

**Enhanced Oil Recovery:
Aqueous Flow Tracer Measurement**

Topical Report

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Laramie, Wyoming

By

Western Research Institute

Laramie, Wyoming

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ABSTRACT

A low detection limit analytical method was developed to measure a suite of benzoic acid and fluorinated benzoic acid compounds intended for use as tracers for enhanced oil recovery operations. Although the new high performance liquid chromatography separation successfully measured the tracers in an aqueous matrix at low part per billion levels, the low detection limits could not be achieved in oil field water due to interference problems with the hydrocarbon-saturated water using the system's UV detector. Commercial instrument vendors were contacted in an effort to determine if mass spectrometry could be used as an alternate detection technique. The results of their work demonstrate that low part per billion analysis of the tracer compounds in oil field water could be achieved using ultra performance liquid chromatography mass spectrometry.

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EXECUTIVE SUMMARY

The petroleum industry uses well-to-well tracer tests to investigate fluid flow paths between injector wells and producer wells in oil reservoirs. Although interwell tracer testing provides valuable information to improve the conformance of enhanced oil recovery (EOR) or water floods of oil reservoirs, it has not been commonly used in Wyoming oil fields. Understanding these flow paths is particularly important in EOR applications since EOR fluids are expensive to purchase and/or process. The overall objective of understanding the flow paths is to use the information to increase oil production.

In July 2005, the University of Wyoming Enhanced Oil Recovery Institute (EORI) contracted with Western Research Institute (WRI) to develop a more efficient analytical method of measuring a suite of fluorinated benzoic acid (FBA) tracers for use in Wyoming oil fields. Using a novel high performance liquid chromatography (HPLC) separation, eight tracers were successfully measured in an aqueous matrix at low part per billion levels in less than ten minutes analysis time using conventional ultraviolet (UV) absorbance detection. Although these results were better than the hydrological results reported in the literature, suitable detection limits could not be obtained in oil field water due to interference problems with the hydrocarbon-saturated water using the UV absorbance detector.

The tracer detection limit is a crucial issue in field reservoir work because the amount of chemical tracer that must be injected down-hole is directly related to the amount that can be detected after migration and diffusion through the underground reservoir. In early 2006, WRI contacted instrument vendors to see if an alternate detection technique such as mass spectrometry (MS) could provide lower detection limits. One of the vendors was able to successfully perform low part per billion detection limit analysis of fluorobenzoate tracers in oil field water sample utilizing ultra performance liquid chromatography (UPLC) in conjunction with MS as the detector.

Task 73 was subsequently initiated in late 2006. One of the first experiments conducted was an oil/water partition study to determine the solubilities of the fluorobenzoates in oil/water mixtures. The results of the study verified that the tracers partition favorably into the aqueous phase of the oil field water. Very nearly all of the chemical tracer was detected in the aqueous phase (and was not diluted into the oil phase) which meant that for field work, the cost of the tracers could be kept to a minimum. Having reached that significant conclusion, a UPLC/MS instrument was purchased for low-level detection limit tracer analysis. The instrument was installed in early 2007, and initial method development activities were conducted for the analysis of the FBA tracers in oil field water.

At the request of EORI, the scope of work for Task 73 was redirected in late 2007. The focus was shifted from fluorinated benzoic acid tracer studies to defining a tracer or other type(s) of chemical compound(s) that could be used to help determine the complex chemical interaction that exists in underground reservoir oil, indigenous rock formation, and the type of water used in water floods. Redirection of the scope of work was based on the finding that low-salinity water flooding showed more promise to increase oil production than understanding EOR flow characteristics, i.e., understanding the low-salinity mechanism was deemed to have more economic impact than developing and demonstrating a tracers method.

The subject of this Topical Report deals only with the original scope of work and not the redirected effort. The main focus of this Topical Report is to document the unique analytical procedures for performing ultra-trace determination of FBA tracers in aqueous matrices.

INTRODUCTION

The purpose of Task 73 Enhanced Oil Recovery: Aqueous Flow Tracer Measurement is to provide the University of Wyoming Enhanced Oil Recovery Institute (EORI) and the U.S. Department of Energy (DOE) with an ultra-low detection limit tracer test measurement capability that can be used to evaluate and improve enhanced oil recovery (EOR) and water flood operations. Specific activities within this Task include: a tracer oil/water partition study, the purchase and installation of a new UPLC/MS instrument, and initial method development activities related to the quantitative measurement of fluorinated benzoic acid (FBA) tracer compounds at low detection limits in oil field water.

Background

Tracers are chemical compounds that are added to fluid systems so that flow patterns may be determined. Tracer measurements can be used in a qualitative manner to determine whether or not a particular fluid flow exists, or in a quantitative manner to determine flow velocities and patterns. Ideally, tracers should be non-reactive and should not be naturally-occurring in the fluid system being studied. Classifications of tracers include; but are not limited to; visible color dye, fluorescent, radioisotope, anion, and aromatic acid compounds.

