



## Short communication

# Direct sensitive simultaneous determination of fluorinated benzoic acids in oil reservoir waters by ultra high-performance liquid chromatography–tandem mass spectrometry

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## ABSTRACT

A direct ultra-high performance reverse-phase HPLC (UHPLC) – electrospray MS/MS method was developed for the simultaneous determination of 16 fluorinated benzoic acids (FBAs) in oil reservoir waters. The separation was achieved within 5 min in a non-linear gradient mode using a 1-ml sample aliquot. The method detection limits were in the lower ng/ml range (between 0.05 and 50 ng/ml, depending on the compound) owing to the use of the travelling-wave collision cell technology. The method developed was more sensitive, faster (by avoiding sample preconcentration and purification steps) and more robust than the GC/MS methods currently used in oil industries. The accuracy of the method was verified by comparison with GC/MS results. It was applied to the determination of FBAs in water samples coming from reservoir tracing campaigns.

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## 1. Introduction

Fluorinated benzoic acids (FBAs) are the most widely used tracers in campaigns aimed at the description of oil reservoirs [1,2]. As they are injected in low quantities, ultra-sensitive analytical techniques are required for their determination. The current reference analytical technique is gas chromatography with MS detection (GC/MS) which offers detection limits of 10–100 pg/ml [3,4]. However, the analysis time is long (60 min) and the procedure requiring a complex sample preparation (clean-up, derivatization) is tedious and error-prone (losses or contamination) [5].

The two most commonly used methods for benzoic acids are high-performance liquid chromatography (HPLC) and gas chromatography (GC) [6,7]. As FBAs are nonvolatile and polar, HPLC offers an advantage of the elimination of the need for derivatization and thus of a potentially faster direct analysis. However, the reported HPLC detection limits are three orders of magnitude higher (UV detection) [8–12] and one order of magnitude higher

(MS–MS detection) [13] than those reported by GC–MS. Ways to improve them include the use of ultra high-performance liquid chromatography (UHPLC) [14–16] and the use of the latest generation mass spectrometers.

The objective of this work was to develop a method for the rapid determination of FBA traces in oil reservoir waters matching the sensitivity of the state-of-the-art GC methods [3,4] but avoiding the tedious sample preparation. A compromise needed to be found between peak capacity, chromatographic resolution, sensitivity, matrix effect and analysis time. This was achieved by the combination of UHPLC with multiple reaction monitoring (MRM) MS using travelling-wave collision cell technology (without and with scan-wave mode). This new type of mass analyzer uses a travelling voltage wave on which ions can surf maximizing analysis speed and sensitivity. The signal intensity is further improved in scan-wave mode because the ions are accumulated before being separated according to their mass-to-charge ( $m/z$ ) ratio [17].

## 2. Experimental

### 2.1. Reagents and chemicals

19 FBA standards (purity > 97%) (Table 1) were purchased from Apollo Scientific (Denton, Manchester, UK). The chemicals: acetonitrile (CH<sub>3</sub>CN, Fluka, LC/MS, 99.9%), acetic acid (CH<sub>3</sub>COOH, glacial,

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**Table 1**  
MS/MS optimized conditions for the Xevo TQ MS instrument.

Compound	Chemical formula	Nominal mass (g/mol)	MRM transition	Cone voltage (V)	Collision energy (eV)
2-FBA	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> F	140	138.84 > 94.97	17	10
3-FBA			138.84 > 94.97	17	10
4-FBA			138.84 > 94.97	17	10
2,3-dFBA	C <sub>7</sub> H <sub>4</sub> O <sub>2</sub> F <sub>2</sub>	158	156.84 > 112.97	16	10
2,4-dFBA			156.84 > 112.97	16	10
2,5-dFBA			156.84 > 112.97	16	10
2,6-dFBA	C <sub>8</sub> H <sub>5</sub> O <sub>2</sub> F <sub>3</sub>	176	156.85 > 112.97	16	10
3,4-dFBA			156.85 > 112.97	20	14
3,5-dFBA			156.85 > 112.97	20	12
2,3,4-tFBA	C <sub>9</sub> H <sub>4</sub> O <sub>2</sub> F <sub>6</sub>	258	174.84 > 130.95	14	10
2,3,6-tFBA			174.84 > 130.95	14	10
2,4,5-tFBA			174.84 > 130.95	14	10
2,4,6-tFBA	C <sub>7</sub> H <sub>2</sub> O <sub>2</sub> F <sub>4</sub>	194	174.84 > 130.95	14	10
3,4,5-tFBA			174.85 > 130.95	20	14
2-tFmBA			188.90 > 144.97	22	14
3-tFmBA	C <sub>9</sub> H <sub>4</sub> O <sub>2</sub> F <sub>6</sub>	258	188.90 > 144.97	22	14
4-tFmBA			188.90 > 144.97	22	14
2,3,4,5-tetraFBA			193.00 > 148.95	14	8
3,5bis-tFmBA			257.00 > 212.90	26	18

Abbreviations: F, fluoro; B, benzoic; A, acid; d, di; t, tri; tFm, trifluoromethyl.

