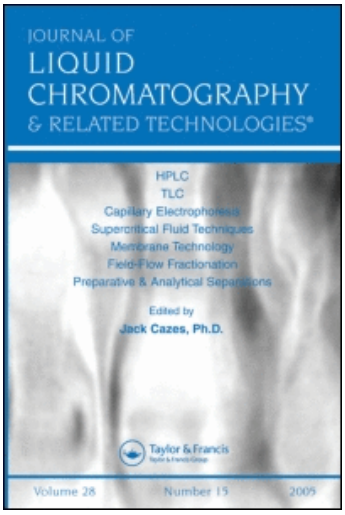

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TRACE ANALYSIS OF FLUORINATED AROMATIC CARBOXYLIC ACIDS IN AQUEOUS RESERVOIR FLUIDS BY HPLC

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ABSTRACT

A straightforward and reliable HPLC method is described, allowing the trace determination of 16 fluorinated aromatic carboxylic acids in aqueous reservoir fluids. Thirteen of these tracer compounds can be determined simultaneously. Concentrations as low as 10 μg/L were determined for selected acids in aqueous reservoir fluids, without sample preparation. The reversed phase column retarded the natural organic background present in aqueous reservoir samples until the selected tracer compounds had been eluted from the column. The use of a diode array detector enabled the identification of the fluorinated benzoic acids. The described technique was used for the reliable determination of the water tracers 2,6-difluorobenzoic acid, 2-fluorobenzoic acid and 3-fluorobenzoic acid in aqueous reservoir samples from a North Sea reservoir.

