Ion chromatographic cation analysis of effluent waters from scale dissolver treatments

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Abstract

Numerous products are available to the oil industry that dissolve barium sulfate and other field scales. Several commercial products were evaluated for dissolution behavior on actual field scale. Testing conditions included temperature, salinity of the make up water and exposure time.

Inductively coupled argon plasma (ICAP) spectroscopy is usually the scientist's first choice for the analyses of cations. Matrix problems needed to be addressed as well as detection limits. An ion chromatographic (IC) method was developed to simultaneously analyze for monovalent and divalent cations. Data was compared to ICAP. The IC method gives an excellent separation and eliminates any need for matrix matching of samples and standards. Low levels of magnesium, calcium, strontium, and barium may be detected in samples with high sodium and/or potassium content. It works particularly well for the scale dissolver samples as the four divalent cations of interest are analyzed in a single chromatogram. Detection limits at or below 0.1 mg/l are possible in this complex matrix. The eluent, methanesulfonic acid (MSA), is certainly strong enough to displace cations from the nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) complexes and other possible complexes.

Keywords: Water analysis; Metal cations; Aminopolycarboxylates

1. Introduction

Alkaline earth metal sulfates form when separate geologically stable brines are mixed during oil production. The mixture, supersaturated with a sparingly soluble salt, subsequently deposits the salt on producing formation, pipework and valves. Such solids represent an economic loss as well as potential safety and environmental hazards. Barium and strontium sulfates comprise much of the problematic deposits. Radium sulfate commonly coprecipitates with these sulfates imparting a radioactive character [1]. Prevention is therefore preferred but removal may become necessary as the treatment of last resort.

Carbonate scales are also encountered during oil production but are easily removed with simple mineral acids [2]. There are no simple solutions to the barium/strontium sulfate problem. Dissolving them is both complex and expensive. Each treatment may cost several hundred thousand dollars in materials with equipment, labor and lost oil production exceeding the cost of materials. This obviates the need for laboratory testing of candidate inhibitors.

Temperature, agitation, diluent composition and dissolver concentration are all known to affect dissolver performance on any one scale [3]. Thus these variables were investigated during the dissolver

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study. The analytical method of choice for determination of soluble divalent cations was to be inductively coupled argon plasma emission spectroscopy (ICAPES).

Although dissolvers are proprietary formulations, they are known to generally comprise strongly alkaline solutions of divalent cation sequestrant aminopolycarboxylates. Sodium, potassium and ammonium ion concentrations are usually 3–5 M and the presence of organic accelerants, wetting agents and co-chelants are to be expected. Total dissolved solids contents may be as high as 300 g/l.

The effluent dissolver solutions contain both chelated divalent ions and high concentrations of free sulfate. As such, they are highly sensitive to variations in pH which render the complexes unstable, leading to rapid reprecipitation of the sulfate salts.

Due to the demanding matrix and sample preparation concerns, it was decided to investigate both ICAPES and ion chromatography (IC) as potential methods for the determination of the four ions of interest (magnesium, calcium, strontium and barium).

2. Experimental

2.1. Instrumentation

The IC method presented was performed on a Dionex 4500i ion chromatograph equipped with a gradient pump [plumbed with polyether ether ketone (PEEK) tubing and fittings], conductivity detector housed in a pulsed electrochemical detection (PED) module, eluent degas module (EDM-2) supplied with helium, autosampler and AI-450 software. The columns used were: (1) cation trap column [4] (24×9 mm, high-capacity cation-exchange resin in the hydrogen (hydronium) form; (2) Dionex IonPac CG12 guard column [5] (50×4 mm); and (3) Dionex IonPac CS12 analytical column [5] (250×4 mm). The columns were used with a Dionex Cation Self-Regenerating Suppressor CSRS-I (4 mm) [6] operating in the recycle mode at a current setting of 3.

