METHODS DEVELOPMENT FOR THE ANALYSIS OF NAPHTHALENE SULFONATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

The use of naphthalene sulfonates as geothermal tracer is a recent development in tracer technology. Naphthalene sulfonates are polyaromatic fluorescent compounds found to be suitable conservative tracers in high temperature reservoirs. They have been proven to be excellent tracers because they are non-toxic, have low level of detection (ppb), absent in the reservoir, detectable by fluorescence spectroscopy, affordable and thermally stable. It has been successfully tested in various fields like the Dixie Valley geothermal system in Nevada, USA and at the PGI MakBan field in the Philippines.

Tracer tests using three naphthasulfonates will be undertaken at the Leyte Geothermal Production Field (LGPF) and Mindanao Geothermal Production Field (MGPF) to study the reservoir flow patterns. Based on the initial method development conducted, three of the di-substituted compounds (2,6-NDS, 1,5-NDS and 1,6-NDS) may be used since results showed good peak separation, fast analysis time, high purity and low cost. In case of unavailability of any one of these compounds, 2,7-NDS may be also be used. Analyses were conducted using Waters C18 reverse phase column (300 x 4.6 mm) and mobile solution consisting of 3.17 mM Na_2HPO_4, 6.21 mM KH_2PO_4, 5.0 mM $C_{16}H_{36}NPO_4$ (TBAP), 25% CH_3OH and 75% H_2O, at flowrate of 1.2 ml/min.

Further method development was conducted using a Merck Chromolith column (30 x 4.6 mm, "chalk-type"). More efficient analysis of the naphthasulfonate compounds was obtained compared to the Waters C18 column. Analysis time was shortened by up to 80%, at a mobile flow rate of 2.5 ml/min. Calibration runs showed acceptable repeatability and linearity (r^2>0.995) for the three compounds. Precision tests indicate acceptable recoveries of standards as samples. Recovery tests on unacidified brine samples showed acceptable recoveries, from 98-104%.

1.0 INTRODUCTION

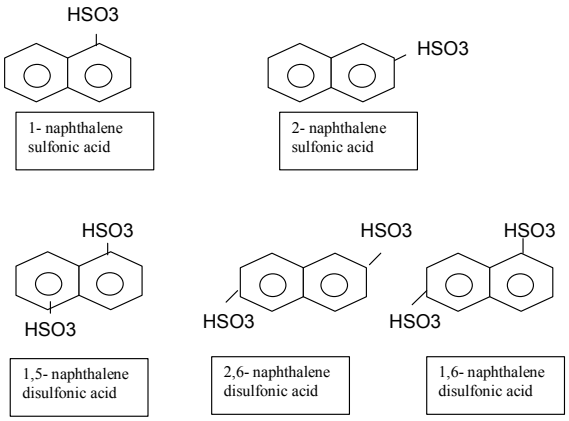
Naphthalene sulfonates are polyaromatic fluorescent compounds found to be suitable conservative tracers in high temperature reservoirs. They have been proven to be excellent tracers because they are non-toxic, have low level of detection (ppb), absent in the reservoir, detectable by fluorescence spectroscopy, affordable and thermally stable. It has been successfully tested in various high temperature geothermal fields like the Dixie Valley geothermal system in Nevada, USA and at the PGI MakBan field in the Philippines (Rose et al., 2002).

Table 1 shows the excitation/emission maxima wavelengths of the naphtha compounds. It is at these wavelengths that maximum fluorescence is obtained.

Table 1. Excitation/emission maxima

Compound	Excitation/ Emission (nm)
2,6-NDS	225 / 342
1,5-NDS	218 / 334
2,7-NDA	226 / 339
1,3,6-NTA	228 / 342
1-NSA	217 / 333
2-NSA	220 / 336

The structures of some of the naphthasulfonate compounds tested in the laboratory are shown below. UV-fluorescence is due to the aromatic bonds. Samples were obtained from Yick-Vic Chemicals, Hongkong. (Rose et al., 2002).



Tracer tests will be undertaken at the LGPF and MGPF fields to study the reservoir flow patterns. Three naphthasulfonate compounds will be needed for injection into test wells, and the choice will depend on the result of this initial method development.