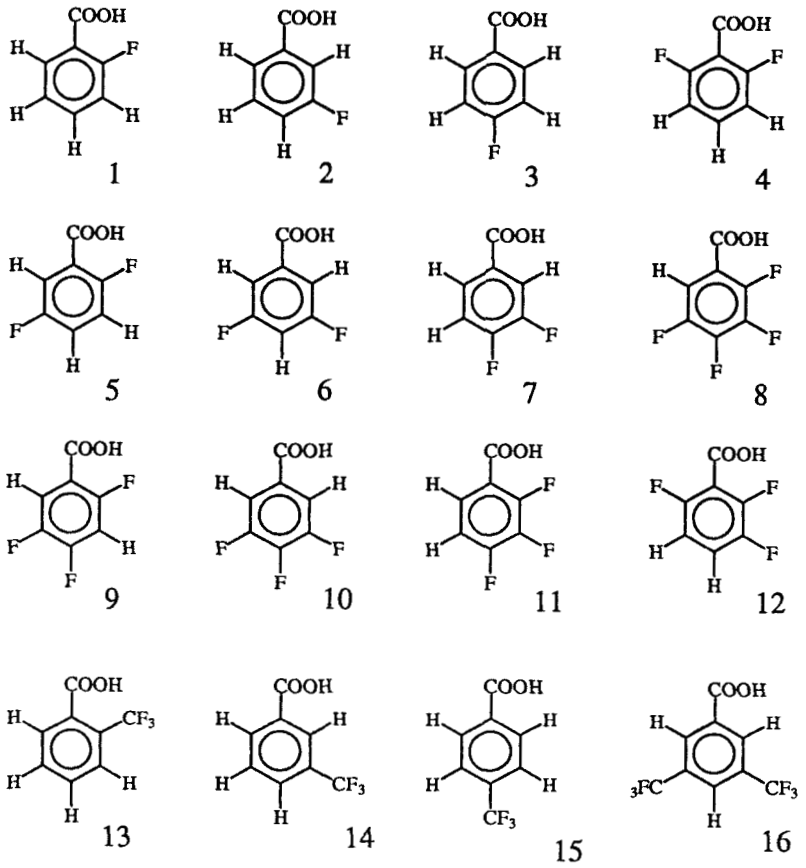

Figure 1. Structures of the 16 fluorinated aromatic carboxylic acids investigated during this work. The compounds are: **1**: 2-fluorobenzoic acid (2-FBA), **2**: 3-fluorobenzoic acid (3-FBA), **3**: 4-fluorobenzoic acid (4-FBA), **4**: 2,6-difluorobenzoic acid (2,6-DFBA), **5**: 2,5-difluorobenzoic acid (2,5-DFBA), **6**: 3,5-difluorobenzoic acid (3,5-DFBA), **7**: 3,4-difluorobenzoic acid (3,4-DFBA), **8**: 2,3,4,5-tetrafluorobenzoic acid (2,3,4,5-TFBA), **9**: 2,4,5-trifluorobenzoic acid (2,4,5-TFBA),**10**: 3,4,5-trifluorobenzoic acid (3,4,5-TFBA), **11**: 2,3,4-trifluorobenzoic acid (2,3,4-TFBA), **12**: 2,3,6-trifluorobenzoic acid (2,3,6-TFBA), **13**: 2-(trifluoromethyl)benzoic acid (2-triFmeBA), **14**: 3-(trifluoromethyl)benzoic acid (3-triFmeBA), **15**: 4-(trifluoromethyl)benzoic acid (4-triFmeBA), **16**: 3,5-di-(trifluoromethyl)benzoic acid (3,5-ditriFmeBA).

INTRODUCTION

A good reservoir description is necessary for an optimum oil recovery strategy. Tracers are fundamental tools for the description of petroleum reservoirs and have to satisfy properties such as no matrix interaction, high stability under reservoir conditions, and ultra low detection limits. Today, mainly HTO or radio-labelled inorganic ions such as $S^{14}CN^-$ or $^{36}Cl^-$ are used as water tracers in oil reservoir studies. A larger number of tracers will enhance the potential for improved reservoir evaluation. Therefore, many compounds have been investigated in recent years by different research groups, in order to find new tracer molecules. Recently, some compounds among a group of fluorinated aromatic carboxylic acids, have been found to be good water tracers.[1,2,3,4] The analytical procedures which enables the detection of these compounds at low concentrations, is now the factor which definitely decides if an application as tracer in aqueous reservoir fluids is suitable or not.

Several analytical methods are under investigation at our institute to find a reliable method for the trace, or even ultra trace determination, of this new group of tracer molecules. This paper reports a new HPLC method for the trace determination of this group of fluorinated aromatic carboxylic acids in aqueous reservoir fluids. Figure 1 shows the 16 fluorinated benzoic acids investigated in this paper.

MATERIALS AND METHODS

Equipment

Chromatography was carried out with a HP 1050 modular HPLC system, containing a quaternary high pressure pump with helium degassing, a HP 1050 autosampler (Hewlett-Packard; Waldbronn, Germany), and a column oven (Krococil). The detector used for routine analysis was a SPD-10A UV detector (Shimadzu; Tokyo, Japan). Spectra of the fluorinated carboxylic acids were recorded either with a HP 1050 Diode array detector or a HP 1100 Diode-array detector (Hewlett-Packard; Waldbronn, Germany).

The chromatographic data were processed with the HP Chemstation (Hewlett-Packard; Waldbronn, Germany). All separations were carried out on a 10 μm C18-Bondapak (300 x 4,6 mm) reversed phased column, from Waters (UK).

Table 1

Composition of the Artificial Formation Water

NaCl	36.85 mg/L
KCl	0.63 mg/L
$CaCl_2$ x $2H_2O$	3.8 mg/L
$MgCl_2$ x $6H_2O$	2.55 mg/L
$BaCl_2$ x $2H_2O$	0.1 mg/L
$SrCl_2$ x $6H_2O$	0.4 mg/L
$NaHCO_3$	0.2 mg/L
Na_2SO_4	0.05 mg/L
10mL crude oil/L	

Table 2

Analytical Conditions for the Analysis of the 16 Fluorinated Aromatic Carboxylic Acids

Mobile Phase A

Run Time	0.0 min	7.0 min	8.0 min	11.0 min
% Modifier	16	16	80	80

Mobile Phase B

Run Time	0.0 min	2.0 min	5.0 min	10.0 min	13.0 min
% Modifier	10	10	30	80	80

Typical Mobile Phase

Run Time	0.0 min	7.0 min	8.0 min	11.0 min
% Modifier	(15-25)	(15-25)	(80)	(80)

Column: 10 μg C_{18}-Bondapak column (300 mm x 4.6 mm. Column temperature: 35°C. Detection wavelength: $\lambda = 223$nm. Mobile phase: flow - 2.5 mL/min, organic modifier - acetonitrile, buffer - 5 mM phosphate buffer; pH: 4.3.

