analysis.

## Conditions

### Anion Method

Columns:	Dionex IonPac AG18-4µm Capillary Guard, 0.4 × 35 mm (P/N 076033) Dionex IonPac AS18-4µm Capillary, 0.4 × 150 mm (P/N 082314)
Eluent Source:	Thermo Scientific Dionex EGC-KOH cartridge (Capillary) (P/N 072076) with Thermo Scientific Dionex CR-ATC Continuously Regenerated Anion Trap Column (P/N 072078)
Gradient:	12–15 mM KOH (0–3 min), 15–22 mM KOH (3–4 min), 22 mM KOH (4–11 min), 12 mM KOH (11–16 min)
Flow Rate:	0.01 mL/min
Column Temperature:	30 °C
Injection Volume:	0.4 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300 Anion Capillary Electrolytic Suppressor (P/N 072052), recycle mode, 8 mA
Background Conductance:	<0.7 µS
Noise:	<1 nS
System Backpressure:	~2000 psi

### Cation Method

Columns:	Dionex IonPac CG16 Capillary Guard, 0.5 × 50 mm (P/N 075402) Dionex IonPac CS16 Capillary, 0.5 × 250 mm (P/N 075401)
Eluent Source:	Thermo Scientific Dionex EGC-MSA cartridge (Capillary) (P/N 072077) with Thermo Scientific Dionex CR-CTC II Continuously Regenerated Cation Trap Column (P/N 072079)
Gradient:	20–30 mM MSA (0–10 min), 30–55 mM MSA (10–18 min), 55 mM MSA (18–31 min), 20 mM MSA (31–37 min)
Flow Rate:	0.010 mL/min
Column Temperature:	40 °C
Injection Volume:	0.4 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ CCES™ 300 Cation Capillary Electrolytic Suppressor (P/N 072053), recycle mode, 11 mA
Background Conductance:	1 µS
Noise:	<1 nS
System Backpressure:	1300 psi

## Preparation of Standards

To prepare 1000 mg/L stock solutions, accurately weigh the amounts indicated in Table 1, transfer to a 100 mL volumetric flask, and fill to the mark with DI water. Mix thoroughly. Concentrated standards should be stable for at least one month when stored at 4 °C.

Table 1: Mass of chemical to prepare a 100 mL stock standard.

Analyte	Chemical	Mass (g)
<b>Acetate</b>	Sodium acetate	0.139
<b>Barium</b>	Barium chloride	0.178
<b>Formate</b>	Sodium formate	0.151
<b>Nitrate</b>	Sodium nitrate	0.115
<b>Strontium</b>	Strontium chloride	0.304

## Working Standard Solutions

Prepare the highest concentration working standard solution by pipetting the appropriate amount of 1000 mg/L stock solution into a 100 mL volumetric flask and diluting to the mark with DI water. Prepare the lower concentration working standards by diluting the highest concentration working standard with DI water (Table 2). Store standard solutions at 4 °C when not in use.

Table 2. Anion and cation standard mixtures.

	Level	1	2	3	4	5	6	7	8
		Concentration (mg/L)							
Anions	<b>Acetate</b>	0.02	0.05	0.1	0.2	0.5	1.0	2.5	5.0
	<b>Bromide</b>								
	<b>Chloride</b>	1.6	4	8	16	40	80	200	400
	<b>Fluoride</b>	0.02	0.05	0.1	0.2	0.5	1.0	2.5	5.0
	<b>Formate</b>								
	<b>Nitrate</b>								
	<b>Sulfate</b>								
Cations	<b>Ammonium</b>	0.025	0.05	0.1	0.25	0.5	1.0	2.5	5.0
	<b>Barium</b>	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10
	<b>Calcium</b>	0.025	0.05	0.1	0.25	0.5	1.0	2.5	5.0
	<b>Lithium</b>								
	<b>Magnesium</b>								
	<b>Potassium</b>								
	<b>Sodium</b>	0.4	0.8	2.0	4.0	8.0	20	40	200
	<b>Strontium</b>	0.05	0.1	0.2	0.5	1.0	2.0	5.0	10

## Sample Preparation

Samples were filtered with 0.2 µm polyethersulfone (PES) syringe filters (Thermo Scientific P/N 42213-PS) and stored at 4 °C. Samples were diluted as indicated with 18 MΩ-cm resistivity degassed DI water.

