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Article

Detection of Naphthalene Sulfonates from Highly Saline Brines with High-Performance Liquid Chromatography in Conjunction with Fluorescence Detection and Solid-Phase Extraction

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A procedure is developed for the simultaneous determination of 1-naphthalene sulfonate, 2-naphthalene sulfonate, 1,5-naphthalene disulfonate, 1,6-naphthalene disulfonate, 2,6-naphthalene disulfonate and 2,7-naphthalene disulfonate from highly saline geothermal brines using ion-pair high-performance liquid chromatography with fluorescence detection after solid-phase extraction. The substances are baseline separated within 33 min and recoveries in brines with salinities of up to 175 g/L NaCl are 100% (± 10) by solid-phase extraction. For the overall method, the method quantification limits of the analytes are between 0.05 and 0.4 μg/L. The method is also shown to be feasible for matrices encountered in deep geothermal reservoirs.

Introduction

Naphthalene sulfonates (NS) are highly water-soluble compounds that have a pK_{OW} of <2, indicating a high mobility in aquatic systems (1). Furthermore, NS show fluorescence and are therefore easily detected at low concentrations. Due to these qualities, along with temperature stability up to at least 250°C and under reducing conditions (3, 4), NS are being established as tracers for flow and transport in deep geothermal reservoirs (3–6). NS are also important substances in the chemical industry, being included in the *List of High Production Volume Chemicals* of the Organisation for Economic Cooperation and Development (OECD) (7). They are primarily used as tanning agents and as intermediates in the production of azo-dyes and pharmaceuticals. Some NS have a low biodegradability and are therefore not removed in wastewater treatment plants, and little is known about their toxicity (8). Therefore, detection and investigation of these substances has been occurring for many years.

Most of the analytical techniques for the detection of these substances are based on high-performance liquid chromatography (HPLC), which uses an ion-pairing agent to achieve a sufficient retardation and separation of the analytes on the column (9–14). References for optimization of ion-pair chromatography are given by Rudzinski *et al.* (15). Anion-exchange chromatography methods have also been developed (16). Capillary electrophoresis methods have also been investigated, showing a sufficient separation by using different additives to neutralize the analytes (17). Unfortunately, the detection limits of capillary electrophoresis were only in the low to sub-mg/L range combined with pre-separation enrichment (18). Gas chromatographic methods have also been developed, but are not often used because of the difficulties encountered in the derivatization of the NS compounds (19).

For matrix separation and concentration of NS, solid-phase extraction (SPE) methods are common. Most researchers have used conventional reversed-phase solid phases in combination with ion-pairing agents (11, 13). Anion-exchange, polymeric and organic carbon solid phases have also been investigated (10–12). A summary of the analytical methods for NS that were published before 1995 has been given by Reemtsma (20). However, existing analytical methods for the simultaneous analysis of NS isomers are limited to river, coastal and bank filtrate waters (2, 12, 13), or industrial wastewaters (9–11).

Depending on the application, the analyte and the matrix, most researchers in this field have been able to achieve detection limits in the low to sub-μg/L range (2, 3, 9–14). However, the trace-level detection of NS using SPE has not yet been described for geothermal brines that have salinities up to 150 g/L total dissolved solids (TDS) and potentially high amounts of organic compounds from previously used fracking gels or additives to the drilling fluid.

Experimental

Reagents

Napthalene-1-sulfonic acid sodium salt (>95%, 1-NS), naphthalene-2-sulfonic acid sodium salt (>98%, 2-NS), 1,5-naphthalene disulfonic acid disodium salt (1, 5-NDS), 1,6-naphthalene disulfonic acid disodium salt (>98%, 1,6-NDS), 2,6-naphthalene disulfonic acid disodium salt (>95%, 2,6-NDS), 2,7-naphthalene disulfonic acid disodium salt (2, 7-NDS) and the internal standard 2-naphthol-3,6-disulfonic acid sodium salt (>70%, 2-OH-3,6 NDS) were obtained from TCI Europe (Zwijndrecht, Belgium). Tetrabutyl ammonium bromide (TBAB; HPLC grade), cetyltrimethyl ammonium bromide (CTMAB; 99 +), methanol (HPLC fluorescence grade), disodium sulphate (pA), disodium hydrogen phosphate (analytical reagent grade), potassium dihydrogen phosphate (analytical reagent grade), sodium chloride (99.5%) and hydrochloric acid (37%, Suprapur) were received from Fischer Scientific GmbH (Schwerte, Germany). Ultrapure water was obtained from a combined water purification system consisting of Elix 5 (Progard 1 silver cartridge) and Milli-Q Gradient A10 (Quantum Ex Ultrapure Organex + Q-Gard 1 cartridge), both from Millipore (Schwalbach, Germany).