The ICAPES was performed on a Thermo Jarrell Ash-9000 Instrument. This instrument acquires intensity of all peaks simultaneously. Scandium was added to each sample as an internal standard to

compensate for any density or viscosity effects in the nebulizer. Sample introduction was by autosampler and peristaltic pump using silicone tubing at 1.6 ml/min rate. The sample introduction system was flushed for 60 s with Milli-Q water between samples. Sample data was automatically acquired for four sets of 10 s and averaged. The peaks were measured with fixed detectors at the following wavelengths (nm): calcium 317.933, magnesium 279.079, strontium 421.552, barium 493.409 and scandium 361.300.

2.2. Reagents

The water used to dilute samples and standards for IC and ICAPES was distilled water passed through a Millipore Milli-Q system.

Cation standards were prepared from Plasmachem sodium ICP standard 10 000 μg/g in 2% nitric acid, Plasmachem magnesium atomic absorption standard 1000 ppm (w/v) in 2% nitric acid, Plasmachem calcium atomic absorption standard 1000 ppm (w/v) in 2% nitric acid, Plasmachem strontium atomic absorption standard 1000 ppm (w/v) in 2% nitric acid, and Plasmachem barium atomic absorption standard 1000 ppm (w/v) in 2% nitric acid. For IC, four different concentrations of mixed standards were prepared by dilution with Milli-Q water. For ICAPES, one mixed standard of 20 ppm (w/v) was prepared using Milli-Q water. Scandium internal standard was added to achieve a concentration of 7.5 ppm (w/v).

Two IC eluents were prepared from methanesulfonic acid (greater than 99% purity) and Milli-Q water. All eluents were degassed with helium and subsequently kept under a blanket of helium (compressed gas, 99.995% pure).

Five commercial scale dissolvers were obtained from three different companies. Low-sulfate sea water (LSSW) is a process fluid manufactured with an ion-selective membrane on some oil platforms. This was synthesized by dissolving the following reagent-grade chemicals to 1 l in distilled water: 25.594 g sodium chloride, 0.667 g potassium chloride, 0.752 g calcium chloride (dihydrate), 3.846 g magnesium chloride (hexahydrate) and 0.096 g sodium sulfate. The resultant LSSW contains 10,099

mg/l sodium, 350 mg/l potassium, 460 mg/l magnesium, 205 mg/l calcium, 17,548 mg/l chloride, and 65 mg/l sulfate.

2.3. Sample preparation

The scale used in this study was obtained from internal tubing of the Dolly Varden (Cook Inlet, AK, USA) Well D-11 in 1989. It was about 2 mm thick and was sized to be 1 cm^2. The average chip weight was 0.68 g. About 4 g of these chips were immersed in a solution made of 50 ml of scale dissolver and 150 ml of distilled water or low-sulfate sea water. Testing conditions included temperatures of 68°C, 85°C and 105°C; salinity of the make up water; and exposure time. At prescribed times, 1 ml aliquots of dissolver solution were removed and diluted to 25 ml.

For IC analyses, samples were diluted again by dilution factors of 2 to 10 using Milli-Q water. For ICAPES, samples were diluted 0.5 ml to 25 ml unless the ion of interest equaled or exceeded 20 mg/l in which case a dilution of 0.25 ml per 50 ml was used. Scandium internal standard was added to all ICAPES samples to match standards and achieve a final concentration of 7.5 ppm.

2.4. Procedure

The gradient IC conditions are listed in Table 1.

3. Results and discussion

3.1. Calibration data

The cation standards for IC were calibrated using a four-point calibration for each ion. The graph was extended through the origin although the chromatogram was not run. The calibration data in Table 2 illustrate good correlation coefficients. Fig. 1 is a chromatogram of one of these standards and shows excellent separation of sodium, potassium, magnesium, calcium, strontium and barium.

The cation standards for ICAPES were calibrated using a two-point linear calibration. A Milli-Q water sample with scandium internal standard was used as a zero calibration point and a 20 ppm standard with scandium internal standard was the other point.