It is important to use 18 MΩ-cm resistivity DI water for sample preparation as well as eluent and autosampler flush solutions to avoid system contamination, decreased sensitivity, and poor calibration. Degassing the DI water by vacuum filtration prior to use is a good practice.

## System Preparation and Configuration

Refer to Thermo Scientific Technical Note 131, *Configuring High-Pressure Capillary IC on the Modular IC System*,<sup>3</sup> for flow diagrams, configuration, and system setup information. For conditioning and installation of columns and electrolytic devices refer to the product specific instruction manuals.

## Results and Discussion

SAGD process water samples were obtained from different stages of oil sands processing, as evident by the difference in color (Figure 2). Information regarding the precise stage from which these samples were obtained was not available, but the concentration of ions, as described below, should provide some insight and indicate their suitability for use as boiler feedstock for additional in situ oil sands extractions.

Capillary IC was used to take advantage of the approximately 100-fold less water consumption (and waste generated) compared to a standard bore system. As a result of the low flow rate (0.01 mL/min), the system can be left always on and ready to run samples, eliminating the time required for system startup and equilibration following the initial setup.



Figure 2. Filtered SAGD process water samples 1 and 2.

### Anion Method

The efficiency of a column is increased proportionately as the particle size is reduced.<sup>4</sup> Consequently, when using smaller particle columns, higher flow rates or shorter columns can be used to achieve peak separation comparable to that of larger particle size columns, but in a shorter period of time. For the data presented here, a 0.4 × 150 mm Dionex IonPac AS18-4µm column was used because of its higher efficiencies (50–60%) compared to a column of the same length using 7.5 µm resin particles.<sup>5</sup> To increase the separation of the early eluting anions (fluoride, acetate, and formate) a gradient from 12–15 mM KOH was used over the first three minutes of the run, followed by a gradient from 15–29 mM KOH from three to four min, with 29 mM KOH maintained for the remainder of the method. All analytes eluted within 10 min.

### Method Linear Calibration Ranges

To determine the linear calibration ranges, the peak responses to concentration were determined using triplicate injections of calibration standards over a 200-fold dilution range (Table 3). Plotting peak area versus concentration demonstrated linearity for the concentration ranges used, as exemplified by the chloride calibration curve (Figure 3). The exception was acetate, which exhibited a quadratic fit relationship to concentration. Coefficient of determinations ( $r^2$ ) ranged from 0.9992 to 1.00.

Table 3: Anion calibration ranges and fitting results.

Analyte	Concentration (mg/L)	$r^2$
Fluoride	0.02–5.0	0.9997
Acetate*	0.02–5.0	0.9997
Formate	0.02–5.0	0.9992
Chloride	1.6–400	1.000
Bromide	0.02–5.0	0.9993
Sulfate	0.02–5.0	0.9997
Nitrate	0.02–5.0	0.9992

$n = 3$ ; \* Quadratic curve fit

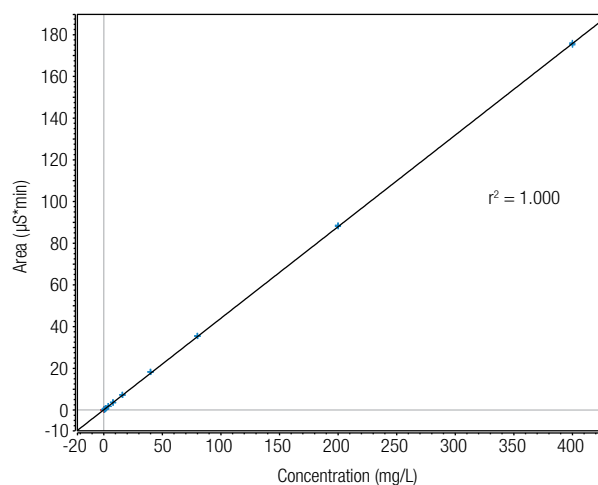


Figure 3. Chloride calibration curve.