Apparatus and procedure

The chromatographic experiments were performed with a Varian (Palo Alto, CA) Prostar HPLC system. The system

included a Prostar 363 fluorescence detector, a Prostar 325 UV-visible detector, two Prostar 210 high-pressure pumps, a Prostar 410 autosampler with a column thermostat and a vacuum solvent degassing unit. The separation columns were an ODS-AQ from YMC Europe (Dinslaken, Germany) with guard-column, a Luna C18(2) from Phenomenex (Torrance, CA), a Luna PFP(2) from Phenomenex and a Varian Pursuit XR-s C18 column, all with 150 × 2 mm I.D. and 3 μm particle diameter. The columns were set with the aid of a thermostat at 35°C and sample volumes of 25 μL were injected. The flow rate was 0.25 mL/min. The final chromatographic conditions were as follows: eluent A was 100% water and eluent B was water–methanol (50:50, *v*/*v*) and both consisted of 5 mM TBAB, 4 g/L disodium sulphate and 40 μL/L 37% hydrochloric acid. The starting conditions were 45% eluent B up to 3 min. Then, a linear gradient to 55% eluent B at 14 min was performed to elute the disulfonates. Afterwards, eluent B was increased to 75% at 18 min. Then, eluent B was kept constant up to 27 min to elute the monosulfonates. To equilibrate the system, eluent B was reduced to 55% within 30 s and then kept constant up to 33 min.

To achieve the lowest detection limit possible, the fluorescence maxima of the NS were determined using a Cary Eclipse 50 fluorescence spectrometer from Varian.

For SPE, two different kinds of polymer based solid-phase materials and one C18-packing were investigated. Respectively, these were: Strata X-RP from Phenomenex, Bond Elut Plexa from Varian and Bakerbond Octadecyl Silica from Mallinckrodt Baker (Phillipsburgh, NJ). All columns had 500 mg sorbent material and a reservoir for 6 mL of sample volume. The extracting procedure was as follows: conditioning the sorbent with 10 mL of methanol, conditioning the sorbent with 10 mL of pure water and afterwards conditioning the sorbent with 10 mL of conditioning solution. The conditioning solution consisted of 2.5 mL of 100 mM TBAB solution, 2.5 mL of 100 mM potassium dihydrogen phosphate solution and 2.5 mL of 65 mM disodium hydrogen phosphate solution added to 50 mL pure water, resulting in a pH of 6.1. The same amounts of buffer and ion-pair solutions were added to 50 mL of sample before the extraction of the analytes. After the extraction, the sorbent was washed with 10 mL of conditioning solution, the cartridges were dried and later the analytes were eluted using 4 mL methanol. During the extraction, washing and eluting procedures, the maximum flow rates were kept below 2 mL/min, and during the conditioning, the flow rates were kept below 5 mL/min. After the elution, the methanol was evaporated from the extract in a nitrogen steam at 60°C until completely dry. Afterwards, the samples were dissolved in 4 mL of pure water.

The major anion analyses were conducted on a DIONEX 500 using electrochemically suppressed conductivity detection. For separation, an AS11-HC column was used with potassium hydroxide as the eluent. Cations were analyzed on a DIONEX 320 using electrochemically suppressed conductivity detection. The separation was conducted on a CS16 column, using methane sulfonic acid as the eluent.

Calibration and validation

The linear range of the method was estimated using a 10-point calibration curve with an analyte-concentration ranging from 0.025 to 2.5 μg/L. The uppermost concentration was stated as the standard with the highest concentration within the 95% confidence interval of the calibration curve. For all analytes, the upper limit in the linear range was restricted by the measurement limit of the fluorescence detector, resulting in peak area cutoff. Using these concentrations, at least seven points were in the 95% confidence interval for every analyte.

