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Ultra-trace determination of fluorinated aromatic carboxylic acids in aqueous reservoir fluids using solid-phase extraction in combination with gas chromatography–mass spectrometry

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Abstract

A method is presented for the ultra-trace determination of 16 fluorinated aromatic carboxylic acids in aqueous reservoir fluids. Up to 15 acids can be determined simultaneously. Solid-phase extraction on Isolute ENV+ cartridges and derivatization with diazomethane prior to gas chromatography–mass spectrometry enabled the reliable determination of the fluorinated acids as methyl esters in the ppt range. Determination of selected fluorinated aromatic carboxylic acids in aqueous reservoir samples, injected as water tracers in North Sea reservoirs, confirmed the applicability of the method.

Keywords: Water analysis; Carboxylic acids; Benzoic acids; Fluorobenzoic acids

1. Introduction

Fluorinated aromatic carboxylic acids have been used as water tracers earlier [1–7] but the relatively low sensitivity of high-performance liquid chromatography (HPLC)–UV techniques limited the number of suitable compounds, keeping in mind the high price of most fluorinated carboxylic acids.

Determination of carboxylic acids using gas chromatography (GC) – after derivatization – is a standard procedure and well described in the analytical literature. Alkylation or silylation are the most common derivatization reactions for carboxylic acids. Derivatization can also be used to enhance the detectability of the analytes. Electron-capture detection and electron-capture negative ionization mass spectrometry (MS) are highly sensitive detection techniques for analytes containing multiple halogen atoms. The introduction of multiple halogen atoms into the analyte molecule or the increase of the number of halogen atoms will increase the detectability [8].

Nevertheless, the major concern during this work was to enable GC–MS for the determination of the fluorinated carboxylic acids in aqueous reservoir fluids. Three things had to be taken into account: first, a suitable derivatization reagent had to be found. Some of the benzoic acids are substituted in one or both *ortho* positions (2-fluoro-, 2-trifluoromethyl- and 2,6-difluorobenzoic acid). Sterical hindrance and/or electronic effects as inductive effects or mesomeric effects are known to reduce the yield

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of normal alkylation reactions of carboxylic acids [9]. Diazomethane is a well known reagent for the instant and careful methylation of sterically difficult accessible functions [10]. Next, the analytes have to be separated from the naturally high content of inorganic and organic material present in aqueous reservoir samples. Third, the fluorinated aromatic carboxylic acids have to be pre-concentrated to enable detection in the sub-ppb range. Solid-phase extraction (SPE) is a suitable method to pre-concentrate analytes and to separate them from interfering compounds at the same time.

The low detection limits of the method, described in this paper, enables the use of 16 fluorinated aromatic carboxylic acids as water or water–oil partitioning tracers even in large reservoirs. Fig. 1 shows all 16 acids investigated in this paper.

2. Experimental

2.1. Equipment

For all GC–MS measurements a Fisons Series 8000 gas chromatograph equipped with a capillary split/splitless injection port and coupled to a Fisons MD 800 quadrupole benchtop mass spectrometer (Fisons, Manchester, UK) was used. An electron