### Determination of Anion Concentrations in SAGD Process Water

Water samples from SAGD oil extraction were diluted 20- and 10-fold for SAGD 1 and SAGD 2, respectively, so that they were within the calibration ranges (Figure 4). In this Figure, the lower chromatogram is an expanded view of the upper for easier visualization of the lower concentration analyte peaks. In SAGD 1, chloride and bromide were 4-fold higher than in SAGD 2, but there was >3-fold less fluoride and sulfate, while acetate and formate were not detected despite loading a dilution that contained ~5-fold more chloride than was present in the SAGD 2 dilution (Figure 5). In SAGD 2, the predominant anion, chloride, was followed in concentration by acetate at ~14-fold lower concentration, and then sulfate, with lesser amounts of formate, bromide, and fluoride.

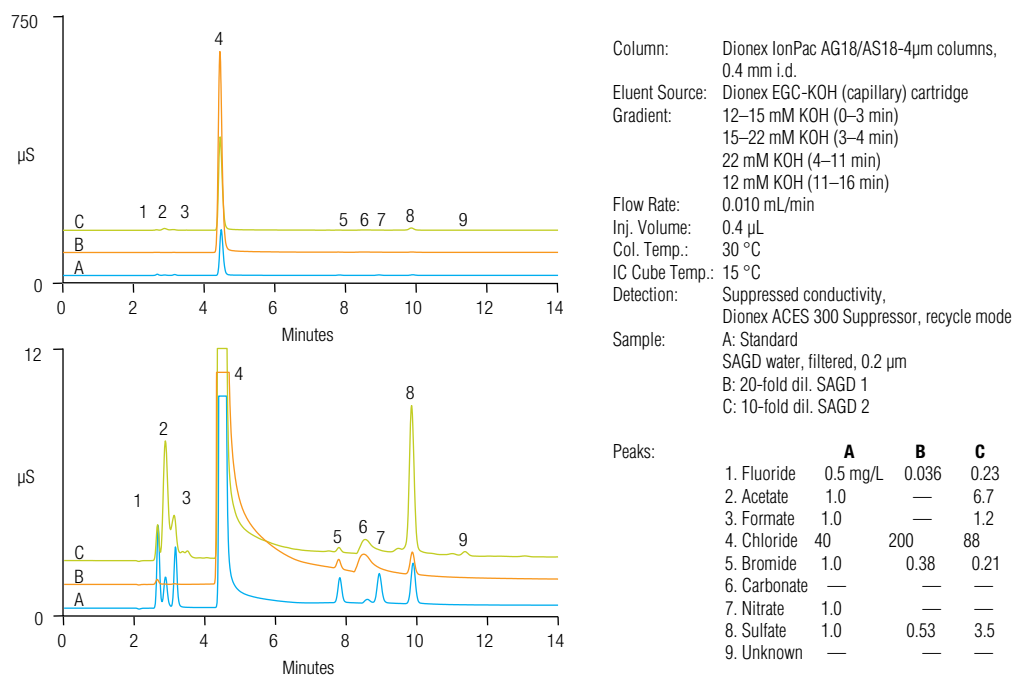


Figure 4. Determination of anions in SAGD process water.