The calculation of the method quantification limits (MQL) and method detection limits (MDL) for the overall method were calculated with the MS-Excel Macro ValiData Version 3.02 (Roher-Wegscheider-Neuböck, Leoben, Austria), according to the standard DIN 32645. An 11-point linear regression line ranging from 0.025 to 0.5 μg/L with a confidence interval of 95% was used. The uppermost and lowermost concentrations were extracted threefold and the concentration levels in between were extracted twice. All samples were injected and measured once.

Results and Discussion

All NS show a strong fluorescence at a very similar wavelength, with the exception of the internal standard 2-OH-3,6 NDS

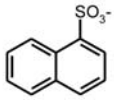
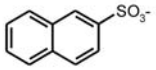
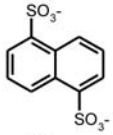
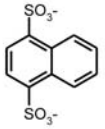
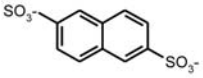
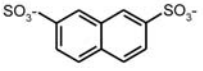
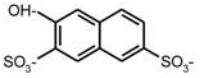
Compound	Chemical structure	Excitation / Emission max. [nm]
1- Naphthalene monosulfonate		222/332
2- Naphthalene monosulfonate		224/337
1,5-Naphthalene disulfonate		224/333
1,6-Naphthalene disulfonate		229/340
2,6-Naphthalene disulfonate		230/345
2,7-Naphthalene disulfonate		229/340
2-Naphthol-3,6-disulfonate		235/470

Figure 1. Structures and fluorescence excitation and emission maximum for 1-NMS, 2-NMS, 1,5-NDS, 1,6-NDS, 2,6-NDS, 2,7-NDS and 2-OH-3,6-NDS.

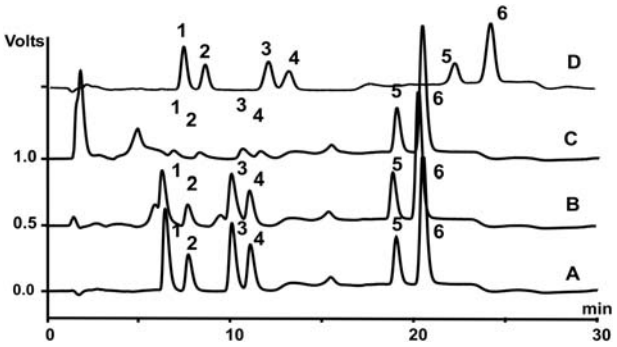


Figure 2. Chromatogram of a 10 mg/L mix-standard consisting of 2,6-NDS (peak 1), 1,5-NDS (peak 2), 2,7-NDS (peak 3), 1,6-NDS (peak 4), 1-NMS (peak 5) and 2-NMS (peak 6) in pure water (A), 10 g/L NaCl (B), and 100 g/L NaCl (C) using a Phenomenex Luna C18(2) column and direct injection. A chromatogram of a 0.4 mg/L mix-standard, consisting of the same analytes after SPE in 100 g/L NaCl, using a YMC ODS-AQ column is given in chromatogram (D).

(Figure 1). The measured values are nearly the same as those found by Rose *et al.* (3). Therefore, a mean wavelength maximum of 225 in excitation and 338 in emission was chosen to detect all analytes. To further improve detection limits for selected analytes, the wavelengths can be adjusted for each analyte according to the data provided in Figure 1. The difference in emission wavelength of the internal standard and the analytes are >100 nm. Therefore, no spectral cross interference was found between analytes and the internal standard.

With the method described previously, all analytes can be sufficiently separated. With the exception of 1,6-NDS and 2,7-NDS, the resolution factor (Rs) always exceeds 1.5, indicating a baseline separation. The Rs of 1,6-NDS and 2,7-NDS is 1.32. A chromatogram is given in Figure 2. Furthermore, one may observe that the separation is strongly affected by the salinity of the injected sample. By increasing the salinity of the sample to 10 g/L NaCl, the peak broadening of the naphthalene disulfonates becomes significant and separation efficiency decreases. At a salinity of 100 g/L NaCl, significant concentrations of the disulfonates show no retention on the column. For the naphthalene monosulfonates, no correlation between change in retention time and high salinity in the sample can be found (Figure 2). This phenomenon can be attributed to the possibility of the monosulfonates undergoing additional hydrophobic interactions with the stationary phase.