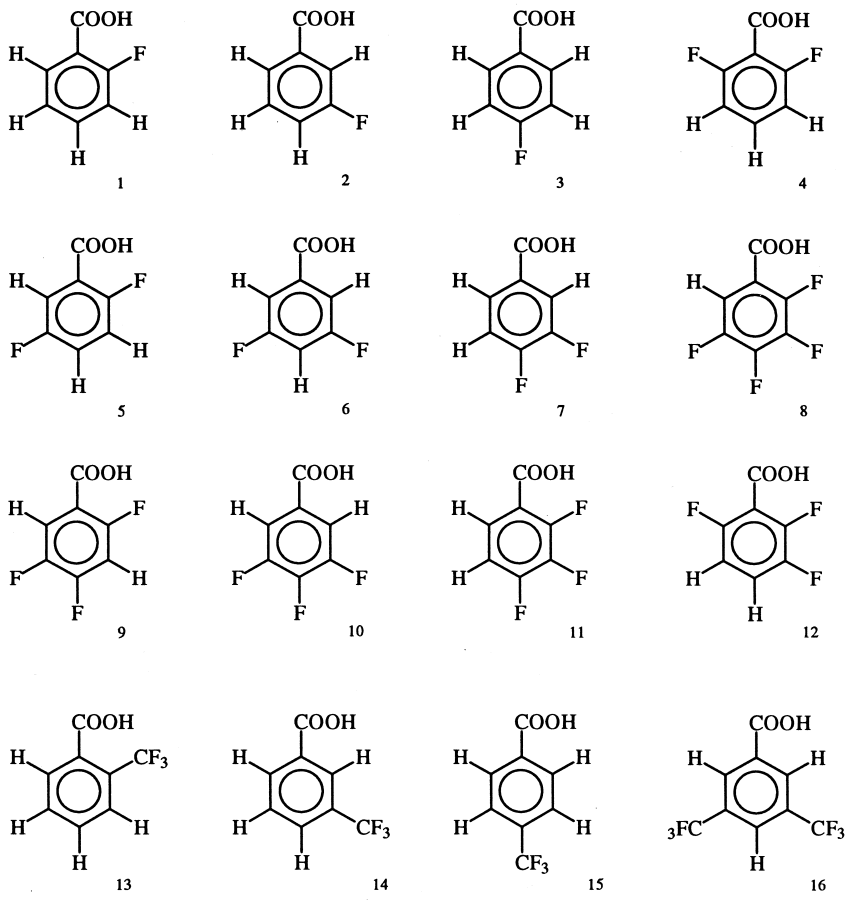

Fig. 1. Structures of the 16 fluorinated aromatic carboxylic acids investigated during this work. The compounds are: 1: 2-fluorobenzoic acid (2-FBA); 2: 3-fluorobenzoic acid (3-FBA); 3: 4-fluorobenzoic acid (4-FBA); 4: 2,6-difluorobenzoic acid (2,6-DFBA); 5: 2,5-difluorobenzoic acid (2,5-DFBA); 6: 3,5-difluorobenzoic 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)

impact ion source was used for all analyses. Several capillary columns were examined, but mainly two capillary columns were used for separation: a HP-5 (10 m×0.1 mm, 0.17 μm) (Hewlett-Packard, Waldbronn, Germany) and a J&W DB-1701 (20 m×0.1 mm, 0.4 μm) (J&W Scientific, Folsom, CA, USA). The MassLab data system (Fisons) was used for data handling. High-purity helium (6.0 quality; AGA, Oslo, Norway) was used as carrier gas. The detailed analytical conditions are described in Table 1.

SPE was carried out with disposable Isolute ENV+ cartridges (No. 915-0020-C); containing 200 mg sorbent material (International Sorbent Technology, Mid Glamorgan, UK). A Masterflex eight-channel peristaltic pump (Cole Palmer, Chicago, IL, USA) was used to pump the samples through the extraction cartridges. A heating block with N_2 supply from Liebisch (Bielefeld, Germany) was used for evaporation of the extracts. A diazomethane generator from Aldrich (Steinheim, Germany) (No. Z10159-1) was used for reagent synthesis.

2.2. Chemicals

1-Methyl-3-nitro-1-nitrosoguanidine (MNNG) 97% – the diazomethane precursor – was purchased from Aldrich. All 16 fluorinated aromatic carboxylic acids (purum quality: ≥97%) were supplied by Fluorochem (Old Glossop, UK). The solid-phase extracts were eluted with acetonitrile (HPLC grade), purchased from Rathburn (Walkerburn, UK). Hydrochloric acid (30%, Suprapur), used for pH adjustment, was supplied from Merck (Darmstadt, Germany). Ether and all other chemicals, as the drying agent Na_2SO_4 and NaOH for generation of diazomethane were analytical-reagent grade and all supplied by Merck.

2.3. Solid-phase extraction

A 250 ml volume of an aqueous reservoir sample was filtered through a 0.45 μ filter (Millipore, UK) to clean the sample of solid matter and droplets of crude oil. Then the pH was adjusted to 1.5 before the sample was pumped through the prepared SPE cartridge. Prior to the application of sample the sorbent material was soaked with acetonitrile and then 10 ml of acetonitrile was passed through the cartridge before the sorbent material was equilibrated to pH 1.5 with 25 ml aqueous hydrochloric acid. Drying the sorbent material between cartridge preparation and sample application can result in an earlier breakthrough of the analytes and hence irreproducible recoveries. There should be always a small volume of liquid on top of the sorbent material.