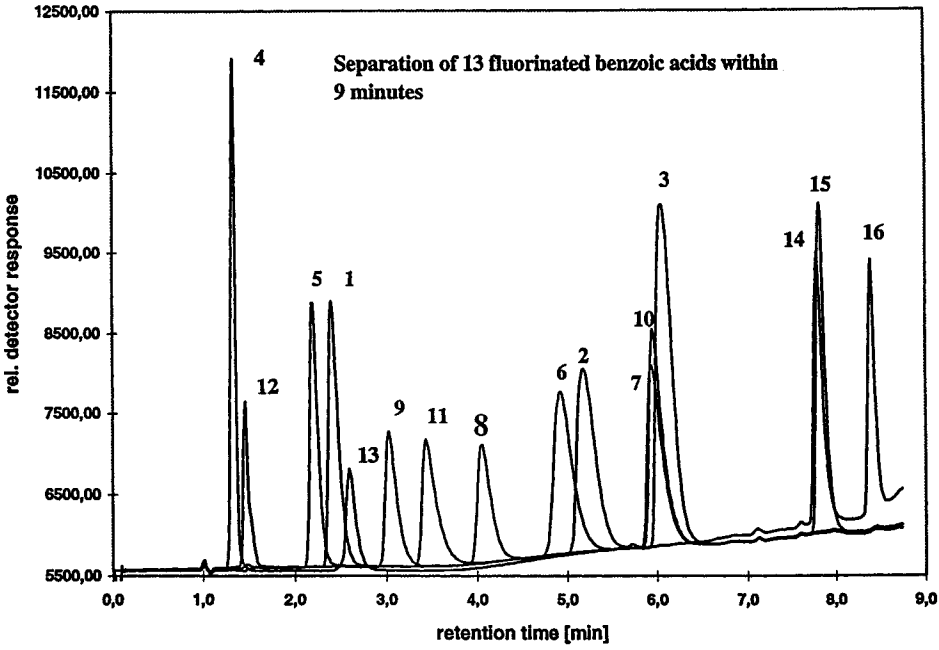

Figure 2. Separation of 13 fluorinated benzoic acids within 9 minutes.

Chemicals

All 16 fluorinated aromatic carboxylic acids (purum quality: 97 %) were supplied from Fluorochem (UK). All other inorganic chemicals, as the phosphate buffer for mobile phase preparation, were analytical grade from Merck (Darmstadt, Germany). Acetonitrile, the mobile phase modifier, was HPLC grade from Rathburn (Walkerburn, Scotland), bidistilled water was used for the preparation of the mobile phase. The buffer solution was filtered through a 0.45μm filter (Millipore: UK) before use.

Preparation of Standards

To ensure both realistic samples and stable experimental conditions during the method development, artificial formation water was used as sample matrix. The composition is shown in Table 1.

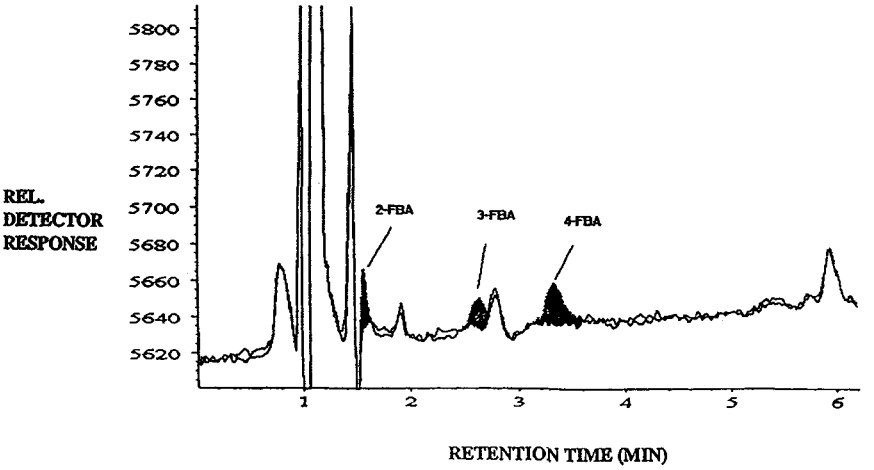

Figure 3. Overlay of two chromatograms of formation water and formation water spiked with four tracer compounds respectively. The concentrations are: 2,6-DFBA: 21,3 µg/L; 2-FBA: 10,1 µg/L; 3-FBA: 9,2 µg/L; 4-FBA: 15,4 µg/L.

