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THE USE OF THE NAPHTHALENE SULFONATES AS TRACERS IN HIGH TEMPERATURE GEOTHERMAL SYSTEMS

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ABSTRACT

*Thermally stable, water-soluble tracers am required in order to test the flow patterns between injection and production wells in high-temperature two-phase **geothermal** systems such as **Bulalo,** where reservoir fluids can exceed 300°C. A detailed analytical method for the simultaneous analysis of six thermally stable naphthalene sulfonate tracers by High Performance Liquid Chromatography is presented. In previous studies summarized in this paper, four of the tracers exhibited no thermal decay after exposure for one week at **330°C,** indicating that they can be used in liquid-dominated geothermal systems having temperatures exceeding 330°C. In a tracer test at the Bulalo geothermal field in Luzon, Philippines, two laboratories independently confirmed tracer **returns** from an injector on the periphery of the field to producers near its center.*

1.0 INTRODUCTION

The uv-fluorescent polyaromatic sulfonates have proven to be excellent tracers in high temperature geothermal reservoirs because they are environmentally benign, very detectable by fluorescence spectroscopy, affordable, and thermally stable. The first successful use of the polyaromatic sulfonates as geothermal tracers involved 1,3,6,8-pyrene tetrasulfonate at the Dixie Valley geothermal system in west central Nevada, USA (Rose et al., 1998).

The naphthalene sulfonates, a subset of the polyaromatic sulfonates, have been used extensively as tanning agents, cement dispersants, and intermediates in the synthesis of dyes. Studies on surfactant toxicity indicate that the naphthalene sulfonates are neither carcinogenic nor mutagenic (Greim et al., 1994). We have studied six naphthalene sulfonates (Figure 1) in the laboratory and have found them to be suitable for use as conservative tracers in high temperature (>300°C) reservoirs (Rose et al., 2001, Rose et al., 2002). Field tests in a number of geothermal reservoirs with temperatures up to 250°C further confirm the long-term stability of these chemicals (Rose et al., 2001, Rose et al., 2002). The excitation and emission peak maxima for each compound are listed in column 3, indicating that all fluoresce in the ultraviolet.

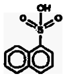
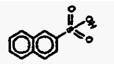
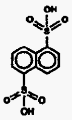
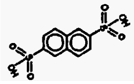
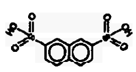
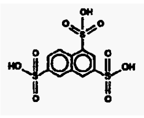
Compound	Structure	Excitation / Emission (nm)
1-naphthalene sulfonic acid		*217 / 333*
2-naphthalene sulfonic acid		***220 / 336***
1,5-naphthalene disulfonic acid		***218 / 334***
***2,6-naphthalene** disulfonic acid*		***225 / 342***
***2,7-naphthalene** disulfonic acid*		*226 / 339*
1,3,6-naphthalene trisulfonic acid		***228 / 342***

Figure 1. Chemical names, structures, and excitation and emission band maxima of six naphthalene sulfonate geothermal tracers studied in the laboratory and in the field.

In this paper we summarize data on the thermal stability of naphthalene sulfonates, and provide details of their analysis in the laboratory. We then present some results of a tracer test at the Bulalo geothennal field that further confirms the utility of these chemicals in high-temperature reservoirs. We present validation of the analybcal methods used through interlaboratory comparison. Unocal patented the use of naphthalene sulfonates to trace movement of reservoir fluids in multiple injection wells in the U.S. in 1993 (Hutchins and Saunders, 1992).

2.0 HPLC ANALYSIS OF THE NAPHTHALENE SULFONATES

The naphthalene sulfonates were analyzed using High Performance Liquid Chromatography (HPLC) with fluorescence detection (Waters Corporation, Milford, MA). HPLC allows for the separation of the polyaromatic sulfonates not only from each other but also from interferences that occur naturally in the reservoir. Using HPLC, any number of polyaromatic sulfonate tracers can, in principle, be analyzed in each other's presence.

In HPLC, high resolution means that compounds can be efficiently separated from each other. In order to take advantage of the high-resolution capability of a reversephase C-18 column (e.g., 50 mm x 4.6 mm Keystone BetaBasic-18, 3 µm), paired-ion chromatography (PIC) was employed. Using PIC reagents in the mobile phase, the very anionic polyaromatic sulfonates are 'paired' in solution with polar cations, or, in our case, tetrabutyl ammonium phosphates. The pairing of negatively charged compounds with positively charged compounds creates neutral, nonpolar compounds with pendant n-butyl chains. Those alkyl chains then are free to interact with the stationary C-18 chains as they flow through the column. It is the interaction of the paired nonpolar n-butyl chains with the stationary nonpolar C-18 stationary phase that allows for the separation of the polyaromatic sulfonates one from another.