3.2. Comparison of ICAP and IC

A typical IC chromatogram is shown in Fig. 2. This chromatogram for dissolver D shows that

Table 1
Gradient IC conditions

Gradient program				
Time (min)	Flow-rate (ml/min)	Eluent 1	Eluent 2	Comment
0.0	1.0	100	0	Equilibrate
6.1	1.0	100	0	Load
7.0	1.0	100	0	Inject
17.0	1.0	100	0	
17.1	1.0	0	100	Eluent step change
27.0	1.0	0	100	Stop run

Eluent 1	16 mM methanesulfonic acid
Eluent 2	40 mM methanesulfonic acid
Columns	Cation Trap Column, Dionex IonPac CG12 column and Dionex IonPac CS12 column
Suppressor	Dionex Cation Self-Regenerating Suppressor CSRS (4 mm)
Mode	Recycle mode at a current setting of 3
Injection	25 μl
Detection	Conductivity
Background	0.5–2.0 μS

Table 2
IC calibration data

No.	Sodium		Potasium		Magnesium	
	mg/l	Peak area	mg/l	Peak area	mg/l	Peak area
1	0.00	0.00000	0.000	0.00000	0.00	0.00000
2	0.50	$3.45120 \cdot 10^7$	0.50	$8.59615 \cdot 10^6$	0.50	$2.23490 \cdot 10^7$
3	4.00	$1.29293 \cdot 10^8$	10.00	$1.62154 \cdot 10^8$	5.00	$2.35742 \cdot 10^8$
4	40.00	$9.08526 \cdot 10^8$	30.00	$4.21985 \cdot 10^8$	15.00	$6.86297 \cdot 10^8$

No.	Calcium		Strontium		Barium	
	mg/l	Peak area	mg/l	Peak area	mg/l	Peak area
1	0.00	0.00000	0.00	0.00000	0.00	0.00000
2	0.50	$1.45991 \cdot 10^7$	0.50	$6.42797 \cdot 10^6$	0.50	$3.82594 \cdot 10^6$
3	10.00	$2.86375 \cdot 10^8$	3.30	$4.30188 \cdot 10^7$	10.00	$8.59984 \cdot 10^7$
4	40.00	$1.11687 \cdot 10^9$	40.00	$5.17327 \cdot 10^8$	40.00	$3.35125 \cdot 10^8$

Quadratic fit correlation coefficients: sodium $R^2 = 1.000$, potassium $R^2 = 1.000$, magnesium $R^2 = 1.000$, calcium $R^2 = 1.000$, strontium $R^2 = 1.000$, barium $R^2 = 1.000$

despite the high concentrations of potassium in the dissolver, the cations of interest (magnesium, calcium, strontium and barium) are detectable.

The data in Table 3 result from the dissolution of scale by dissolver C at 85°C. The entire experiment was completed in duplicate. The three ions of most interest (calcium, strontium and barium) were run by IC and ICAPES techniques from the same sample vial for comparison purposes. Thus, there are two sets of analytical results for each sampling time representing separate but parallel experiments rather than duplicate sampling of one experiment. In both IC and ICAPES, there is a matrix false zero for

calcium and barium and both techniques show good duplication for blank samples. IC reads true zero for strontium.

3.3. Scale dissolver study results

Table 4 shows IC data for dissolved cations over time for Dissolver D. This data confirms that sodium, magnesium, calcium and strontium are not contained in the Dolly Varden scale in appreciable levels. Significant barium dissolution is achieved for the Dolly Varden Scale.