This formation water was then spiked with the tracer compounds in various concentrations. After established analytical conditions, real reservoir samples were used as sample matrix. All samples were filtered through a 0.45 µm filter prior to analysis.

HPLC

All separations were carried out on a reversed phase 10 µ C18-Bondapak column (300 mm x 4,6 mm) purchased from Waters (UK). The detailed analytical conditions are described in Table 2.

RESULTS AND DISCUSSION

The major aim of this study was to enable the determination of trace amounts of the fluorinated carboxylic acids in aqueous reservoir fluids in the presence of high concentrations of both organic and inorganic materials. Earlier papers reported the use of anion exchange chromatography for the simultaneous determination of both fluorinated benzoates and inorganic anions used as tracer molecules.[5] The high and variable ionic strength of aqueous

Table 3

Retention Times for the 16 Fluorinated Benzoic Acids at Given Mobile Phase Conditions

Tracer	Retention Time (Min) Mobile Phase A	Mobile Phase B
2-FBA	2.2	2.4
3-FBA	4.4	5.2
4 FBA	5.6	6.1
2,6 DFBA	1.2	1.3
2,5 DFBA	1.9	2.2
3,5 DFBA	4.0	4.9
3,4-DFBA	5.5	5.9
2,4,5-TFBA	2.5	3.0
2,3,4,5-TFBA	2.9	4.0
2,3,6-TFBA		1.5
3,4,5-TFBA		6.0
2,3,4-TFBA		3.4
2-triFmeBA		2.6
3-triFmeBA		7.7
4-triFmeBA		7.9
3,5-ditriFmeBA		8.4

fluids from oil reservoirs can, however, make the use of ion exchange chromatography unreliable. A better choice for the analysis of fluorinated benzoic acids in such matrices is reversed phase chromatography. Compared to most other organic compounds present in aqueous fluids from oil reservoirs, benzoic acids are very acidic. At the same time, the aromatic ring ensure the tracer compounds retention on reversed phase columns.

In comparison, short chain aliphatic carboxylic acids also naturally present in aqueous oil reservoirs, do not interfere with the stationary phase as strong as the fluorinated aromatic carboxylic acids. By carefully choosing the mobile phase parameters as pH, buffer concentration and the percentage of the organic modifier (acetonitrile), conditions can be achieved where the short chain aliphatic acids are not retained on the column and where the organic background elutes after the detection of the fluorinated tracer compounds by increasing the acetonitrile concentration of the mobile phase.

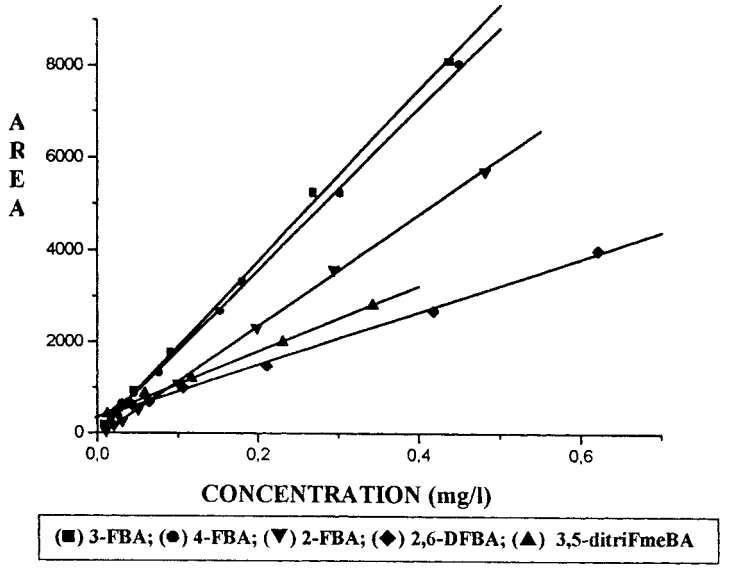

Figure 4. Calibration curves for selected tracer compounds.