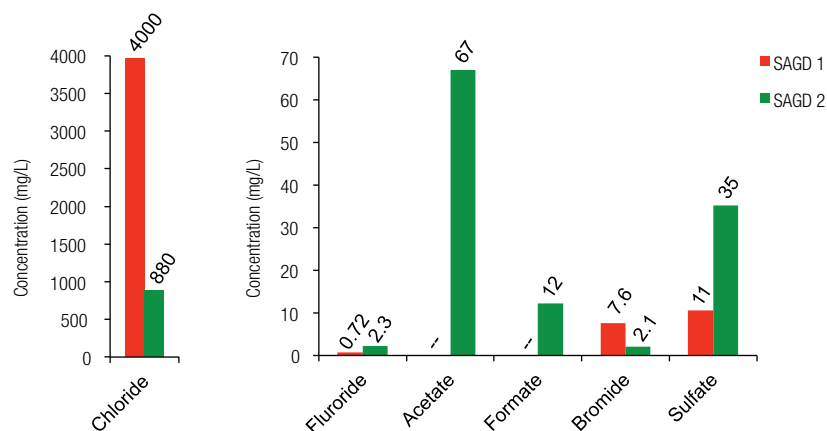


Figure 5. Comparison of anions in SAGD process water. Total anion concentrations are displayed above each bar (mg/L).

### Cation Method

The Dionex IonPac CS16 column was chosen for its high capacity and high resolution of closely eluting analytes of disparate concentration ratio such as sodium and ammonium. Additionally, this column has been used successfully for the analysis of wastewaters from the hydraulic fracturing of shale oil deposits.<sup>6,7</sup> For cation separation, gradients of 20–30 mM MSA (0–10 min) and 30–55 mM MSA (10–18 min) were used to elute all analytes within 33 min.

### Method Linear Calibration Ranges

Plotting peak area versus concentration demonstrated linearity over a 200-fold dilution range. The exception was ammonium, which exhibited a quadratic fit relationship to concentration. The coefficient of determinations ( $r^2$ ) ranged from 0.9989 to 0.9999 (Table 4).

Table 4: Cation calibration ranges and fitting results.

Analyte	Concentration (mg/L)	$r^2$
Lithium	0.025–5	0.9997
Sodium	0.4–200	0.9999
Ammonium*	0.025–5	0.9992
Potassium	0.025–5	0.9993
Magnesium	0.025–5	0.9997
Calcium	0.025–5	0.9998
Strontium	0.05–10	0.9995
Barium	0.05–10	0.9987

$n = 3$ ; \* Quadratic curve fit

### Determination of Cation Concentrations in SAGD Process Water

As with anion analysis, the samples required dilution to ensure that the concentrations were within the calibration ranges. SAGD 1 was diluted 20-fold while SAGD 2 was diluted 5-fold. These dilutions resulted in approximately equivalent amounts of sodium being loaded on the column.

Consistent with the trend in anion concentrations, the concentration of the major cation (sodium) was highest in SAGD 1 (by ~4-fold) while almost all of the other cations were higher in SAGD 2 (Figures 6 and 7).

Both SAGD samples had low concentrations of the scale-forming cations (magnesium, calcium, strontium, and barium) indicating that little softening (to prevent scale buildup) would be required prior to using these solutions as boiler feedwater.