2.0 OBJECTIVES

The objectives of the said activity are:

- To develop and optimize a method for the analysis of naphthalene sulfonates using the Shimadzu LC10Ai HPLC
- To recommend candidate naphthasulfonate compounds for actual field testing based on the accurate and fast separation of test compounds
- To compare the performance of Waters C-18 column and Merck Chromolith column
- To establish analytical precision and conduct brine recovery tests

3.0 METHODOLOGY

3.1 Initialization/optimization of HPLC Operating Parameters Using Waters C-18 Reverse Phase Column

3.1.1 Optimization of HPLC Operating Parameters

The Shimadzu LC10i HPLC of the ERDC Chemistry Laboratory was used for the analysis of naphthasulfonates. Visits and consultation with PGI-MakBan staff (V. Capulong, M. Ramos, A. Peh) were conducted prior to the method development. Some parameters appropriate to our HPLC system were applied, while others were refined to obtain optimum separation and quantitation. Consultations with Peter Rose during his visit to LGPF were also very timely and relevant in the conduct of the method development.

Initially, parameters such as the sensitivity, injection volume and mobile flow rate were experimented with to obtain the optimum settings. Due to time constraints, the recommended excitation/emission wavelength used by P. Rose at EGI for mixed standards were applied. These were the operating parameters obtained and used in the isocratic HPLC analysis of the naphthasulfonate compounds:

Table 2. Shimadzu LC10 operating parameters.

Detector	Shimadzu RF-10XL
Sensitivity	Medium (x32)
Excitation/emission wavelengths	225/333 nm
Analytical Column	Waters C18 reverse phase column 300 x 4.6 mm
Column Temperature	40 ^{o}C
Mobile phase	25% MeOH, 75% water, 3.17 mM Na_2HPO_4, 6.21 mM KH_2PO_4 5.0 mM tetra-butyl ammonium phosphate (TBAP)
Mobile flow rate	1.2 mL/min
Injection volume	50 μL

3.1.2 Single Standard Runs of the Naphtha Compounds

Using the optimized HPLC system, 10 mg/L single standard runs were conducted to obtain the retention time, and ensure sufficient time between peak elution for proper separation.

3.1.3 Mixed Standard/ Calibration Runs

After the single runs, mixed standard runs were conducted to confirm peak separation. Calibration runs using 0.25-2.0 ppb mixed standards were also conducted.

3.2 Further Method Development/Tests Using Merck Chromolith Column

3.2.1 Comparison of Operating Parameters Using Water C-18 Column and Merck Chromolith Column

Some operating parameters were revised to accommodate the use of the Chromolith demo column from Merck in the isocratic HPLC analysis of the naphthasulfonate compounds. Table 3 shows the current settings of the operating parameters.

Table 3. Shimadzu LC10 revised operating parameters.

Parameters	Current Settings
Analytical Column	Merck Chromolith SpeedRod18e, 30 x 4.6mm
Column Temperature	40 ^{o}C
Mobile phase	20% MeOH, 80% water, 3.17 mM Na_2HPO_4, 6.21 mM KH_2PO_4 5.0 mM (TBAP)
Mobile flow rate/ pressure	2.5 mL/min 35 psi
Injection volume	50 μL
Sensitivity	High (x64)
Excitation/emission wavelengths	285/333 nm

3.2.2 Single Standard Runs

10 mg/L single standard runs were conducted to obtain the retention time, and ensure sufficient time between peak elution for proper separation.

3.2.3 Mixed Standard/Calibration Runs

Calibration runs using 0.25-2.0 ppb mixed standards were conducted.

3.2.4 Precision Runs

Repeated injections of standard mixtures were performed to check analytical precision. Standards were analyzed as samples to obtain the recoveries.

3.2.5 Brine Recovery Runs

Recovery of naphthasulfonate compounds in brine samples was conducted to check if matrix effects are encountered.

4.0 RESULTS AND DISCUSSIONS

4.1 Analyses Using Waters C-18 Reversed Phase Column

Seven naphthasulfonate compounds were initially considered for testing, and these are listed in Table 4 below, including the retention times obtained from single standard injections.