Fluorinated derivatives of benzoic acid (fluorobenzoates, FBAs) are a sub-classification of aromatic acid compound tracers. FBAs are chemically distinct compounds ranging in fluorine substitution from three mono-fluorinated isomers through penta-fluorobenzoate. Table 1 lists 17 FBA congeners that are commonly and commercially available. The molecular weights of the congeners vary from 140 through 212 atomic mass units (amu). Although the molecular weights are identical within the mono-, di-, tri-, and tetra-substituted isomers, the highly electronegative nature of fluorine and its position relative to the carboxylic acid plays a significant role in how the congeners can be separated and identified using an analysis tool such as high performance liquid chromatography (HPLC).

The use of FBAs as nonreactive tracers in soil and groundwater studies has been documented (Bowman et. al. 1995, Farnham 2003, McCarthy et. al. 2000). Two of the authors (Bowman, Farnham) were telephoned to inquire about the analytical methodology used to measure the FBAs. The analysis technique generally used was reversed-phase aqueous HPLC, buffered at low pH and using conventional UV absorbance detection at 205 nm. Detection limits on the order of approximately 10 parts per billion (ppb) were generally achieved in the groundwater studies conducted by the authors.

Fluorobenzoates have also proven to be useful tracers in geothermal applications (Adams et. al. 1998). Although FBAs have been successfully used as tracers in groundwater and geothermal features, a literature search did not reveal any use of FBA tracers in oil field reservoir applications.

FBAs as Tracers in EOR Applications

In EOR applications, interwell tracers are added to the oil field injector wells, and the producer wells are periodically sampled and the water is quantitatively analyzed for the tracers. Different tracers are commonly used in reservoirs that contain multiple injectors and producers. The migration times and concentration measurements of the tracers measured at the producers are used to model the fluid flow paths. Once the subsurface flow paths are modeled, the information can be used to improve sweep efficiencies for EOR or water flood projects.

Although well-to-well tracer testing is an efficient means of acquiring valuable reservoir information, it has not been commonly used in Wyoming oil field management practices. In July 2005, EORI contracted with WRI to develop an analytical method for using FBA tracers in a Wyoming oil field application.

HPLC/UV Methodology

WRI telephoned HPLC column manufacturers to ask for their recommendation for the best HPLC column for the separation of fluorobenzoates in aqueous matrices, and a newly-introduced HPLC column was purchased for the tracers method development. Initial activities were performed using six FBAs and two carboxylic aromatic acid compounds prepared in laboratory reagent water. A novel separation was developed using the HPLC/UV equipment already in place at WRI. This instrument is shown in Figure 1.

Using an improved analysis method, the tracers were successfully measured at detection limits of approximately 1-2 ppb in under ten minutes analysis time. Table 2 provides the HPLC/UV method operating conditions that were developed for the new analysis method. Figure 2 is a chromatogram of the tracers separation that was achieved in laboratory reagent water using the new analysis method.

Although the HPLC/UV detection limits were improved by almost an order of magnitude relative to the hydrological results reported in the literature, the improved detection limits could not be replicated when an oil field water sample was used as the sample matrix. It was apparent from the chromatographic results that the hydrocarbon-saturated oil field water exhibited considerable interferences due to dissolved petroleum components using the UV absorbance detector. Even after the oil-field water was pre-extracted with n-heptane to remove most of the hydrocarbons, detection limits of approximately 10 – 40 ppb could only be realized.

For a reservoir tracer study, the net amount of chemical tracer that must be injected down-hole is directly related to the amount that can be detected after diffusion and migration through the reservoir. The ten-fold detection limit increase due to the hydrocarbon interferences thus corresponded to a ten-fold increase in tracer cost. From a cost perspective, it appeared unlikely that an oil-field tracer study could be a financially viable option for oil field use, because the cost of the tracers needed for a representative Wyoming oil field reservoir study would increase from about \$20,000 to \$200,000. This cost estimate was prepared using the six least expensive tracers listed in Table 3.

In late 2005 and early 2006, WRI contacted vendors of HPLC instruments to determine if it was possible to perform the quantitative tracer measurement using mass spectrometry (MS) rather than UV as the detector. Two instrument vendors agreed to analyze the FBAs in an oil-field water sample. The results of the applications work performed by the Waters Corp. showed that low ppb detection limits were indeed possible using a relatively new technique called ultra performance liquid chromatography / mass spectrometry (UPLC/MS).

PARTITION STUDY

Before a UPLC/MS instrument could be purchased, an experimental study was performed to verify that addition of FBA-type tracers to an oil/water mixture would not result in significant solubility of the tracers in the oil phase. Because the cost of the chemical tracers needed for field work is such a crucial issue, the partition study was conducted to determine to what extent the tracers would remain in the aqueous phase vs. how much they would be lost by dilution into the oil phase.

Experimental

Samples—An aqueous solution containing benzoic acid; phthalic acid; 2-fluorobenzoic acid; 4-fluorobenzoic acid; 2,6-difluorobenzoic acid; 3,5-difluorobenzoic acid, and 2,3,4,5-tetrafluorobenzoic acid was spiked into neutral pH Bairoil, WY oil field water containing supernatant oil. Spikes were performed in duplicate using 400 μ L and 800 μ L spike volumes, to achieve desired concentrations of 160 and 320 ppb (w/v) for five of the seven compounds in 100 mL samples in volumetric flasks. The aqueous spike solution was pipetted directly onto the supernatant oil at the top of the sample in the flasks. The samples were mixed by inverting the flask several times, and the flasks were placed in an ultrasonic bath for 15 minutes. The samples were mixed again, then allowed to equilibrate overnight. The following morning, the samples were poured into a graduated cylinder to determine the volumes of the aqueous and supernatant oil phases. The 160 ppb spike sample was found to consist of 74 mL aqueous phase and 26 mL oil phase, while the 320 ppb spike sample was found to consist of 80 mL aqueous phase and 20 mL oil phase. A 10 mL aliquot of the aqueous phase of each sample was removed and washed with 5 mL of n-heptane to extract most of the hydrocarbons. A 4 mL aliquot of the aqueous

phase was removed and acidified to pH 2 for HPLC/UV analysis of the compounds as their acid species.