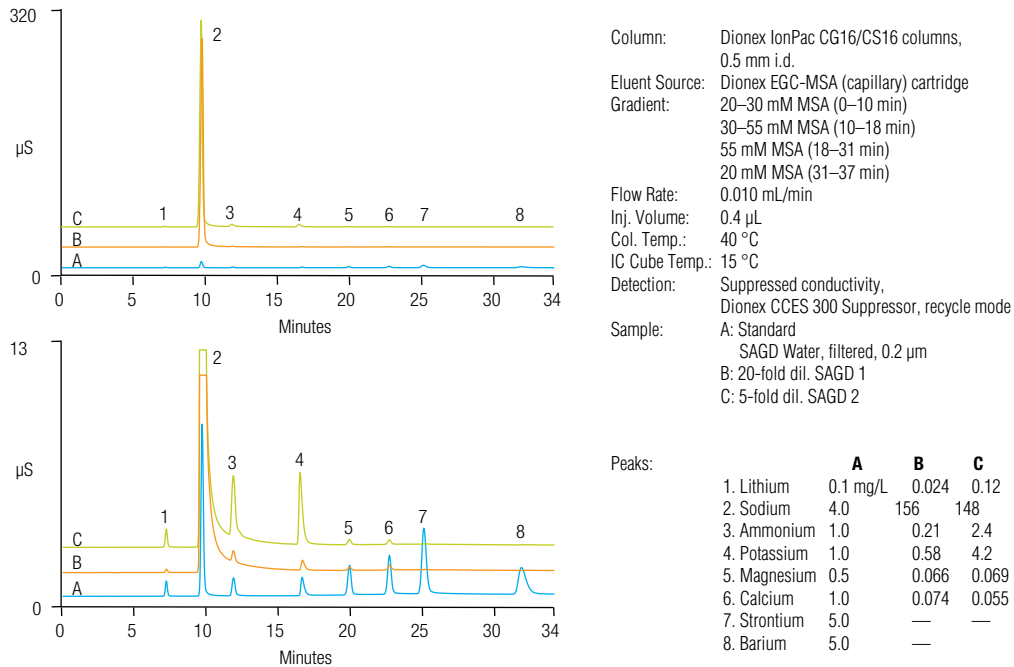


Figure 6. Determination of cations in SAGD process water.

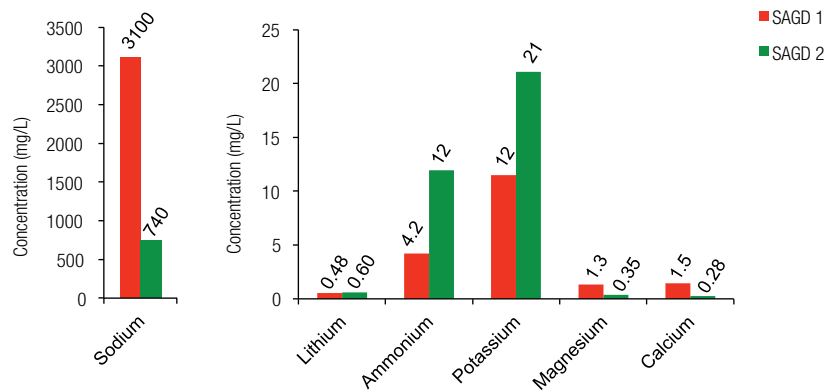


Figure 7. Comparison of cations in SAGD process water. Total cation concentrations are displayed above each bar (mg/L).

Based on the clear coloring of SAGD 1, it could be concluded that it is makeup water, which is used to compensate for water losses that occur during SAGD water treatment. While almost all of the analytes measured were higher in SAGD 2, the primary ions, sodium and chloride, were ~4-fold higher in SAGD 1. Relatively high salt concentrations can be tolerated in boiler feed water<sup>8</sup>, making water such as SAGD 1 appropriate for this purpose. Using high salt water in this way conserves clean water (that may be in short supply) so that it can be used for drinking and agriculture. In contrast, the brown coloring of SAGD 2 suggests that it was likely recovered following mixture with oil sands. This supposition is supported by the higher concentration of organic acids in SAGD 2 compared to SAGD 1, which is consistent with the elevated levels of organic acids found in produced and de-oiled water compared to groundwater.<sup>2</sup> More definitive answers will require analysis of samples whose origins have been more closely tracked, but it is evident that the concentrations of ions can be used to monitor the progression of water through the various stages of water treatment and can indicate the requirement for additional treatment steps.

## Conclusion

This Application Note demonstrates that the concentration of cations and anions in SAGD process water can be accurately determined using the Dionex ICS-5000+ HPLC system with Dionex IonPac AS18-4 $\mu$ m and Dionex IonPac CS16 capillary columns. The chromatographic conditions were optimized so that all of the analytes eluted within 10 and 33 min for anions and cations, respectively. The most abundant anions were chloride, nitrate, and acetate, while sodium, potassium, and ammonium were the most prevalent cations. The low levels of scale-forming cations measured in the analyzed SAGD samples indicate that they are suitable candidates for re-use in additional oil sands processing using SAGD.