Table 1
GC–MS parameters for the analysis of the examinasted fluorinated benzoic acids

Injection		
Mode	Splitless (30 s) for trace concentration Split for ng amounts	Sample volume: 1 μl
Column head pressure	10 p.s.i. (HP-5 column) 20 p.s.i. (J&W DB-1701 column)	
Temperatures		
Injection temperature	250°C	
Interface temperature	250°C	
Source temperature	200°C	
Oven temperature program		
HP-5 column	60°C→2 min, ↑25°C/min, 100°C, ↑3°C/min, 125°C, ↑25°C/min, 275°C→1 min	
J&W DB-1701 column	60°C→2 min, ↑25°C/min, 125°C, ↑3°C/min, 175°C, ↑25°C/min, 275°C→2 min	
Mass spectrometer		
Mode	SIR for trace detection Scanning for mass spectra recording	Electron energy: 70 eV

1 p.s.i.=6894.76 Pa.

The sample was then loaded at a flow-rate of 10 ml/min. After sample loading, the cartridges were dried by a stream of nitrogen, and the fluorinated aromatic carboxylic acids were carefully and quantitatively eluted with 6 ml acetonitrile into vials. The vials were placed into a heating block with N_2 support and carefully evaporated to dryness. The residue was dissolved in 300 μl dry acetonitrile (Na_2SO_4) and transferred to 1.8 ml screwcap vials (Chromacol, Hearts, UK), where 100 μl diazomethane solution was added. A 1 μl aliquot of this final solution was analyzed by GC–MS. For routine analysis of unknown analyte concentrations an internal standard was added prior to sample processing.

2.4. Breakthrough experiments

The breakthrough experiments were carried out in a similar fashion. A 1 l volume of an aqueous reservoir sample from a North Sea Oil Field was spiked with 14 of the fluorinated aromatic carboxylic acids. The spike contained the fluorinated compounds in concentrations between 10 and 40 mg/l. 5 ml of the spike was then added to the reservoir sample to give 0.05 to 0.2 mg/l concentrations. Two replicates were prepared as described above and pumped through the ENV+ cartridges. Fractions of 100 ml were sampled. Preliminary breakthrough tests with selected acids showed no breakdown after 100 ml; analyses were performed with HPLC–UV. Altogether ten 100 ml fractions were processed as described above and finally analyzed by GC–MS.

3. Results and discussion

SPE is a suitable technique both to separate analytes from an interfering sample matrix and to pre-concentrate simultaneously. Depending on the sorbent material chosen, the sample matrix will always have an impact on the performance of SPE. The fluorinated aromatic carboxylic acids are organic compounds and in the normal pH range carboxylate anions. Theoretically both attributes can be used for extraction, thus an anion-exchange material or a ''reversed-phase'' material be candidates for SPE. Nevertheless, the high content of inorganic ions in aqueous reservoir samples will likely lead to an overload of any anion-exchange sorbent material. Reversed-phase materials need to withstand a pH of 1.5. Also the capacity of silica based materials for the polar carboxylic acids was found to be limited. However, the polymeric sorbent material Isolute ENV+, a cross-linked polystyrene material, was found to have both the stability at low pH and a high capacity for polar organic compounds.

The breakthrough experiments were carried out with real reservoir matrices (North Sea Oil Field) and with tracer concentrations higher than expected in reservoir studies to ensure reliable analytical conditions.

GC–MS analyses of all ten 100 ml fractions of the replicate samples (1 l), which were pumped through the SPE cartridges, were used to determine the breakthrough volume. 2,6-Difluorobenzoic acid was found as the first eluting compound in the third fraction. Eight compounds had their breakthrough in the fifth fraction, while 2-fluorobenzoic acid was detected in the fourth fraction. 3,4,5-Trifluorobenzoic was found in the seventh fraction. The 3- and 4-(trifluoromethyl)benzoic acid and the 3,5-di(trifluoromethyl)benzoic acid were not detected in any of the ten fractions. The acids with one or two fluorine atoms in *ortho* position had lower breakthrough volumes while acids substituted with fluorine in the *meta* and/or *para* position had higher breakthrough volumes. This behaviour corresponded to the retention times of the fluorinated acids on C_{18} columns in reversed-phase HPLC [7] and can be explained by two parameters: acidity and molecular size of the compounds. With increasing acidity the breakthrough volume is decreased, while increasing molecular size increases the breakthrough volume due to more effective interactions with the sorbent material.