Aqueous Laboratory Controls—Analogous to the spiking procedure described above, 400 μL and 800 μL spikes were pipetted into 100 mL neutral pH laboratory reagent water. 4 mL aliquots of the resulting solutions were acidified to pH 2 for analysis. The laboratory controls were used to verify not only the spiking procedure using interference-free water, but to also confirm the accuracy of the HPLC/UV instrument calibration.

Aqueous Oil Field Matrix Controls—Portions of Bairoil, WY oil field water containing supernatant oil were pre-extracted with n-heptane to extract most of the hydrocarbons. 400 μL and 800 μL spikes were pipetted into 100 mL of the pre-extracted aqueous sample matrix. 4 mL aliquots were acidified for analysis. The matrix controls were used to verify the spike amounts in the actual matrix without water/oil partition effects.

HPLC/UV Operating Parameters—The same operating conditions described previously and listed in Table 2 were used for the partition study.

Results by HPLC/UV

For the samples and matrix controls, hydrocarbon interferences prevented the integration and quantitation of four of the seven compounds. Suitably-resolved chromatographic peaks were observed for 2-fluorobenzoic acid, benzoic acid, and 2,3,4,5-tetrafluorobenzoic acid. The aqueous laboratory controls showed well-resolved chromatographic peaks for all seven compounds.

The concentrations of the three tracers that could be determined in the 160 and 320 ppb, samples were compared to the concentrations determined in the 160 and 320 ppb matrix controls. It was immediately evident that the tracer recoveries in the samples were approximately 120% of the amounts found in the matrix controls. However, the samples were volumetrically comprised of 74% and 80% aqueous phase, with the remainder comprised of oil. If the tracers partitioned only into the aqueous volume then the concentration results would be expected to be higher. When the volume correction was applied to the sample results, a more accurate calculation was obtained. The pertinent data and calculations are presented in Table 4.

Overall, the results show strong partitioning of the three compounds into the aqueous phase of the sample. The 320 ppb spiked sample partition results are more reliable than the 160 ppb sample results, because the relatively lower matrix background in the 320 ppb samples makes the peak integration and concentration results more accurate.

Based upon the partition results, the aromatic acids and fluorobenzoates appeared to be suitable candidates for underground interwell oil-field tracer studies. EORI recommended that WRI proceed with the purchase of an instrument that could perform the required the low-level detection limit tracer analysis.

LOW-LEVEL DETECTION LIMIT TRACERS METHODOLOGY

UPLC/MS Methodology

Two instrument manufacturers agreed to accept and analyze samples prepared by WRI. FBA standards were spiked into the Bairoil, WY n-heptane extracted oil-field water, and the analysis method developed at WRI (Table 2) was provided to both vendors. The Figure 2 HPLC/UV chromatogram was also provided. The Waters Corp. was able to demonstrate that the hydrocarbon interference using UV detection could be overcome using mass spectrometry as the detector. The results of their effort is compiled in Appendix I of this Topical Report. Appendix I provides the UPLC/MS operating conditions, chromatograms of an FBA standard mix spiked at three concentration levels (400, 40, 4 ppb) in the n-heptane extracted oil-field water matrix, and a chromatogram of the unspiked oil-field water matrix. Using a signal/noise ratio of 2, the detection limits were estimated for the 7 tracer compounds. The estimated detection limits are provided in Table 5. Note that these detection limits are initial results determined from the applications investigation conducted by Waters. Further method development to fine-tune the separation and detection parameters would likely result in improved detection limits.

UPLC/MS Installation and Setup

The same model of instrument used by the Waters Corp. for their applications work was purchased by WRI in late 2006. A suitable laboratory in the main building of WRI was chosen as the location for the new instrument. After the laboratory was prepared according to specifications for electrical, venting, and other physical and environmental requirements, the instrument was installed and set up in early 2007. The initial performance of the UPLC/MS was certified by the Waters service engineer at the time of installation. A photograph of the instrument installed at WRI is presented in Figure 3.

The Waters applications chemist who had performed the initial UPLC/MS tracers methodology arrived at WRI a few months later to set up the method. However, he found the instrument's computer and software to be non-operational. It was presumed that this was due to multiple power failures and outages experienced due to construction activities in the immediate vicinity of the WRI building. The computer was finally repaired two months later with the help of IBM technical assistance.