Previous experiments using a phosphate buffer and tetrabutyl ammonium bromide or hydroxide, as used by other authors (2–3, 9–13), has also provided a successful baseline separation of all analytes. However, in this case, an increasing backpressure of the HPLC column resulted within approximately 50 h, indicating a plugging of the column with precipitating phosphate salts. The same issue has been reported by Rose *et al.* (3). Experiments without phosphate or any additives apart from the ion-pairing agent and acid, to avoid a plugging of the column, resulted in broader peaks and thus a no longer sufficient separation. It seems that the use of phosphate buffer in the eluent always carries the risk of the formation of phosphate precipitates. To avoid this problem, the suggested method is based on using sulphate as a counter ion, thus increasing the overall robustness of the method. The use of sulphate showed no change in backpressure for at least 500 h under standard operating conditions.

Table I
Recovery of NS on Different Solid Phase Sorbents in Percentages (0.5 μg/L of each analyte added to 50 mL samples)

Solid phase sorbent, matrix	Compound					
	1-NMS	2-NMS	1,5-NDS	1,6-NDS	2,6-NDS	2,7-NDS
Strata X-RP	93	96	94	92	93	91
Strata X-RP, 10 g/L NaCl	93	104	93	93	92	92
Strata X-RP, 100 g/L NaCl	98	106	94	94	93	93
Bakerbond	93	95	94	91	90	89
Bakerbond, 100 g/L NaCl	94	97	30	58	28	53
Bondelut Plexa	96	100	91	93	107	92
Bondelut Plexa, 10 g/L NaCl	94	96	91	90	105	90
Bondelut Plexa, 100 g/L NaCl	93	95	8	17	19	19

Changing the stationary phase of the HPLC column has resulted in no significant effects on the separation of NS isomers, as long as the dimensions of the column and the particle size are identical. Most experiments were conducted with an ODS-AQ from YMC Europe but baseline separation was also possible on a Phenomenex Luna C18(2), a Varian XRs-C18 and a Phenomenex Luna PFP(2), as long as the time scheme of the eluent composition was adjusted.

Experiments with ion-pairing agents other than TBAB have also been conducted. In the case of using ion-pairing agents of lower polarity, lower amounts of the agent are required to achieve a sufficient retardation and separation on the column. In the case of CTMAB, for example, the amounts could be reduced to at least 0.05 mM. This, however, has its limitations. It was found that significant amounts of CTMAB are still present in the eluent after 20 h of flushing the column with methanol and water (50:50, *v*/*v*). By installing the flushed column into a liquid chromatograph–mass spectrometer, significant amounts of CTMAB were semi-quantitatively detected. In this experimental setup, a scan in positive mode was performed ranging from 150 to 400 m/z. Details of the experimental setup, the analytical system and the eluents used are given by Nödler *et al.* (21). This indicates that CTMAB sorbs onto the stationary phase and equilibrium of the ion-pairing agent between the column and the eluent cannot be achieved within a reasonable time span. Therefore, a robust method development with CTMAB would be hindered immediately by this physical difficulty. In this method, TBAB was therefore used as the recommended ion-pairing agent.

The recovery of the respective tested solid-phase materials in the SPE is excellent, approaching nearly 100% in samples without NaCl. By adding 100 g/L NaCl to the samples, recoveries of the naphthalene disulfonates on the Bond Elute Plexa and the Bakerbond Octadecyl sorbent significantly decrease, indicating a breakthrough of these substances. Only the Strata X-RP solid-phase material shows no dependency on NaCl concentration within the sample (Table I). This could possibly be attributed to the additional interaction mechanisms of the Strata X-RP phase such as π-π and dipole interactions, as well as additional hydrophobic interactions. Therefore, this sorbent was used in the method development. To study the effects of NaCl on recoveries of NS onto Strata-X-RP sorbents in detail, a test with increasing salinities of up to 175 g/L was performed. Fifty milliliters of brine with increasing salinities of 25 g/L NaCl were spiked with 0.5 μg/L of each analyte. Within this test, no influences of

Table II
Recoveries of NS in High Salinity Brines with Concentrations between 0 and 175 g/L NaCl and in Reservoir Matrix*

Compound	Mean (μg/L)	RSD (%)	Recovery (%)	Recovery in reservoir matrix (%)
1-NMS	0.53	1.54	95	102.9
2-NMS	0.44	9.00	91	101.4
1,5-NDS	0.46	5.48	92	110.9
1,6-NDS	0.43	4.55	96	112.7
2,6-NDS	0.49	1.49	96	100.1
2,7-NDS	0.48	2.28	92	110.8

*Twenty-five g/L steps, $n = 8$, 0.5 μg/L of each analyte added to 50 mL samples.