The separations were mainly carried out on GC columns with an internal diameter of 0.1 mm. Decreasing the column diameter and length give shorter analysis time with the same column efficiency. Another advantage is the lower vacuum achieved in the mass spectrometer due to the lower carrier gas flow and hence a better sensitivity. Not all fluorinated benzoic acids were separated on the time axis. But in combination with the mass axis 14 of the 16 tracer compounds were separated on the HP-5 column and 15 out of 16 on the DB-1701 column.

Neither the 3- and 4-fluorobenzoic acids, nor the 2,6- and the 2,5-difluorobenzoic acids could be separated by retention time on the HP-5 column, while the 2,6- and the 2,5-difluorobenzoic acid were separated by retention time on the DB-1701 column (see Table 2).

Mass spectra of the fluorinated benzoic acids showed the expected fragmentation reactions [11]. The molecular ion was readily detectable for all methyl benzoates. The loss of the methoxy group ([M−31]) is the main fragmentation reaction for all methyl esters of the fluorinated carboxylic acids and leads to the stable benzoyl cation. The benzoyl cation decomposes further by the loss of carbon monoxide. This behaviour is similar for all fluorinated aromatic carboxylic acids and gives three fragments which can be used for detection in the selected ion recording (SIR) mode. Table 2 shows the retention times and actual m/z values for all 16 compounds.

Fig. 2 is a gas chromatogram showing the separation of 14 fluorinated aromatic carboxylic acid methyl esters using the J&W DB-1701 column. The chromatogram was taken in the SIR mode.

Selected fluorinated benzoic acids as 2- and 4-fluorobenzoic acid or 2,6-difluorobenzoic acid have already been injected as water tracers in several North Sea reservoirs. Reservoir samples containing unknown amounts of the injected tracers were routinely analyzed using the described method.

Fig. 3 shows the SIRs of a real reservoir sample containing the internal standard 3-trifluorobenzoic acid (4 μg/l) and an unknown amount of 4-fluorobenzoic acid. The molecular ion (1) and the base peak (4) of the methyl ester of the analyte, present in a given ratio at the defined retention time, confirmed the presence of 4-fluorobenzoic acid in the sample. Fragments (2) (molecular ion) and (3) (base peak) represent the methyl ester of the internal standard 3-(trifluoromethyl)benzoic acid. The increasing background present in the lower chromatogram m/z 123 can make detection difficult and a quantification based on calibration of the base peak response impossible. In cases of high background at m/z 123, the ion current at m/z 154 had to be used for quantification of 4-fluorobenzoic acid.

An internal standard was added to the reservoir samples prior to sample processing. This standard compound should behave in a manner similar to that of the analyte during the sample pre-treatment. This means that all 16 compounds investigated in this work could be used as suitable internal standards for each other, as long as they are not interfering during the GC–MS analysis. Unfortunately all the fluorinated benzoic acids are only available in purum

Table 2
Retention times and masses of the fluorinated aromatic carboxylic acids

Tracer compounds detected as methyl ester	Retention time (min) for columns		Mass (m/z) used for detection mol. peak, base peak, '3rd' peak		
	DB-1701	HP-5	[M]	[M−31]	[M−59]
2-Fluorobenzoic acid	18.9	8.6	154	123	95
3-Fluorobenzoic acid	16.4	7.4	154	123	95
4-Fluorobenzoic acid	16.4	7.4	154	123	95
2,6-Difluorobenzoic acid	17.9	7.7	172	141	113
2,5-Difluorobenzoic acid	17.4	7.7	172	141	113
3,5-Difluorobenzoic acid	14.3	6.3	172	141	113
3,4-Difluorobenzoic acid	16.2	7.2	172	141	113
2,4,5-Trifluorobenzoic acid	15.6	6.8	190	159	131
2,3,4-Trifluorobenzoic acid	16.9	7.5	190	159	131
3,4,5-Trifluorobenzoic acid	14.4	6.4	190	159	141
2,3,6-Trifluorobenzoic acid	17.1	7.2	190	159	131
2,3,4,5-Tetrafluorobenzoic acid	14.7	7.1	208	177	149
2-(Trifluorormethyl)-benzoic acid	18.2	8.1	204	173	145
3-(Trifluoromethyl)-benzoic acid	16.5	7.5	204	173	145
4-(Trifluoromethyl)-benzoic acid	16.1	7.3	204	173	145
3,5-di(Trifluoromethyl)benzoic acid	12.8	5.9	272	241	213