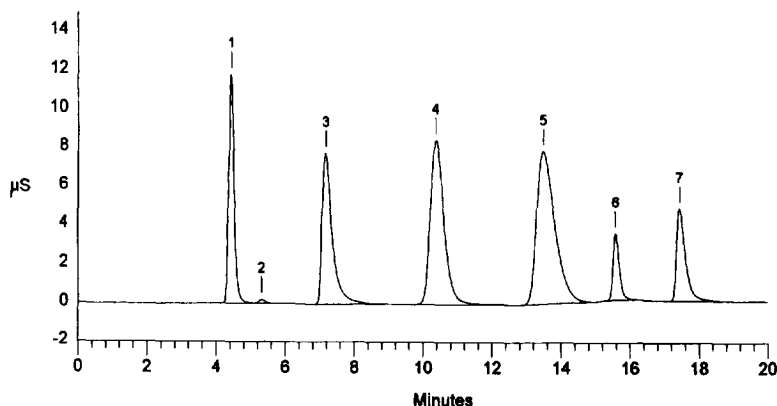Table 5 shows that the five scale dissolvers

Fig. 1. IC cation standard. Peaks: 1=sodium, 4.0 mg/l; 2=unidentified; 3=potassium, 10 mg/l; 4=magnesium, 5.0 mg/l; 5=calcium, 10.0 mg/l; 6=strontium, 3.3 mg/l; 7=barium, 10.0 mg/l.
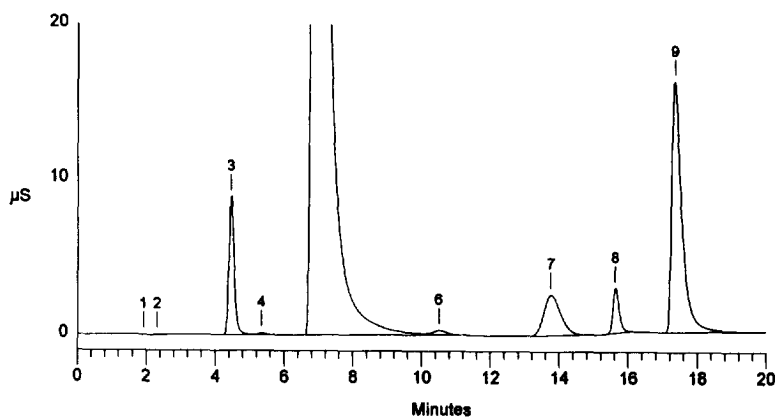
Fig. 2. Scale dissolver D. Peaks: 1, 2=unidentified; 3=sodium, 28.4 mg/l; 4=unidentified; 5=potassium (off scale); 6=magnesium, 1.71 mg/l; 7=calcium, 31.1 mg/l; 8=strontium, 28.1 mg/l; 9=barium, 397 mg/l. The dilution factor of 10 has been applied.

Table 3
IC and ICAPES data

Time (h)	IC data			ICAPES data		
	Calcium (mg/l)	Strontium (mg/l)	Barium (mg/l)	Calcium (mg/l)	Strontium (mg/l)	Barium (mg/l)
0 (Blank)	0.38	0	0.17	1.55	0.40	0.50
0 (Blank)	0.38	0	0.17	1.55	0.40	0.50
1.5	1.27	0.97	11.1	1.91	0.71	11.9
1.5	1.16	0.93	10.3	2.99	0.35	10.0
3.0	1.64	3.10	32.8	2.55	1.88	33.3
3.0	1.37	1.34	22.0	2.70	1.13	23.2
6.0	1.73	4.56	57.0	5.53	3.71	56.2
6.0	1.75	4.08	48.8	3.87	3.05	48.2
24.0	1.90	6.04	82.1	3.26	4.88	78.1
24.0	1.99	5.97	83.4	4.27	4.46	79.5

Table 4
IC data for dissolved cations over time

Time (h)	Dissolver D at 85°C				
	Sodium (mg/l)	Magnesium (mg/l)	Calcium (mg/l)	Strontium (mg/l)	Barium (mg/l)
0	14.0	0.88	0.81	0.23	0.71
3	16.1	1.03	7.99	9.25	142
7.25	16.3	0.61	11.0	18.6	275
24	15.4	0.72	11.7	25.0	360
31.25	15.6	1.47	12.3	26.1	369
48.25	15.5	0.77	11.9	27.5	390
55.0	17.5	1.05	12.3	28.3	394
55.0	15.9	1.86	11.6	28.9	392