Table III
Composition of Brine Taken from the Deep Geothermal Test Site in Bruchsal, Germany*

Anions		Cations	
Compound	Concentration [g/L]	Compound	Concentration [g/L]
Cl^-	73.7	Na^+	39.1
SO_4^{2-}	0.6	K^+	3.3
Br^-	0.3	Mg^{2+}	0.4
		Ca^{2+}	8.0
		Li^+	0.2

*Measurements were conducted by IC.

salinity on the recovery rates can be observed (Table II). The mean recoveries of each analyte, including all salinities, are between 91 and 96%. Also, the use of 20 g/L MgCl2 did not affect the recoveries. The use of SPE has no influence on the chromatograms obtained by HPLC. The chromatograms of spiked samples, including the analyte and inorganic salts after SPE, are nearly the same as chromatograms of standards directly injected to HPLC (Figure 2D). Changes in retention times in this chromatogram are only caused by changing the column from a Phenomenex Luna C18(2) to a YMC ODS-AQ, and a simultaneous variation of the time schedule of the eluent composition.

Finally, the method was tested in an original matrix of a deep geothermal system located in Bruchsal, Germany. Ion-chromatographic measurements show a salinity of over 120 g/L, dominated by Na and Cl (Table III). For this test, 50 mL of sample were spiked with 0.1 μg/L of all analytes and the internal standard. In the analysis, the recoveries of NS are in the range of 100 to 113% (Table II). This shows that the method is feasible for matrices encountered in deep geothermal brines.

The calibration parameters of the overall method, including SPE and HPLC detection, are given in Table IV. For most analytes, the linear range covers a concentration range of nearly two orders of magnitude and is therefore sufficient for standard applications. Also, the MQL of 0.4 μg/L or lower is adequate for most applications. If the detection limit of the method is not sufficient for analysis, the extracting volumes may be increased. This, however, has its limitations. At an extraction volume of 500 mL, the disulfonates show a significant breakthrough on the extraction. The monosulfonates are not at all affected in their recoveries of up to 500 mL (Table V).

Conclusions

A robust method for the simultaneous determination of six NS from highly saline brines was developed. Salinities up to 175 g/L NaCl showed no influence on the recoveries of SPE and the subsequent chromatographic detection. The method was demonstrated to be successfully applicable for the matrices encountered in deep geothermal brines in Northern Europe. By using the SPE method, it is possible to successfully separate the inorganic matrix from the organic ionic analytes. Simultaneously, a preconcentration of the analytes is possible, thus significantly reducing detection limits.

Table IV
Calibration Parameters of the Overall Method, Including SPE and HPLC Detection*

Compound	Linear range (μg/L)	MQL (μg/L)	Absolute MDL (pg)
1-NMS	0.025–1.75	0.05	0.7
2-NMS	0.007–0.75	0.16	2.8
1,5-NDS	0.025–2.00	0.08	4.8
1,6-NDS	0.025–2.00	0.40	10.0
2,6-NDS	0.025–1.50	0.08	1.2
2,7-NDS	0.025–1.75	0.19	3.9

*Method quantification limit and linear range are valid for 50 mL sample extraction, 4 mL re-dissolution and a 25 μL injection of the extract. Details about the calculations are given in the text.

Table V
Mean Recovery and RSD of NS on SPE by Using Different Sample Volumes in 100 g/L NaCl*

Compound	Sample volume (mL)							
	50		100		250		500	
	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]	Recovery [%]	RSD [%]
1-NMS	102	3.9	95	3.3	105	7.9	101	5.2
2-NMS	94	7.9	102	5.7	101	2.4	102	2.6
1,5-NDS	106	3.7	101	2.5	101	2.4	52	13.0
1,6-NDS	106	6.5	100	2.1	93	21.1	46	20.9
2,6-NDS	104	4.5	97	0.9	107	5.5	71	8.5
2,7-NDS	107	3.3	100	3.5	104	8.1	59	8.1

*The samples were spiked with 25 pg absolute of each analyte ($n = 6$).

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