The mobile phase consisted of a phosphate-buffered solution of tetrabutyl ammonium phosphate (TBAP) in various proportions of methanol. The higher the proportion of methanol in the mobile phase, the faster the neutral ion-pairs elute from the column. Through trial and error, the proportion of methanol to water can be optimized to allow for the efficient separation and subsequent simultaneous analysis of several polyaromatic sulfonate tracers.

The excitation and emission peak maxima are shown in Figure 1. These are the detector settings required for the greatest sensitivity for each compound. If the detector cannot be programmed for each analyte's wavelength pair individually, then it is possible to obtain reasonable sensitivity in the simultaneous analysis of all six naphthalene sulfonates by using an excitation setting of 222 nm and an emission setting of 338 nm. Obviously, the compounds 1,3,6-naphthalene trisulfonate, which has an excitation peak maximum at 228 nm, and I-naphthalene sulfonate, which has an excitation peak maximum at 217 nm, are the two compounds whose sensitivity would be most effected. For maximum sensitivity, each compound can be analyzed separately, using the appropriate wavelengths for each.

In order to protect the column, all samples should be filtered. We have found that a 0.45-micron Whatman cellulose nitrate membrane filter is adequate for most brines. Columns occasionally deteriorate, regardless of sample and mobile phase filtering. As a means of prolonging column life, we recommend a thorough rinse after analyzing a set of samples and before shutting down the pump. The composition of the rinsate should resemble that of the mobile phase without salts (e.g., 25% meOH and 75% water). In most cases, a rinse time of approximately 45 min is adequate. If, over time, peak shapes deteriorate and backpressure increases, it may mean that the column is partiilly plugged. It may be possible to clean the column by back flushing a 95% methanol/5% water mix at 55°C at a high flow rate, followed by a 5% methanol/95% water mix, also at 55°C and a high flow rate. Large changes in mobile phase composition should always be made gradually.

With isocratic liquid chromatography, the composition of the mobile phase remains constant throughout each chromatographic analysis. With gradient liquid chromatography, however, the composition of the mobile phase is varied during the run, allowing for an optimization of the mobile phase composition over time.

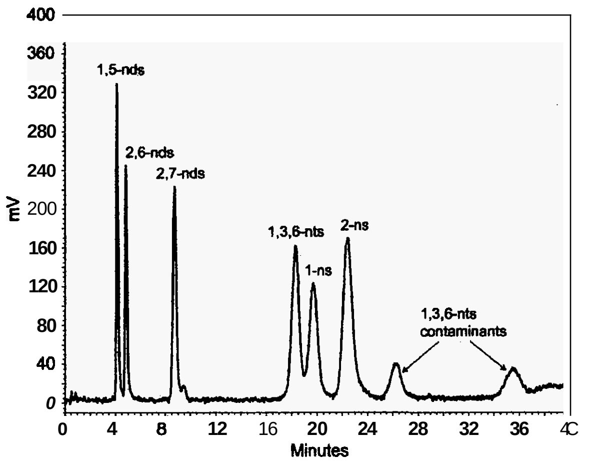


Figure 2. Chromatogram of six naphthalene sulfonate analytes obtained using an isocratic mobile phase.

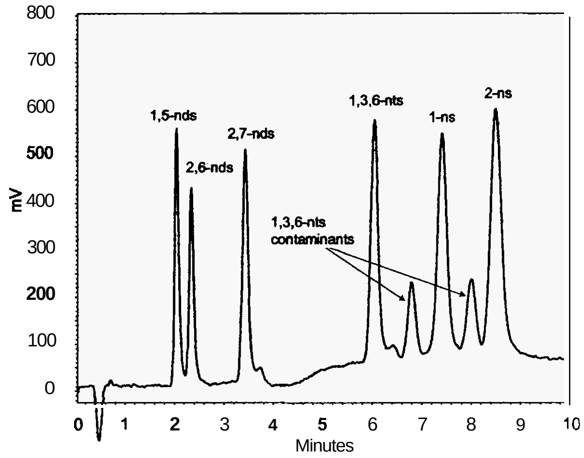


Figure 3. Chromatogram of six naphthalene sulfonate analytes obtained using a gradient mobile phase.