Waters subsequently sent service engineers in two separate visits to place the UPLC/MS back into operational mode after the computer malfunction and repair. As it appeared that the multiple power outages had corrupted the instrument's electronics, two uninterrupted power supply (UPS) units were purchased to prevent this from happening again in the future. One of the UPS units was a conventional 120V unit for the computer. The other UPS was a commercial-grade 240V system to protect the instrument electronics. After the UPS units were installed, the UPLC/MS system was operated successfully in a variety of analysis modes. Method development activities aimed at separating a more comprehensive suite of FBA and aromatic acid tracers and lowering the detection limits were finally initiated in late 2007. About this time, EORI notified WRI that their focus was being redirected by the Wyoming State EOR Commission. Work on the tracers method in oil-field water was suspended when EORI formally requested in late 2007 that the project be redirected.

This Topical Report was prepared to document the work performed for the tracer measurement component of Task 73. A subsequent, Final Topical Report will be issued in April 2009 for the redirected work effort.

CONCLUSIONS

A novel HPLC/UV method was developed for the analysis of fluorobenzoic acid and aromatic acid tracer compounds in aqueous matrices. Eight tracers were successfully measured in an aqueous matrix at low part per billion levels in less than ten minutes analysis time using conventional UV absorbance detection. The method operating conditions described in this Topical Report provide improved results from the hydrological results reported in the literature, and the new method is useful for the analysis of FBA and aromatic acids as tracers in hydrological applications.

Although the levels of tracers that can be detected by the new method are about an order of magnitude lower than the hydrological results reported in the literature, the low detection limits could not be obtained in oil-field water due to interference problems with the hydrocarbon-saturated water using the UV detector. WRI submitted tracer mixtures in oil-field water to two instrument manufacturers to see if low detection limits could be obtained using mass spectrometry as the chromatographic detector. The Waters Corp. was able to demonstrate that low-level analysis of fluorobenzoic and aromatic acid tracer compounds could indeed be achieved in oil-field water using a technique known as UPLC/MS. The method operating conditions developed by the Waters Corp. are included in this Topical Report, and provide the basis for a new method to successfully analyze FBA and aromatic acid tracers at low part per billion levels in oil-field water matrices.

ACKNOWLEDGMENTS

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Table 1. FBA Congeners

Fluorobenzoate	M.W.	CAS	Formula
2-Fluorobenzoic acid	140	445-29-4	C ₇ H ₅ FO ₂
3-Fluorobenzoic acid	140	455-38-9	C ₇ H ₅ FO ₂
4-Fluorobenzoic acid	140	456-22-4	C ₇ H ₅ FO ₂
2,3-Difluorobenzoic acid	158	4519-39-5	C ₇ H ₄ F ₂ O ₂
2,4-Difluorobenzoic acid	158	1583-58-0	C ₇ H ₄ F ₂ O ₂
2,5-Difluorobenzoic acid	158	2991-28-8	C ₇ H ₄ F ₂ O ₂
2,6-Difluorobenzoic acid	158	385-00-2	C ₇ H ₄ F ₂ O ₂
3,4-Difluorobenzoic acid	158	455-86-7	C ₇ H ₄ F ₂ O ₂
3,5-Difluorobenzoic acid	158	455-40-3	C ₇ H ₄ F ₂ O ₂
2,3,4-Trifluorobenzoic acid	176	61079-72-9	C ₇ H ₃ F ₃ O ₂
2,3,5-Trifluorobenzoic acid	176	654-87-5	C ₇ H ₃ F ₃ O ₂
2,3,6-Trifluorobenzoic acid	176	2358-29-4	C ₇ H ₃ F ₃ O ₂
2,4,5-Trifluorobenzoic acid	176	446-17-3	C ₇ H ₃ F ₃ O ₂
2,4,6-Trifluorobenzoic acid	176	28314-80-9	C ₇ H ₃ F ₃ O ₂
3,4,5-Trifluorobenzoic acid	176	121602-93-5	C ₇ H ₃ F ₃ O ₂
2,3,4,5-Tetrafluorobenzoic acid	194	1201-31-6	C ₇ H ₂ F ₄ O ₂
Pentafluorobenzoic acid	212	602-94-8	C ₇ HF ₅ O ₂

Table 2. HPLC/UV Operating Conditions

<u>Pump/Controller:</u>	Waters 600
<u>Column:</u>	Phenomenex Synergi 4μ Hydro-RP 80A, 150 x 4.6 mm (Part # 00F-4375-E0)
<u>Guard Column:</u>	Phenomenex Aqueous Phase C-18 (Part # AJ0-7511)
<u>Mobile Phase:</u>	65% aqueous 0.02M H₃PO₄, 0.02M KH₂PO₄ 35% CH₃CN (isocratic)
<u>Flow Rate:</u>	1.0 mL/min
<u>UV/Vis Detector:</u>	Waters 2487 at 230 nm
<u>Autosampler:</u>	Waters 717, 100 μl injection

Table 3. FBA Price List (Oakwood Chemicals, 2006)