Table 4. Single standard runs.

Compound	Retention time (minutes)
2,6-NDS	12.2
1,5-NDS	14.5
2,7-NDS	22.4
1,6-NDS	25.5
1,3,6-NTA	43
1-NSA	64
2-NSA	72

The di-substituted sulfonate compounds showed good well-defined Gaussian elution peaks. Sufficient lag time between peaks was also noted for good separation. The tri- and mono-substituted compounds elute at later times, showing broad peaks, and contaminant peaks (eg. 1-NSA has 2-NSA impurities). These peaks also were not integrated properly due to limitations of the LC-10 software, e.g. peak processing, baseline correction, etc.

Only the di-substituted (2,6-NDS, 1,5-NDS, 2,7-NDA and 1,6-NDS) compounds were considered for the mixed standard calibration runs, since good peak separation and acceptable total run of less than 30 minutes was achieved. Table 5 summarizes the results of the 1 and 10 ppb mixed standard runs for these compounds.

Table 5. Mixed standard runs.

Compound	10 ppb mixed		1 ppb mixed	
	RT (min)	Peak Area	RT (min)	Peak Area
2,6-NDA	12.11	439455	12.11	44663
1,5-NDS	14.80	203520	14.78	27155
2,7-NDA	22.75	398490	22.81	21718
1,6-NDS	25.54	320908	25.49	33681

Expectedly, 2,6-NDA is the most sensitive at the set excitation/emission wavelengths of 225/333 nm since its optimum wavelength is very near the wavelength settings, as seen in Table 1. The least sensitive is 1,5-NDS. Very

good detection can still be achieved even at 1 ppb level.

Calibration standards ranging from 0.25 to 2.00 ppb were performed. Table 6 summarizes the results of these runs.

Table 6. Mixed standard calibration runs.

Conc. (ppb)	Peak Area			
	2,6-NDS	1,5-NDS	2,7-NDS	1,6-NDS
0.25	15074	5464	ND	ND
0.50	17461	6739	13131	3528
1.00	41459	21035	35120	20643
1.50	62569	25437	49999	25648
2.00	83762	43729	72731	88265

For the 0.25 ppb run only 2,6-NDA and 1,5-NDS were detected. Based on EGI and PGI experience, detection limit of 0.30 ppb was obtained. This is also confirmed by the poor recovery of the 0.25 ppb run. Good runs were obtained for the 0.50 to 2.00 ppb runs. Acceptable linearity, however, has not been established since runs were not duplicated due to time constraints.

Table 7 below summarizes the commercial properties of the naphthasulfonates from Yick-vic Chemicals. Most compounds have acceptable % purities of >90%, except 1,3,6-NTA and 1-NSA. In terms of purity and cost, the di-substituted components show good acceptability for testing.

Table 7. Commercial properties of the naphthasulfonate compounds.

Component	Assay	Impurity
2,6-NDS	99.2%	2,7-NDS (0.71%)
1,5-NDS	96.8%	
2,7-NDS	93.0%	2,6-NDS (1.62%)
1,6-NDS	99.8%	
1,3,6-NTA	86.5%	
1-NSA	75.0%	2-NSA (24%)
2-NSA	99.7%	

It was then recommended that three of the di-substituted compounds (2,6-NDS, 1,5-NDS and 1,6-NDS) be used for initial injection due to good peak separation, fast analysis time, high purity and low cost. In case of unavailability of any one of these compounds, 2,7-NDS may be also be used.

4.2 Analyses Using Merck Chromolith Column

The Merck Chromolith column is a very short "chalk type" column, densely packed with macropores to allow rapid transit of the mobile phase and mesopores to create a large surface area ensuring efficient and rapid separations, with very low pressures. The mobile phase flow rate using the Waters C18 column was 1.2ml/min, with pressure of up to 200 psi. However, in using the Chromolith column, 2.5ml/min flow has pressure of only 35 psi. Hence, faster analysis time and more efficient separation is expected. The excitation/emission wavelengths were set at 285/333 nm, as more stable baseline is observed in this setting. The sensitivity was also increased to attenuate the naphthasulfonate peaks.