The six naphthalene sulfonates shown in Figure 1 can be separated isocratically using a 50-mm reverse phase C-18 column as described above in combination with an appropriate guard column. Figure 2 shows an isocratic chromatogram of the six analytes with a mobile phase consisting of 20% HPLC-grade methanol and 80% HPLC-grade water. The injection volume was 200 microliters and the flow rate of the mobile phase was maintained at 2.5 ml/min. The concentrations of Na_2HPO_4 and KH_2PO_4 in the mobile phase were 3.17 mM and 6.21 mM respectively and the concentration of the TBAP ion-pairing agent was 5.0 mM. Using these concentrations of salts, the pH of the mobile phase was about 6. The mobile phase was filtered through a 0.45-micron nylon filter. The column temperature was constant at 35°C. The column backpressure was approximately 2800 psi.

The long run time *shown* in Figure 2 was required, since the 1,3,6-naphthalene trisulfonate contained fluorescent contaminants (possibly isomers of 1,3,6-naphthalene trisulfonate) that had to be eluted before a subsequent injection. An even longer run time would be required to obtain baseline separation between 1,3,6-naphthalene trisulfonate and 1-naphthalene sulfonate. Such long run times require large volumes of mobile-phase solvents and result in poorer resolution and lower sensitivity due to peak broadening.

Using gradient chromatography, however, it is possible to reduce the run time from 40 minutes to less than 10 minutes, as shown by the chromatogram in Figure 3. The first mobile phase consisted of a solution of 3.17 mM Na_2HPO_4, 6.21 mM KH_2PO_4, and 5.0 mM TBAP in 25%/75% methanol/water. The second mobile phase consisted of the same concentrations of salts in 30%/70% methanol/water. Each mobile phase was filtered through a 0.45-micron nylon filter. The pH of each mobile phase was naturally about 6.

The chromatogram in Figure 3 was obtained by first flowing phase one at a rate of 2.5 ml/min. At 2.25 minutes into the run, a control valve switched mobile phases from phase one to phase two, allowing phase two to flow through the column for the next five minutes. At 7.25 minutes into the run, the control valve was switched back to phase one for the remaining 2.25 minutes of the analysis, for a total run time of 10 minutes. The column temperature was constant at 35°C. The maximum backpressure was approximately 2800 psi.

Using the gradient method, the two 1,3,6-naphthalene trisulfonate contaminants now elute before and after 1-naphthalene sulfonate, respectively. With a run time that is only one fourth as long as required by the isocratic method, only one fourth of the mobile phase solvent volume is likewise required. In addition, the resolution is improved.

Larger injection volumes result in lower detection limits, since, for a given concentration, larger injection volumes result in more analyte flowing through the detector flow cell. Lower detection limits allow for a reduction in the mass of tracer required to achieve measurable breakthrough. It is therefore preferable to use the largest injection volume that the instrument and the chromatographic conditions will allow. Using an injection volume of 200 microliters with the conditions described above, the detection limit of each of the naphthalene sulfonates was less than 0.1 ppb. By optimizing the detector excitation and emission wavelengths for each tracer, the detection limits can be reduced even further.

3.0 DECAY KINETICS OF THE NAPHTHALENE SULFONATES

The decay kinetics of the six naphthalene-sulfonate tracer candidates was studied using autoclave batch reactors under controlled conditions designed to simulate a geothermal environment (Rose et al., 2001, Rose et al., 2002). Plotted in Figure 4 is half-life vs. temperature for each compound. The dotted line representing the four compounds 1-naphthalene sulfonate, 2-naphthalene sulfonate, 2,6-naphthalene disulfonate, and 2,7-naphthalene disulfonate is an approximation. These four compounds were sufficiently thermally stable that no decay was observed upon exposure of each compound to simulated geothermal conditions for one week at 330°C. We suspect that these compounds are sufficiently Stable for use in geothermal reservoirs at least as hot as 330°C. Also shown for comparison in Figure 4 are the half-life vs. temperature plots for the two xanthene dyes fluorescein and rhodamine WT, as well as the polyaromatic sulfonate 1,3,6,8-pyrene tetrasulfonate.

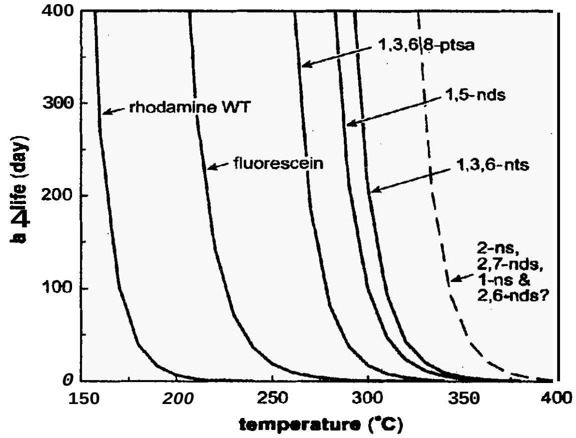


Figure 4. Plot of half-life vs. temperature for several polyaromatic sulfonate tracers as well as for two xanthene dyes as determined from decay kinetics data measured at EGI.