FBA	\$ / gm
2-Fluorobenzoic acid	\$ 0.17
4-Fluorobenzoic acid	\$ 0.35
2,6-Difluorobenzoic acid	\$ 0.49
3-Fluorobenzoic acid	\$ 0.89
3,5-Difluorobenzoic acid	\$ 0.99
2,3,4,5-Tetrafluorobenzoic acid	\$ 1.02
2,5-Difluorobenzoic acid	\$ 1.46
2,3,4-Trifluorobenzoic acid	\$ 1.46
2,4,5-Trifluorobenzoic acid	\$ 1.46
3,4-Difluorobenzoic acid	\$ 3.72
Pentafluorobenzoic acid	\$ 4.08
2,3-Difluorobenzoic acid	\$ 5.72
2,4-Difluorobenzoic acid	\$ 5.72
2,3,6-Trifluorobenzoic acid	\$ 8.12
2,4,6-Trifluorobenzoic acid	\$ 28.00
3,4,5-Trifluorobenzoic acid	\$ 28.00
2,3,5-Trifluorobenzoic acid	\$ 37.60

Table 4. Partition Data

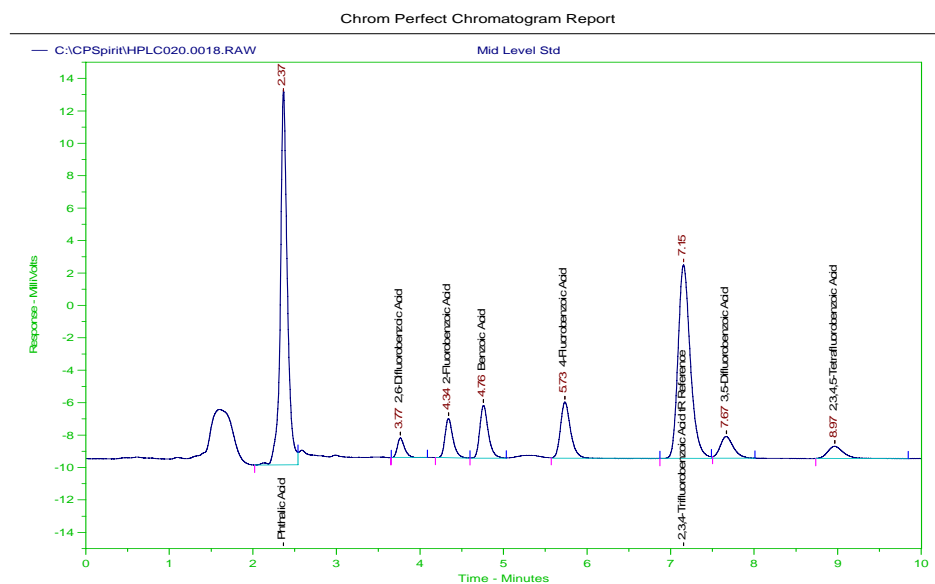
Experiment/Description	2-FBA, ppb	Benzoic Acid, ppb	2,3,4,5-FBA, ppb
160 ppb Sample	232	208	274
160 ppb Matrix Control	193	170	184
Water/Oil Volume Correction Factor	0.74	0.74	0.74
Corrected Sample Concentration	172	154	203
Partition Into Aqueous Phase	89%	91%	110%
320 ppb Sample	406	372	460
320 ppb Matrix Control	347	308	349
Water/Oil Volume Correction Factor	0.80	0.80	0.80
Corrected Sample Concentration	325	298	368
Partition Into Aqueous Phase	94%	97%	105%

Table 5. Estimated Tracer Detection Limits by UPLC/MS

Tracer Compound	Ion, m/z (SIR)	Approximate Retention Time	Estimated Detection Limit (S/N=2)	Reference Chromatogram in Stackplot (Appendix A)
Benzoic Acid	121	2.2 minutes	4 ppb	Top (red)
2-Fluorobenzoic Acid	139	1.4 minutes	4 ppb	Second from Top (green)
4-Fluorobenzoic Acid	139	3.0 minutes	4 ppb	Second from Top (green)
2,6-Difluorobenzoic Acid	157	0.5 minutes	10 ppb	Third from Top (blue)
3,5-Difluorobenzoic Acid	157	4.0 minutes	10 ppb	Third from Top (blue)
Phthalic Acid	165	0.6 minutes	1 ppb	Second from bottom (violet)
2,3,4,5-Tetrafluorobenzoic Acid	193	3.1 minutes	4 ppb	Bottom (magenta)



Figure 1. HPLC/UV Instrument



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Figure 2. FBA Separation in Laboratory Water Using HPLC/UV



Figure 3. UPLC/MS Instrument Installed in WRI Laboratory

APPENDIX A

UPLC/MS Method and Chromatographic Data (Courtesy Of Waters Corp.)



Untitled

Instrument Method: 02 AceticAcid 20% MeOH ES neg

Stored: 1/27/2006 11:41:09 AM PST

Method Information

Comments

Modified User System

Locked No

Method Id 1589

Method Version 10

Edit User

Source S/W Info Empower 2 Software Build 2154 DB ID: 707600768

ZQ2000 Instrument Setup

Configuration

Mode Operate

Gas On

Gas Threshold 100

Function 1

Type SIR Span 0.40

Ion Mode ES-

Start Time 0.00

End Time 5.00

Inter-Channel Delay 0.01

Inter-Scan Delay 0.10

SIR Channels

	Channel	Mass (Da)	Dwell (sec)	Cone (Volts)
1	1	121	0.02	15
2	2	139	0.02	15
3	3	157	0.02	15
4	4	165	0.02	15
5	5	193	0.02	15