To confirm the retention time and ensure sufficient time between peak elution, 10 mg/L single standard runs of the three recommended naphthasulfonate compounds were conducted. Table 8 compares the results between the Chromolith column and the Waters C18 column.

Table 8. 10 ppb Single standard runs.

Compound	Retention time (mins)	
	C18 Column	Chromolith
2,6-NDS	12.2	2.29
1,5-NDS	14.5	2.65
1,6-NDS	25.5	5.05

The relative elution times of the naphthasulfonate compounds are similar for both columns. However, it can be noted that using the Merck Chromolith column has shortened the analysis time by up to 80% as compared to using the C18 column. The use of lower polarity mobile phase (20% MeOH) was also applied to improve separation between 2,6-NDA and 1,5-NDS, since overlapping of these two peaks were observed when using the 25% MeOH mobile phase.

Figure 1 show sample chromatograms of runs using the Waters C-18 column and the Merck Chromolith Column.

Calibration runs using 0.25-5.0 ppb mixed standards were conducted. Several calibration runs were made to confirm repeatability and linearity of standard concentrations. Figure 2 shows a graph of one of the calibration runs

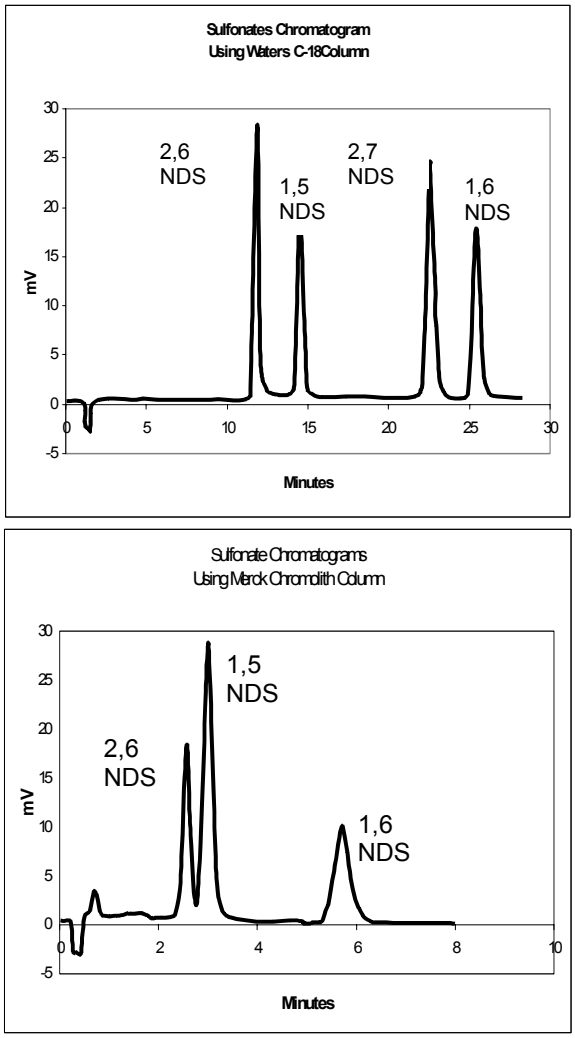


Figure 1. Napthasulfonate chromatograms

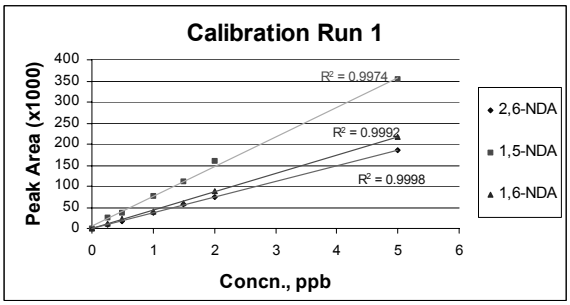


Figure 2. Calibration run of the di-sulfonates.

showing the trend lines and the R^2 value of each series. As can be seen, the standard series of 0.25-5.0 ppb shows good linearity as indicated by their high R^2 values, generally >0.995.

To check the performance of the instrument and column, we performed duplicate injections of each standard mixture. We also analyzed each standard as sample to compare the analyzed values to the theoretical concentration. Table 9 shows the results.