4.0 TRACER TESTING AT BULALO

The Bulalo geothermal field is a hot, two-phase geothermal reservoir that has provided a large amount of electrical power to Luzon for more than two decades (Golla et *al.*, 2001). Brine and cooling tower condensate produced from the field has been injected since it began commercial operation in 1979 (Sta. Maria et *al.*, 1995). These waste fluids are now injected into a number of deep wells at distances of 1.0 to 2.5 km from the production zone. Early attempts to quanti injection returns using fluorescein from specific wells were largely unsuccessful because the high reservoir temperatures caused breakdown of this chemical tracer.

The more thermally stable naphthalene sulfonates were chosen for recent tracer tests to determine the rate of return of waste brine and cooling tower condensate injected at several wells on the western edge of the field. With measured temperatures exceeding 300°C in some deep production wells, Bulalo provides a challenging environment for verifying the measured thermal stability of the naphthalene sulfonates.

On January 24,2001,450 kg of 1,5-naphthalene disutfonate (Yick-Vic Chemicals, Hong Kong) was injected into well Bul-69, located about 1 km from the southwest edge of the Bulalo production zone. Cooling tower condensate was continuously injected into the well over the subsequent year. Selected producing wells in the field were monitored for the tracer by PGI over the subsequent year. Since this was the first time napthalene sulfonates were analyzed by PGI, a subset of samples was sent to the EGI laboratory in Salt Lake City, Utah, USA for confirmatory analysis.

Shown in Figure 5 are the returns of 1,5-naphthalene disulfonate to well Bul-08 as measured by both PGI and EGI. The two return curves match remarkably well, as each produced almost identical first arrivals and peak maxima. Such reproducibility provides confidence in the performance of the tracer.

The return curves each show a relative minimum at approximately 113 days into the test. The

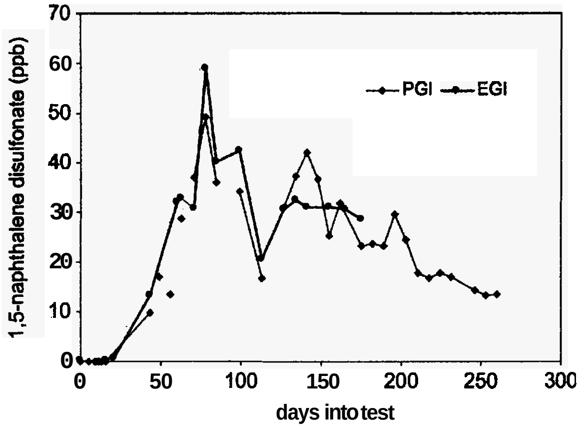


Figure 5. Return of the tracer 1,5-naphthalene disulfonate from Bul-69 to Bul-08 as measured independently by PGI and EGI.

analytical chemists at both PGI and EGI suspected this minimum point to be in error, since it was an anomaly in the otherwise gradual tracer decay following the curve's peak. Each lab confirmed its analysis of the suspected point, however, by replicating the result through repeated analyses.

The Bul-08 return curve can be explained as two superimposed curves, representing two major flow paths between Bul-69 and Bul-08. The first path shows tracer returns with a first arrival of approximately 37 days and a peak return at approximately 78 days into the test. The first arrival for the tracer returning via the slower path is indeterminate, but its peak is at approximately 140 days. Tracer returns from Bul-69 to wells with shallow entries in proximity to Bul-08 indicate relatively rapid returns, whereas tracer returns from Bul-69 to wells in proximity to Bul-08 that have only deep entries indicate slower returns (Capuno, unpublished data). Since Bul-08 has both shallow and deep fluid entries, it is reasonable to assume that the first peak in the Bul-08 return curve represents a relatively rapid, shallow flow path, whereas the second peak represents a slower, deeper flow path.

5.0 CONCLUSIONS

Six naphthalene sulfonates that are suitable for use in high temperature geothermal systems can be analyzed simultaneously using paired-ion reversephase liquid chromatography. Using an isocratic mobile phase, the run time is approximately 14 minutes, whereas the use of a gradient mobile phase results in a run time less than 10 minutes. In addition to being environmentally benign and very affordable, these fluorescent tracers have detection limits below 0.1 ppb.

A tracer test was recently conduced at the Bulalo, Philippines geothermal field using 1,5-naphthalene disulfonate. Excellent agreement by two laboratories was observed in the analysis of produced tracer.

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