Nevertheless, reservoir samples can contain interfering compounds eluting in the retention time window "reserved" for the fluorinated benzoic acids. Especially petroleum industry related chemicals, often present close to oil field installations (e.g. corrosion inhibitors), might interfere with the tracer analysis. Therefore the mobile phase composition has to be optimised for a given sample matrix.

All the evident tracer compounds have a distinct UV spectrum, due to the aromatic ring in the molecule, with two more or less distinguished absorption maxima near λ =270 nm and λ =223 nm, respectively, before the UV cut off is reached below 200 nm. The number and the position of the F- and CF_3-substituents explain the shift in the absorption maxima.

Detection is always a question of signal/noise ratio. Experiments showed that a wavelength of 223 nm gave a superior detector response with an acceptable background noise. Lower wavelength gave better response, but the background noise increased even faster. The response at higher wavelengths (e.g. λ = 270 nm) gave enhanced selectivity and hence less interference with organic substances possibly present in the reservoir sample; but the detector response at this wavelength was too low for a tracer application.

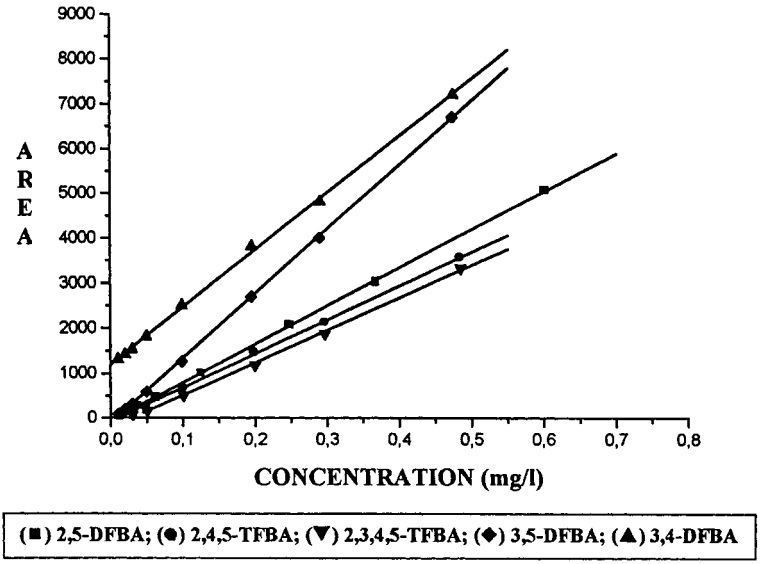

Figure 5. Calibration curves for selected tracer compounds.

The separation of 13 fluorinated benzoic acids out of the group of 16 tracer compounds within 9 minutes is shown in Figure 2. The mobile phase composition (mobile phase B) is described in Table 2. The separation of 13 analytes needs a rather long retention time window, thus increasing the probability of interference due to co-eluting substances present in a real sample.

Figure 3 shows an overlay of two chromatograms: A chromatogram of a reservoir sample and a chromatogram of the same reservoir sample spiked with 2,6-difluorobenzoic acid, 2-fluorobenzoic acid, 3-fluorobenzoic acid, and 4-fluorobenzoic acid. The detected tracer peaks are filled black. The tracer concentrations are in the range from 9 to 22 μg/L. In the retention time window between ca 1,5 min and 5,5 minutes, the chromatogram is almost free from interfering compounds. As it can be seen, the 2,6-difluorobenzoic acid (retention time 1,2 min) is not detectable at these low concentrations due to interference from non-retaining materials present in the sample. As shown in this example, the detection of 2,6-difluorobenzoic acid can be critical at low concentrations. A lower acetonitrile concentration and/or a pH-adjustment towards lower values can, however, increase the retention time of the tracer and avoid the interference with the little retained components.