ACQ-BSM Instrument Setup

Comment

Solvent Selection A A1

Solvent Selection B B2

Low Pressure Limit 0(psi)

High Pressure Limit 15000(psi)

Solvent Name A Acetic Acid

Solvent Name B

Switch 1 No Change

Switch 2 No Change

Switch 3 No Change

Seal Wash 5.0(min)

Chart Out 1 System Pressure

Reported by User: System

Report Method: Untitled

Report Method ID:111

Page: 1 of 3

Project Name: WRI3

Date Printed:

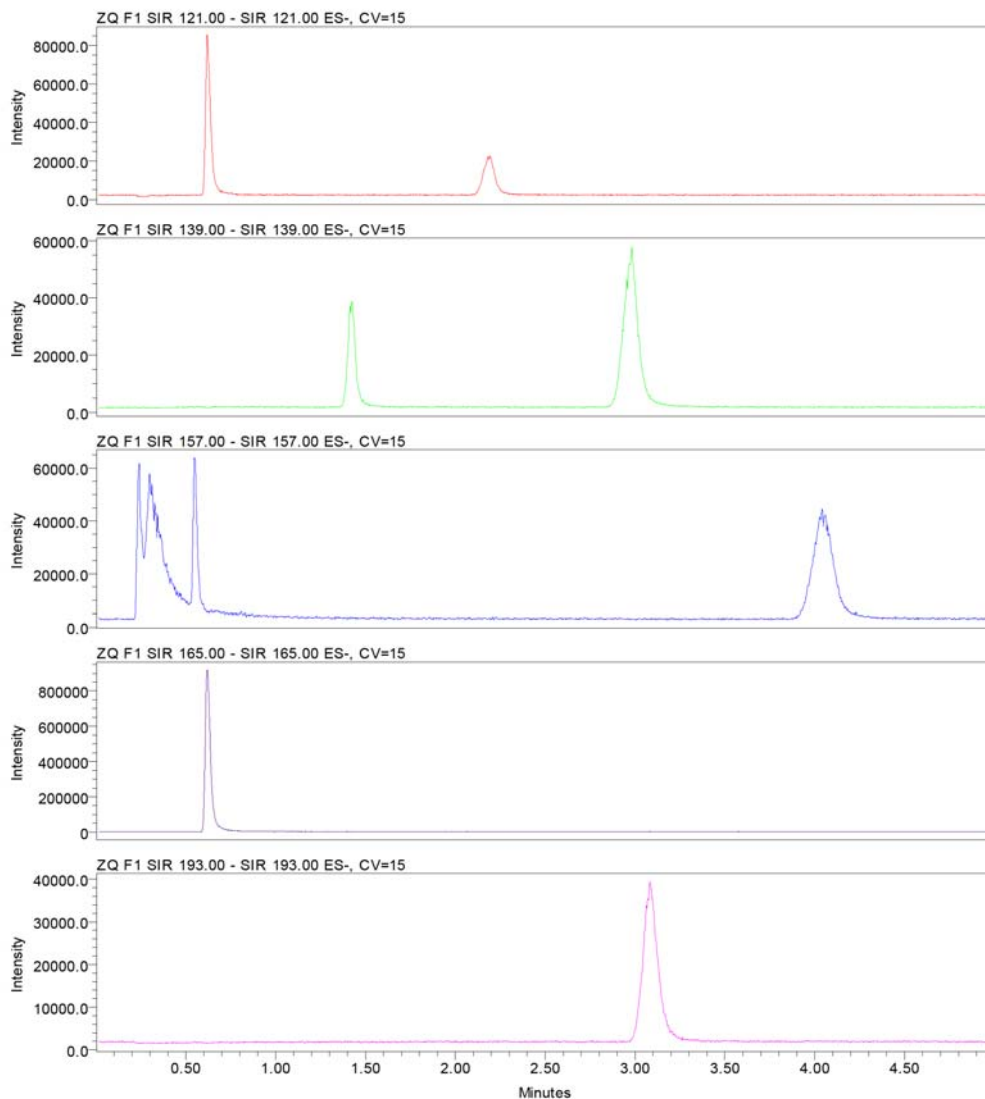
12/15/2008

9:58:19 AM US/Pacific



400 pg/ul FBA