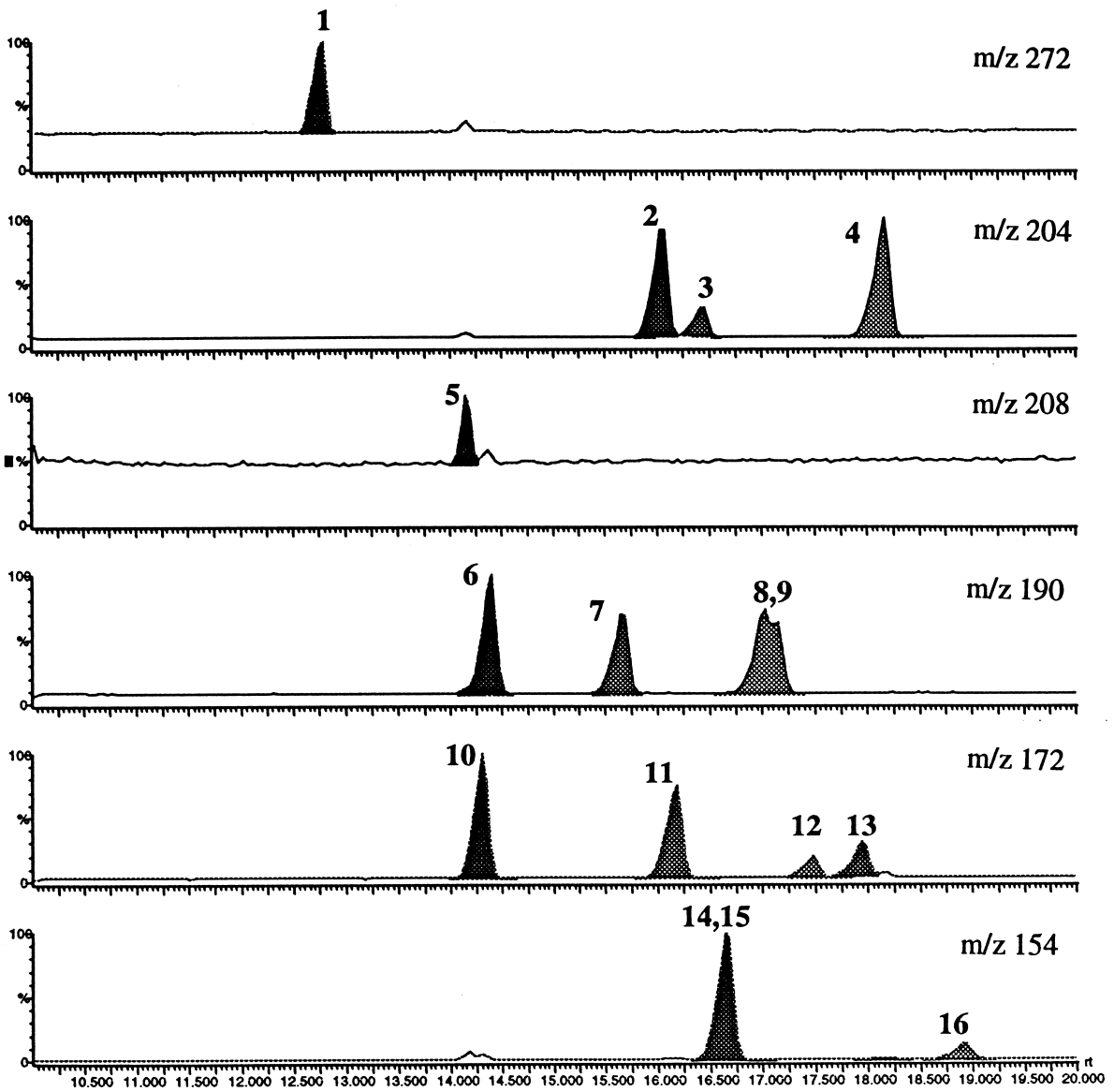

Fig. 2. SIRs showing the separation of 14 fluorinated benzoic acid methyl esters on the DB-1701 column. The response at the given m/z values, representing the molecular mass of the analytes, are shown as a function of the retention time. 1: 3,5-ditriFmeBA (12.8 min); 2: 4-triFmeBA (16.1 min); 3: 3-triFmeBA (16.5 min); 4: 2-triFmeBA (18.2 min); 5: 2,3,4,5-tFBA (14.2 min); 6: 3,4,5-tFBA (14.4 min); 7: 2,4,5-tFBA (15.6 min); 8+9: 2,3,4-tFBA/2,3,6-tFBA (17.0/17.1 min); 10: 3,5-dFBA (14.3 min); 11: 3,4-dFBA (16.2 min); 12: 2,5-dFBA; (17.4 min); 13: 2,6-dFBA; (17.9 min); 14+15: 3-FBA/4-FBA (16.4 min) 16: 2-FBA (18.9 min).

quality (≥97%). To ensure that the internal standard was not contaminated with any of the tracers, the 3-(trifluoromethyl)benzoic acid was selected as internal standard. No aromatic carboxylic acid, with fluorine substituted in the benzene ring, can be formed during production of 3- (trifluoromethyl)benzoic acid. Nevertheless the purity of the internal standard limits the accuracy of the quantification.

Standard solutions containing the tracers: 2-fluorobenzoic acid, 4-fluorobenzoic acid and 2,6-difluoro-