Riedel-de Haën, 100%), formic acid (HCOOH, Fluka, 98%, MS grade), sodium hydroxide (NaOH, Rectapur, Prolabo, 98% min), ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>, ReagentPlus, 99%), were purchased from Sigma–Aldrich (Saint-Quentin, Fallaviers, France). Ultra-pure water (18.2 MΩ cm) obtained from a Millipore system (systems Elix 3 and Advantage, Millipore, Saint-Quentin, France) was used throughout.

## 2.2. Standards and samples

Standard solutions (300 μg/ml) were prepared by dissolving between 14.0 and 25.8 mg (accurately weighed) of a FBA in 40 ml water and 10 ml 3975 μg/ml NH<sub>4</sub>HCO<sub>3</sub> solution. They were stored at 4 °C in the dark up to four months (the stability of their concentrations after four months of storage was confirmed within 10%). Working solutions were prepared by appropriate dilution of the stock solutions with water. Reservoir water samples spiked with a mixed standard solution at different concentrations (between 500 ng/ml and 100 pg/ml) were used for the method development. The analysed samples were oil reservoir waters from three tracing campaigns.

The samples were filtered through a GHP Acrodisc 13-mm syringe filter (0.2 μm GHP membrane, Pall Life Sciences, Interchim, France). The samples showed low to middle salinity (<10 g/L equivalent NaCl). In the case of higher salt content, samples should be diluted with 0.1% HCOOH prior to filtration in order to avoid the formation of a salt deposit on the cones and signal suppression [16].

## 2.3. Apparatus

An Acquity UPLC system (Waters Corp., Milford, MA) including a binary solvent pump, a cooled autosampler, an Acquity UPLC BEH C<sub>18</sub> column, 50 mm × 2.1 mm (1.7 μm particles, Waters) with a matching Vanguard precolumn was used.

The detectors were: a diode-array UV detector (Acquity) used at 265 nm, a TQD (quadrupole–hexapole–quadrupole in T-wave mode) (Waters, Milford, MA) or XevoTQ (quadrupole–T–wave–quadrupole in scan wave mode) MS with an orthogonal Z-spray–electrospray interface (Waters). A hybrid mass spectrometer ESI-QTOF (QSTAR XL, Sciex, ON, Canada) was used in the method development.

## 2.4. Procedures

### 2.4.1. Chromatographic separation

The parameters studied included: mobile phase composition (H<sub>2</sub>O/CH<sub>3</sub>CN containing 0.1% of HCOOH or CH<sub>3</sub>COOH), LC-gradients and columns (Acquity UPLC BEH C<sub>18</sub> column: 2.1 mm × 50 mm, particle size 1.7 μm, and Acquity BEH HILIC column: 1 mm × 150 mm, 1.7 μm). Because of the target analytes and the detection in ESI<sub>neg</sub> mode, it was decided not to work with an ion-pairing agent, such as trifluoroacetic acid (TFA) or heptafluorobutyric acid (HFBA).

Mobile phase was a mixture of water (A) and acetonitrile (B), both containing 0.1% HCOOH. The elution gradient (non-linear hyperbole) was: 0 min (5% B), 0.2 min (10% B), 1.8 min (28% B), 2.5 min (80% B), 3.2 min (80% B), and 4 min (5% B) for 1 min. The gradient steps after 2.5 min served to clean and re-equilibrate the column to guarantee the repeatability of the analysis. Total analysis time was 5 min, column equilibration included. The injected volume was 10 μL (or more if a sample was diluted). The flow rate was 0.85 ml/min, the column temperature was 45 °C and the autosampler temperature was 5 °C.

### 2.4.2. Mass spectrometric conditions

MS/MS data acquisition was performed with the electrospray source operating in negative mode (ESI<sub>neg</sub>) under the MRM conditions listed in Table 1. The MS parameters were optimized for each instrument (see Supplementary Data file and detailed procedure described elsewhere [18]). The optimized values for the Xevo TQ MS instrument were: capillary voltage 2.50 kV; source temperature 150 °C; desolvation temperature 400 °C; extractor voltage 3 V; RF lens 0.4 V. Nitrogen was used as both the nebulizing gas and the desolvation gas. Cone gas and desolvation gas flows were set at 20 L/h flow and 1000 L/h respectively. Argon was used as collision gas with a pressure of  $2 \times 10^{-3}$  mbar in the T-wave cell. Dwell times of 0.010 s/scan for 2,3,4,5-tetraFBA and 3,5bis-tFmBA and 0.017 or 0.025 s/scan for the other FBAs, were selected. The Masslynx software (Waters Corp., Milford, MA) was used to process data. Quantification was based on peak area.

## 3. Results and discussion

### 3.1. Choice of chromatographic conditions

Acetonitrile was selected owing to its lesser toxicity than methanol. Despite the FBAs pK<sub>a</sub> values being below 4, it was

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