Chromatogram Stackplot



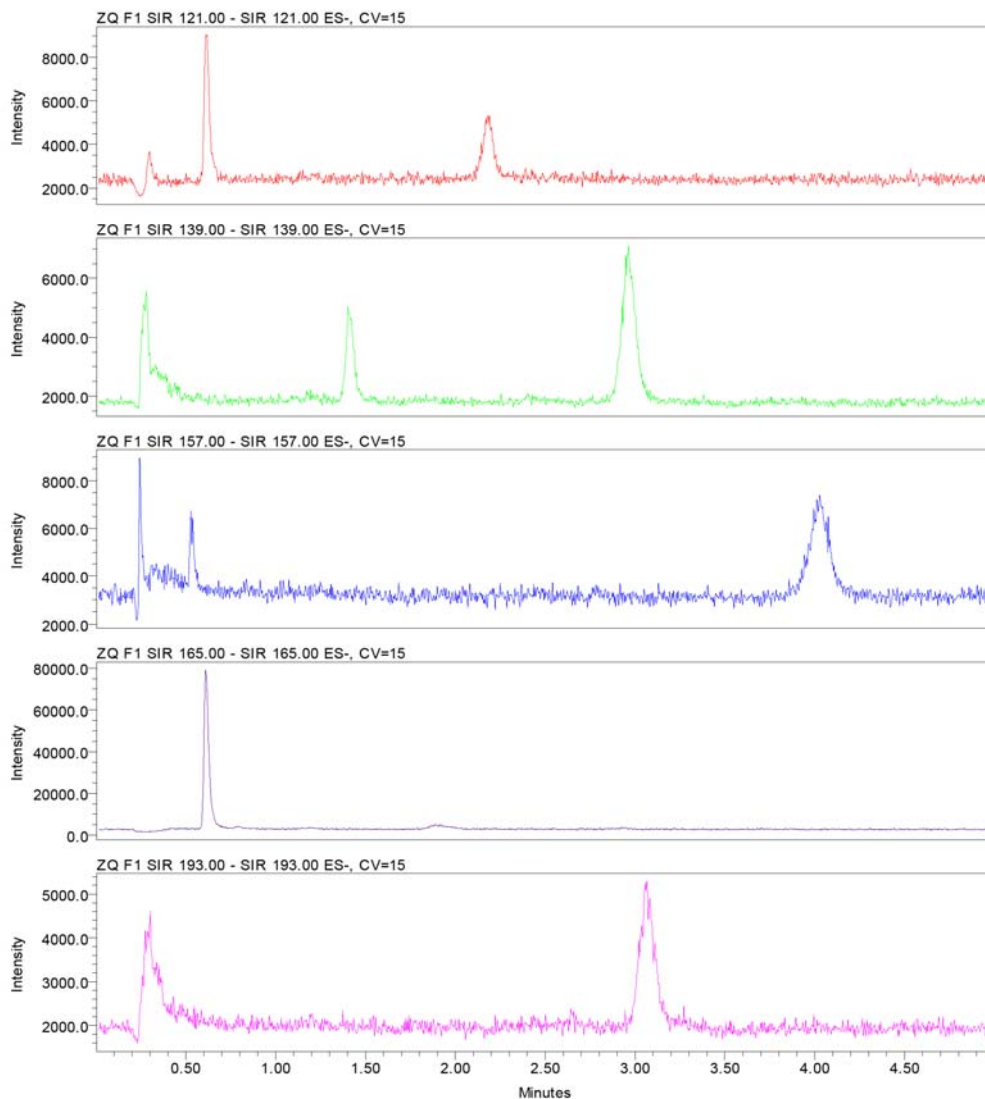
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Report Method: Chromatogram Stackplot
Report Method ID: 1460
Page: 1 of 1

Project Name: WR3
Date Printed:
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40 pg/ul FBA in matrix

Chromatogram Stackplot



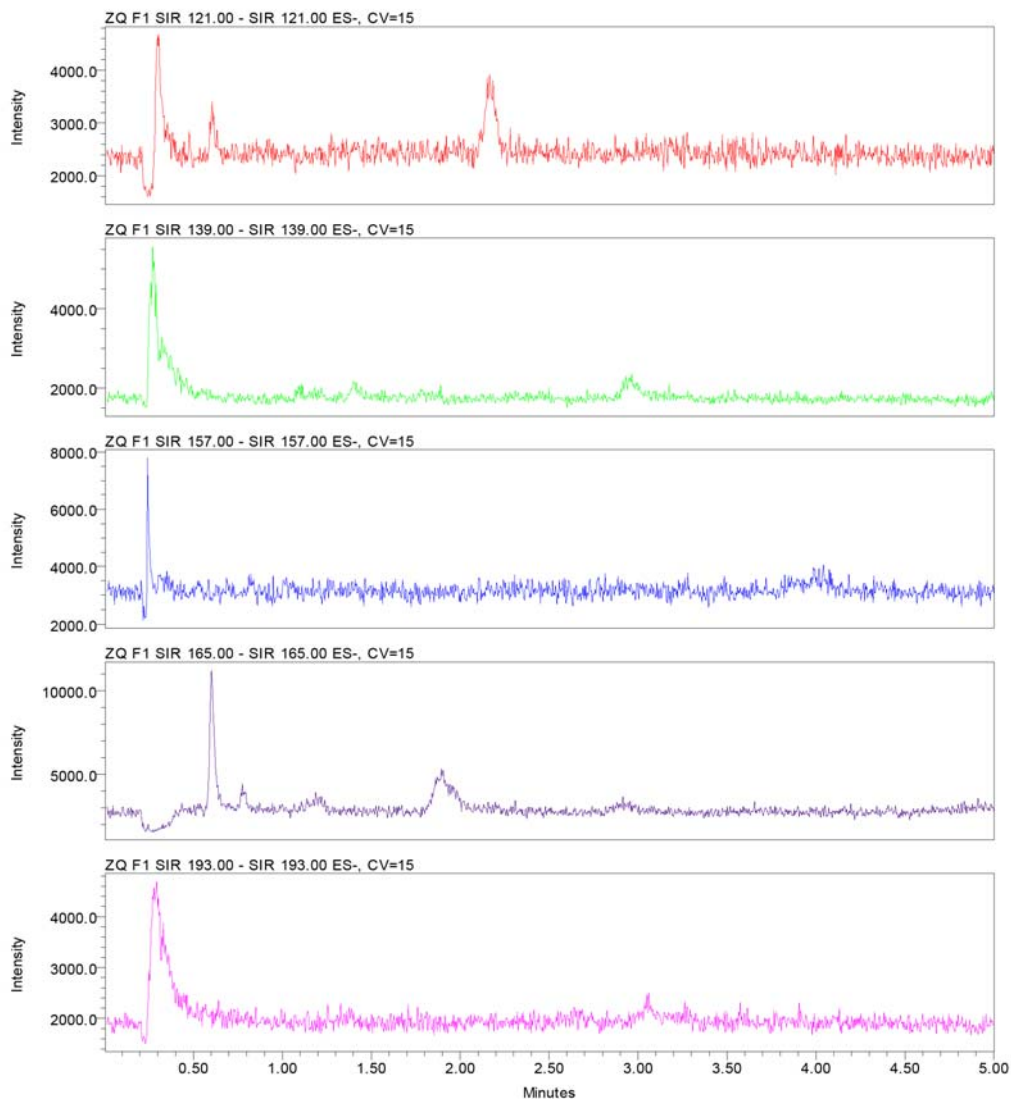
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Report Method ID: 1461
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4 pg/ul in matrix