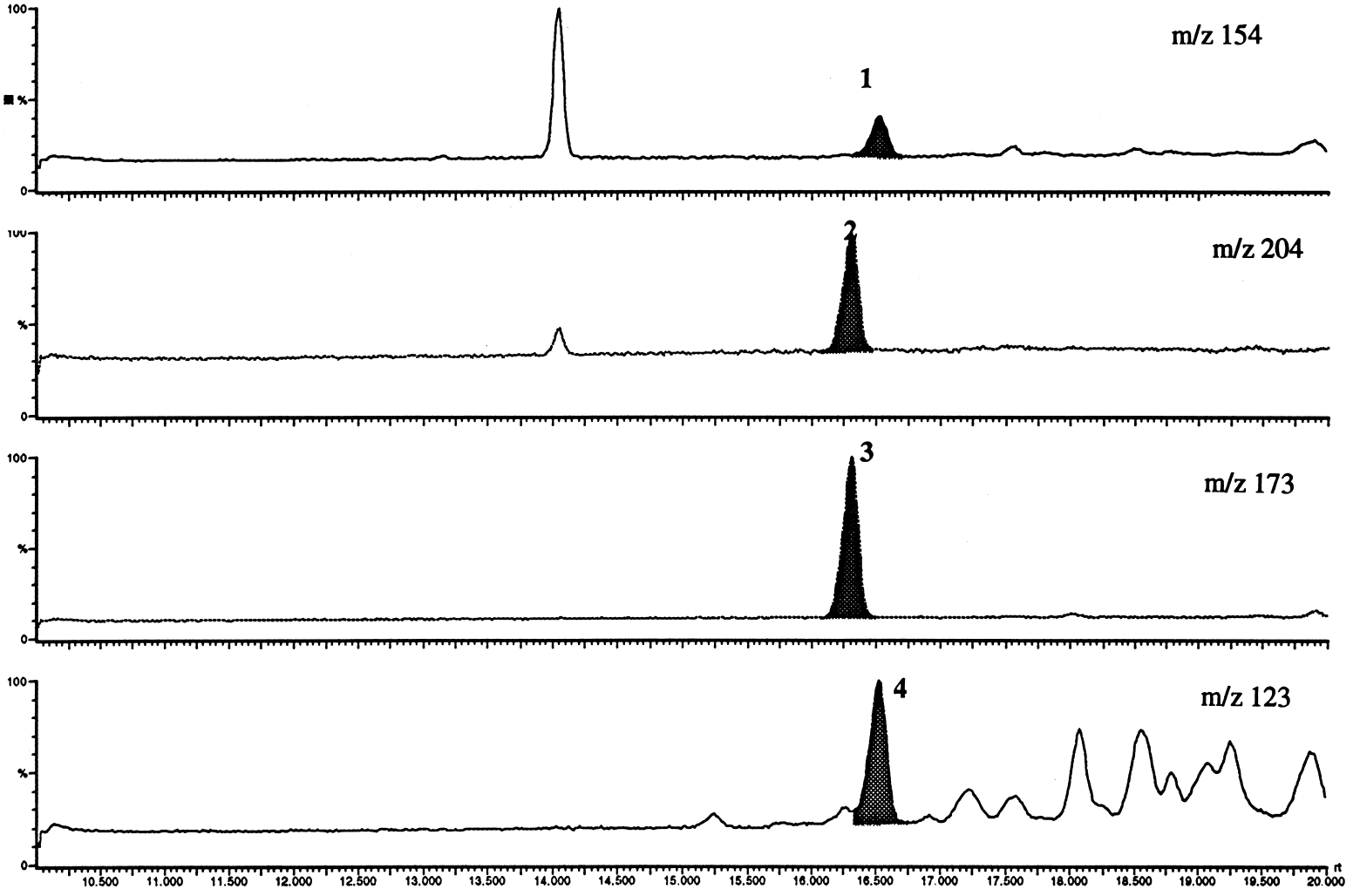

Fig. 3. SIRs of a real sample containing an unknown amount of the water tracer 4-FBA and the internal standard 3-triFmeBA. The presence of the analyte is confirmed by detection of the molecular ion (1) and the base peak (4) (of the methyl ester) at the same retention time (16.5 min). The internal standard (2: molecular ion; 3: base peak) is added prior to sample processing.