Table 5
Comparison of scale dissolver performance at 85°C

Time (h)	Barium concentrations (mg/l) by IC				
	Dissolver A	Dissolver B	Dissolver C	Dissolver D	Dissolver E
0	0	4	10	18	0
3	3450	2210	2925	3350	2525
7.25	5575	4225	4850	6875	4625
24	7975	7150	7775	9000	7725
31.25	7525	7425	8850	9225	7875
48.25	8175	7925	9050	9750	8575
55.0	8263	8325	8425	9825	8238

exhibited a similar style of barium dissolution. The initial rate of dissolution was rapid, but as the available sequestrant was exhausted, the rate of further dissolution was retarded. All dissolvers approached a similar calculated maximum dissolution level. Dissolver D was chosen as the most efficient product due to its more rapid, early rate. Even dissolver B would have become saturated if the duration of the experiment had been longer than 56 h. Dissolver D had dissolved its full capacity of scale in less than 24 h.

Temperature was shown to have a profound effect on dissolver performance in Table 6. The rate of dissolution increased substantially with increasing temperature. Raising the system temperature from 68°C to 85°C produced a three-fold increase in the rate of dissolution. Lowering the test temperature to 50°C resulted in the dissolver being incompletely saturated at the termination of the experiment.

When the dissolver was diluted in LSSW instead

of distilled water, there was a reduction in its rate of dissolution and ultimate capacity (Table 7).

Agitation of the dissolver was found to improve dissolver performance, but this was not quantified by the scientist due to difficulties measuring and reproducing dissolver flow-rate past stationary scale pieces.

4. Conclusions

Closely matched results would not necessarily be expected from parallel experiments, but the IC data generally (there were many such comparisons) showed closer agreement between parallel experiments than the ICAPES data. IC also gave lower false positive data on blank matrix samples. Previous comparative work had shown that ICAPES data on similar matrices would similarly deviate from known data points. Trend and comparative results were desired from this experiment and thus the scientist conducting the work chose IC as the primary ana-

Table 6
Thermal dissolution behavior of dissolver D

Time (h)	Barium concentrations (mg/l) by IC		
	Temperature (°C)		
	50	68	85
0	14.25	9.75	17.75
3	na	na	3550
7.25	2205	3800	6875
24	5525	7725	9000
31.25	6450	8250	9225
48.25	7250	8950	9750
55.0	7550	9150	9825

na=Not available.

Table 7
Effect of diluent on dissolver D

Time (h)	Percent theoretical barium dissolution for IC data (85°C)	
	Distilled water	LSSW
0	0	0
3	40	not available
7.25	78	39
24	102	67
31.25	105	64
48.25	111	86
55.0	111	72

lytical technique. IC can also provide good analytical data for other types of scale besides barium sulfate that may be studied in the future.

The difference in dissolver performance was remarkable. There was a six-fold difference in performance between the best and worst dissolver on this particular scale. Such a difference is likely to result in either success or failure of the treatment dependent upon which dissolver were selected.

In such a high ionic strength environment, it is unlikely for low sulfate sea water to cause a noticeable salinity effect. Sodium exchange with the sequestrant counter ions is known to affect the solubility of barium sequestrant complexes. However, the presence of calcium and magnesium in the low sulfate sea water is also likely to complex with, and thus remove, active dissolver prior to the experiment. This would explain the slight (<10%) reduction in ultimate capacity of the dissolver due to a change of diluent. The difference in capacity would approximate the 8% removal of sequestrant by LSSW divalent cations, assuming a 25% solution of a 1 M sequestrant dissolver.

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