Chromatogram Stackplot



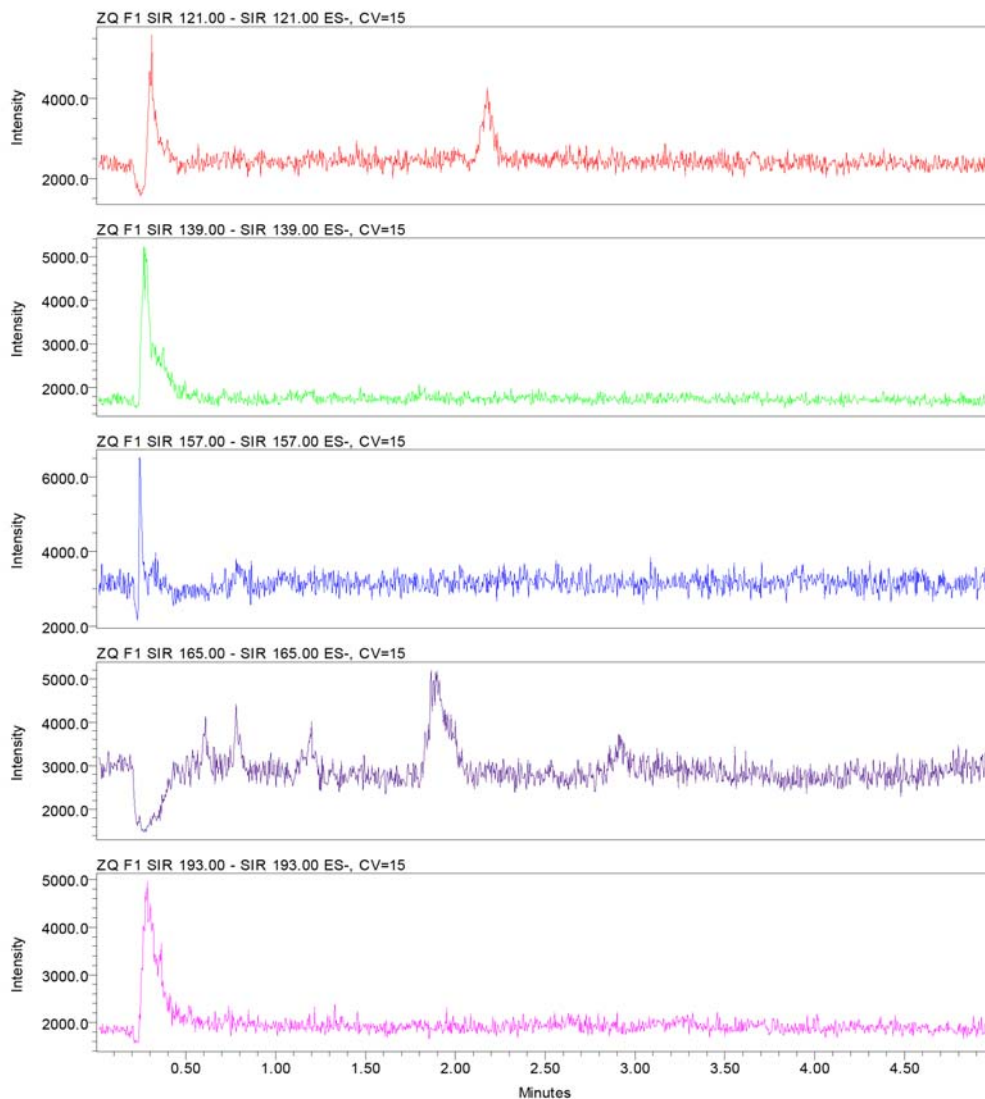
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Matrix Only
Heptane Extracted Oil Field water



Chromatogram Stackplot



Reported by User: System
Report Method: Chromatogram Stackplot
Report Method ID: 1461
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