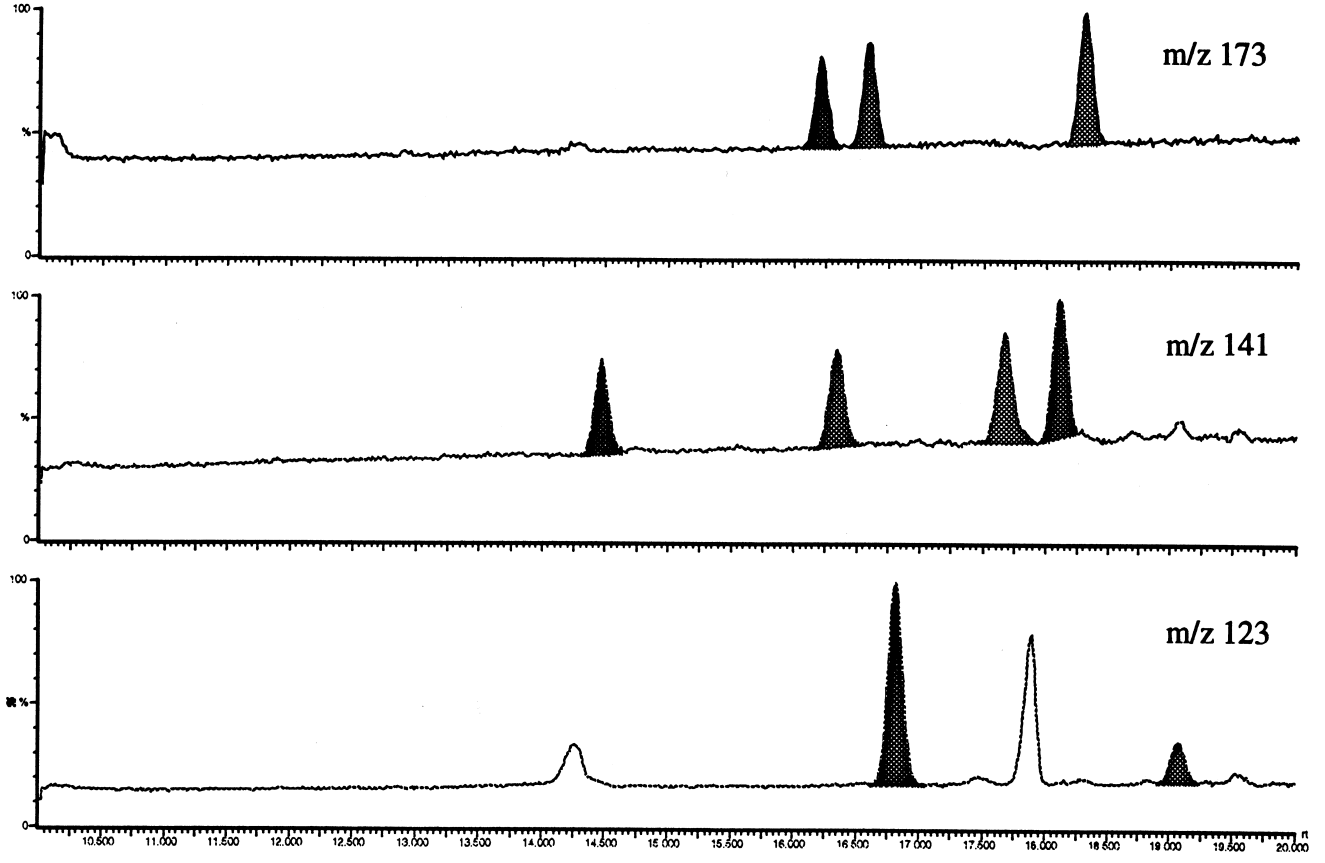

Fig. 4. SIRs of a real reservoir sample (North Sea Reservoir) spiked with selected water tracers (concentration: 0.1 to 0.5 μg/l). Upper panel: in order of retention time: 4-triFmeBA, 3-triFmeBA and 2-fluoromethyl benzoic acid. Middel panel: 3,5-DFBA, 3,4-DFBA, 2,5-DFBA and 2,6-DFBA. Lower panel: 3- and 4-FBA (co-eluting), 2-FBA (all detected as methyl esters).

Table 3
Reproducibility of the described method

	Area ratio 4-FBA/ISTD	Concentration (μg/l)	Standard deviation
Sample A-prep 1	0.2583	0.50	
Sample A-prep 1	0.2672	0.53	
Sample A-prep 2	0.2648	0.52	
Sample A-prep 2	0.2356	0.43	0.04
Sample B-prep 1	0.2261	0.40	
Sample B-prep 1	0.2145	0.36	
Sample B-prep 2	0.2284	0.40	
Sample B-prep 2	0.2367	0.43	0.03
Sample C-prep 1	0.3169	0.60	
Sample C-prep 1	0.3039	0.64	
Sample C-prep 2	0.2927	0.68	
Sample C-prep 2	0.3264	0.71	0.05

Experimental conditions as in Table 1 (DB-701 column).

benzoic acid in the concentration range from 0.4 to 40 μg/l and the internal standard 3-(trifluoromethyl) benzoic acid were prepared and processed as previously described. The calibration curves, based on SIR either of the molecular ions ([M]) or the benzoyl cations ([M−31]) of the tracer compounds, showed a linear response for the examined compounds within the selected concentration range. The linear coefficients were between 0.99498 and 0.99992 for the examined tracers.

Chromatograms of a real sample spiked with selected benzoic acids (concentrations between 0.1 and 0.5 μg/l) are shown in Fig. 4. One liter of sample was processed. After evaporation of the extract, the residue in this case was dissolved in 100 μl acetonitrile and 100 μl of diazomethane solution was added.

The reproducibility of the method is shown in Table 3. Real reservoir samples from North Sea reservoirs, containing unknown amounts of 4-fluorobenzoic acids, were each pre-concentrated in parallel on two cartridges and each pre-treated sample was analyzed twice by GC–MS. Standard deviations of about 0.05 μg/l for tracer concentrations below 1 μg/l in real reservoir samples were obtained, showing the applicability of the procedure for ultra-trace determination of tracer compounds in aqueous reservoir samples.

4. Conclusions

An analytical method for ultra-trace determination of fluorinated carboxylic acids, used as water tracers, in aqueous reservoir fluids has been established. The method combines SPE on Isolute ENV+ sorbent with GC–MS and enabled detection of tracer concentrations down to 0.1 μg/l after derivatization with diazomethane. Improvements are also possible. The use of larger extraction cartridges will enable the processing of larger sample volumes and hence lowering the detection limits. An internal standard with higher purity (if available) can give a more accurate quantification of the tracer molecules.

Nevertheless, the described analytical procedure increases the number of available water tracers (water–oil partitioning tracers) with 16 fluorinated benzoic acids. A better and more detailed reservoir description and hence a better oil recovery is then made possible.

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