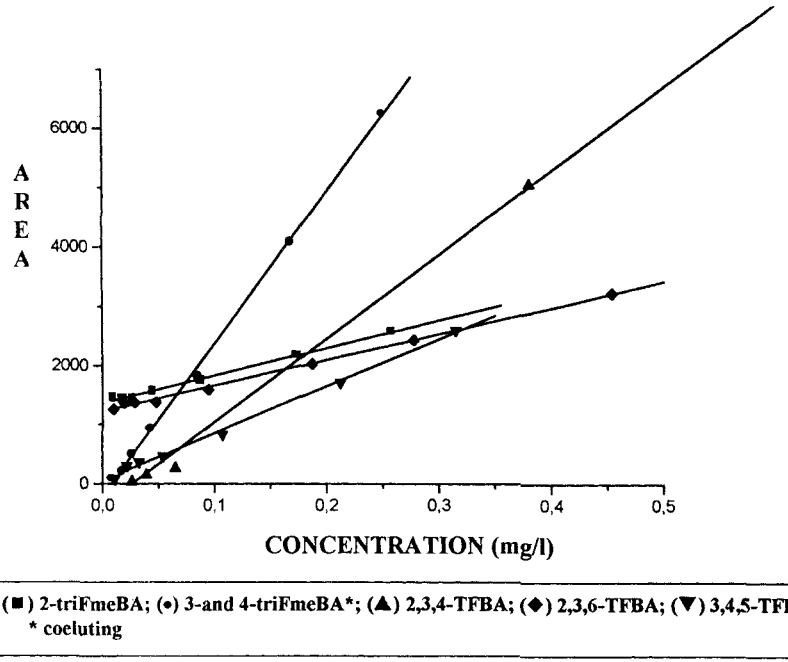

Figure 6. Calibration curves for selected tracer compounds.

With the exception of Figure 2, the mobile phase contained a low modifier concentration, typically between 15 and 25% acetonitrile, until the last tracer was detected. Then an acetonitrile gradient cleaned the column from the retarded organic background. Typical analytical conditions are shown in Table 2. The retention times for all fluorinated benzoic acids for given mobile phase conditions are listed in Table 3. As long as interfering substances were absent within the retention time window, tracer concentrations of about 10 μg/L have been detected for all compounds.

Standards were made from artificial formation water spiked with the selected tracer compounds in the concentration range from 10 μg/L up to 700 μg/L. The calibration curves ($n \geq 4$) show linearity for the relationship between the peak areas and the concentration of the tracer compounds from the detection limit up to 0,7 mg/L. The curves of all fluorinated benzoic acids are shown in Figures 4, 5 and 6. The linear coefficients were 0.9995 or better for all tracer candidates.