## References

1. Canadian Association of Petroleum Producers. *About Canada's Oil Sands*; Calgary, AB, 2013. <http://www.capp.ca/getdoc.aspx?DocId=228182&DT=NTV> (accessed January 25, 2015).
2. Kawaguchi, H.; Li, Z.; Masuda, Y.; Sato, K.; and Nakagawa, H. Dissolved Organic Compounds in Reused Process Water for Steam-Assisted Gravity Drainage Oil Sands Extraction. *Water Res.*, **2012**, *16*, 5566–5574.
3. Thermo Fisher Scientific. Thermo Scientific Technical Note 131, *Configuring High-Pressure Capillary IC on the Modular IC System*, TN70352\_E, Sunnyvale, CA, **2012**.
4. Snyder, L.R.; Kirkland, J.J.; Dolan, J.W. *Introduction to Modern Liquid Chromatography*, 3rd ed.; Wiley and Sons: Hoboken, NJ, **2010**.
5. Thermo Fisher Scientific. Thermo Scientific White Paper 70631, *Benefits of Using 4  $\mu$ m Particle-Size Columns*, WP70631\_E, Sunnyvale, CA, **2013**.
6. Thermo Fisher Scientific. Thermo Scientific Application Note 1094, *Determination of Cations in Hydraulic Fracturing Flowback Water from the Marcellus Shale*, AN71085\_E, Sunnyvale, CA, **2014**.
7. Thermo Fisher Scientific. Thermo Scientific Application Note 1105, *Determination of Anions and Cations in Produced Water from Hydraulic Fracturing*, AN71255\_E, Sunnyvale, CA, **2014**.
8. Alberta Innovates. *New SAGD Technologies Show Promise in Reducing Environmental Impact of Oil Sand Production*; Calgary, AB, 2014. [http://albertainnovates.ca/media/20420/sagd\\_technologies\\_ogm\\_lightbown.pdf](http://albertainnovates.ca/media/20420/sagd_technologies_ogm_lightbown.pdf) (accessed February, 9, 2015).

## [www.thermofisher.com/chromatography](http://www.thermofisher.com/chromatography)

©2016 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

<b>Africa</b> +43 1 333 50 34 0	<b>Denmark</b> +45 70 23 62 60	<b>Japan</b> +81 6 6885 1213	<b>Russia/CIS</b> +43 1 333 50 34 0
<b>Australia</b> +61 3 9757 4300	<b>Europe-Other</b> +43 1 333 50 34 0	<b>Korea</b> +82 2 3420 8600	<b>Singapore</b> +65 6289 1190
<b>Austria</b> +43 810 282 206	<b>Finland</b> +358 9 3291 0200	<b>Latin America</b> +1 561 688 8700	<b>Sweden</b> +46 8 556 468 00
<b>Belgium</b> +32 53 73 42 41	<b>France</b> +33 1 60 92 48 00	<b>Middle East</b> +43 1 333 50 34 0	<b>Switzerland</b> +41 61 716 77 00
<b>Brazil</b> +55 11 3731 5140	<b>Germany</b> +49 6103 408 1014	<b>Netherlands</b> +31 76 579 55 55	<b>Taiwan</b> +886 2 8751 6655
<b>Canada</b> +1 800 530 8447	<b>India</b> +91 22 6742 9494	<b>New Zealand</b> +64 9 980 6700	<b>UK/Ireland</b> +44 1442 233555
<b>China</b> 800 810 5118 (free call domestic) 400 650 5118	<b>Italy</b> +39 02 950 591	<b>Norway</b> +46 8 556 468 00	<b>USA</b> +1 800 532 4752

**Thermo**  
SCIENTIFIC

A Thermo Fisher Scientific Brand