Table 9. Precision and recovery runs for the standards.

Conc. ppb	2,6-NDS		1,5-NDS		1,6-NDS	
0.25	0.28 *(109)*		0.19 *(76)*		0.32 *(128)*	
1.00	0.96 *(95.5)*		0.94 *(94.5)*		0.70 *(69)*	
1.50	1.58 *(105)*	1.61 *(107) (COV 1.3%)*	1.50 *(98.3)*	1.61 *(107) (COV 6.1%)*	1.38 *(91.7)*	1.43 *(95.1) (COV 2.6%)*
2.00	2.02 *(101)*	2.00 *(99.9) (COV 1.0%)*	1.93 *(96.4)*	1.98 *(98.9) (COV 1.8%)*	1.93 *(96.5)*	2.13 *(106) (COV 7.0%)*
5.00	4.61 *(92.2)*	4.99 *(99.8) (COV 5.5%)*	4.80 *(96)*	5.12 *(102) (COV 4.4%)*	4.03 *(81)*	4.84 *(97) (COV 12.8%)*

Generally good recoveries were obtained for 2,6 NDS and 1,5 NDS standards > 0.50 ppb. Relatively poor recoveries of the 1,6-NDS may be due to improper peak integration due to broadening of the peak, as it is the latest compound to elute. Duplicate analysis showed good agreement between runs with COV for the first 2 peaks ranging from 1.0% - 6.1%. Again relatively poorer precision was obtained for 1,6 NDS, although at this concentration level, this variation is still acceptable.

Recovery tests were done by adding a spike of 2.5 ppb standard to both acidified and unacidified brine samples from MG-16. Below is the table of the results for the recovery test.

Acceptable recoveries, ranging from 98-104%, were obtained using the unacidifed brine sample. Interference from the N=O in HNO_3 acid used may attribute for the poor recovery in acidified samples.

Table 10. Recovery tests in brine.

Compound Name	Acidified Brine Sample		Unacidified Brine Sample	
	Concn., ppb	% Recovery	Concn., ppb	% Recovery
2,6-NDS	3.36	134.53	2.55	102.88
1,5-NDS	2.72	108.81	2.59	103.70
1,6-NDS	2.92	116.89	2.46	98.60

5.0 CONCLUSIONS AND RECOMMENDATIONS

Based on the method development and testing conducted on the naphthasulfonate compounds, the following are our conclusions and recommendations:

- Calibration runs using mixed di-sulfonates standards showed good runs from 0.50-2.00 ppb. For the 0.25 ppb standard run, only 2,6-NDS and 1,5-NDS were detected.

- It is recommended that three of the di-substituted compounds (2,6-NDS, 1,5-NDS and 1,6-NDS) be used for initial injection due to good peak separation, fast analysis time, high purity and low cost. In case of unavailability of any one of these compounds, 2,7-NDS may be also be used.

- More efficient analysis of the naphthasulfonate compounds was obtained using the Merck Chromolith column (30 x 4.6 mm, "chalk-type) as compared to the Waters C18 (300 x 4.6mm) column. Analysis time was shortened by up to 80%, at a mobile flow rate of 2.5 ml/min.

- Calibration runs showed acceptable repeatability and good linearity (r^2>0.995) for the three compounds.

- Precision tests indicate acceptable recoveries of standards as samples.

- Recovery tests on brine samples showed acceptable recoveries of the compounds, ranging from 98-104% in unacidified brine samples.

- The HPLC system has been optimized and is ready for analysis during tracer injection.

REFERENCES

Capulong, V., Peh, A. (pers. comm.). PGI MakBan

Lu, C.A., Gonda, R., and Magdadaro, M. (2002). Method development for the analysis of naphthasulfonates by high pressure liquid chromatography. PNOC-EDC internal report.

Merck Chromolith Column Product Brochures.

Rose, P.E, Capulong, V., Peh, A., Kilbourn, P. and Kasteler, C. (2002). The use of the naphthalene sulfonates as tracers in high temperature geothermal system. *Proceeding of the 27th Annual PNOC-EDC Geothermal Conference.*

Shimadzu LC-10 HPLC Operations Manuals.