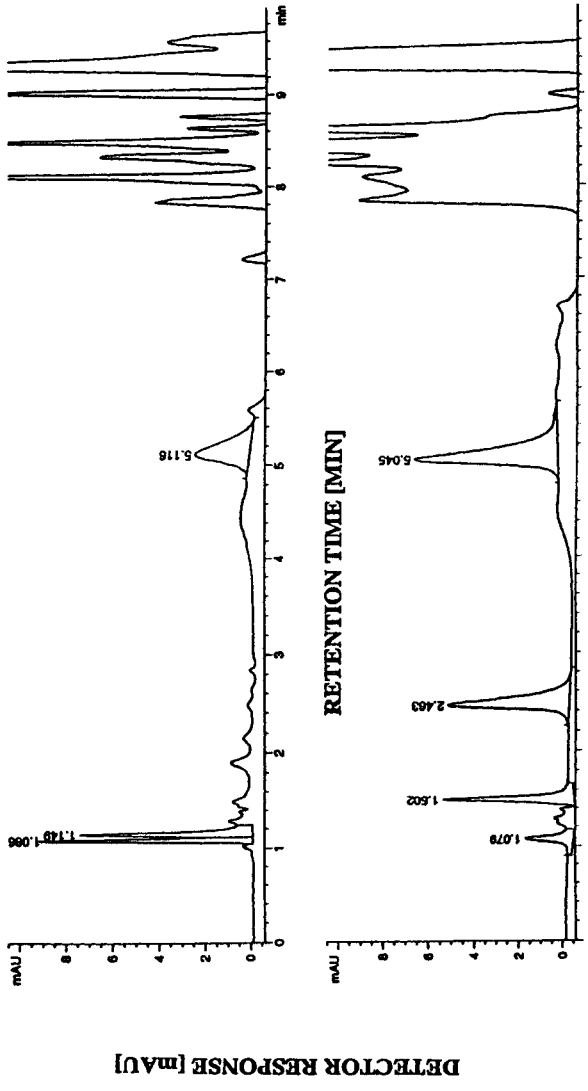

Figure 7. A chromatogram of a reservoir sample after breakthrough of the 3-fluorobenzoic acid (above) and a standard spiked with the tracer compounds 2,6-difluorobenzoic acid, 2-fluorobenzoic acid and 3-fluorobenzoic acid. The compound eluting at 5,1 min is identified as the 3-fluorobenzoic acid. A spectrum taken at the peak apex confirmed this result (see Figure 8).

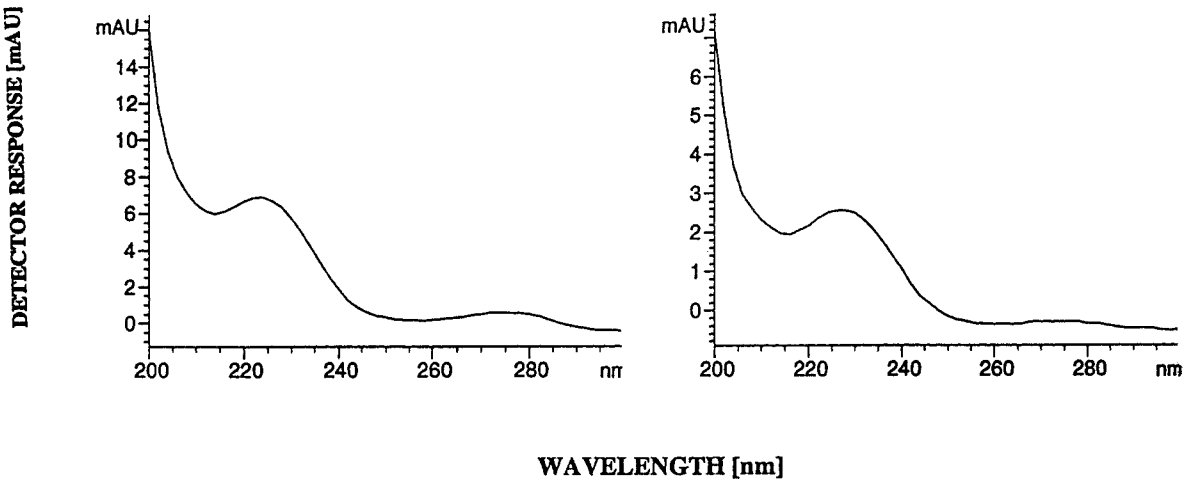

Figure 8. Spectra taken from the 3-fluorobenzoic acid: standard (left) and sample (right).

The compounds 2,6-difluorobenzoic acid, 2-fluorobenzoic acid and 3-fluorobenzoic acid and 4-fluorobenzoic acids have been injected as water tracers in North Sea reservoirs and were already analysed routinely, using the described method. Figure 7 shows the chromatograms of a standard spiked with the tracers injected into the reservoir and a reservoir sample from a production well, after breakthrough of the 3-fluorobenzoic acid.

The retention time window between 1.5 min and 6 min is almost free from background. The tracer is identified and quantified by comparison with the standard. The spectrum taken (Figure 8) confirmed the identity of the analyte. The organic background present in the sample did not interfere and eluted with the increasing acetonitrile concentration after 6 minutes.

CONCLUSION

A straightforward sensitive HPLC method for the determination of trace amounts of fluorinated benzoic acids in aqueous reservoir fluids without sample pre-treatment has been developed. North Sea reservoir samples containing selected tracer candidates have been analysed routinely, showing the applicability of this method.

In combination with a sample preparation and pre-concentration step this method should give the possibility to achieve detection limits in the sub ppb range.

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