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Sensitive simultaneous determination of 19 fluorobenzoic acids in saline waters by solid-phase extraction and liquid chromatography–tandem mass spectrometry

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ABSTRACT

A solid-phase extraction (SPE) procedure using C_{18} stationary phase was optimized for the preconcentration of 19 fluorinated derivatives of benzoic acid (FBA): mono-, di-, tri-, and tetrafluorosubstituted in the ring, trifluoromethylbenzoic acid and 3,5-bistrifluoromethyl benzoic acid from undiluted salt-rich (>20%) reservoir waters. Quantitative (>90%) retention/elution of 16 out of 19 analyte compounds was achieved allowing a fourfold preconcentration factor accompanied by the elimination of >99% of salt. For the three most polar compounds (2,6-dFBA, 2,3,6-tFBA, and 2,4,6-tFBA) the non-quantitative recoveries (>70%) were corrected by dedicated custom-synthesized deuterated internal standards. The FBAs were determined by HPLC – MS/MS revisited in terms of a choice of column, elution conditions and MS/MS signal acquisition parameters allowing the baseline separation and a gain in sensitivity. For a sample intake of 4 mL, detection limits for all the compounds in a reservoir water sample containing more than 20% salt were between 0.01 and 0.05 ng/mL which represents a gain of a factor of 10–20 in comparison with the state-of the art LC–MS/MS procedures for samples of similar complexity.

1. Introduction

Derivatives of benzoic acid with one or more fluorine atoms, or one or more trifluoromethyl groups, attached to the aromatic ring are the most common currently used non-radioactive passive water tracers for oil field applications [1]. As a tracing campaign involves a set of several different compounds (out of more than 20 commercially available), there is a need for methods for their simultaneous determination in an oil reservoir water matrix. Low detection limits are critical as they determine the quantity of the tracers necessary to be used and thus the cost and the environmental impact of the campaign. The matrix differs depending on the sample origin but it is usually rich in salts (reaching in some cases up to 30%) and organic constituents [2].

The lowest detection limits (down to 0.01 ng/mL) were obtained by gas chromatography (GC)-MS but lengthy (24 h) and tedious sample preparation procedures including matrix removal and derivatization were necessary [3]. The incomplete and strongly compound-dependent yields required compound specific isotope dilution calibration that was proposed for six species determined to achieve accurate analysis [4,5].

The alternative is the use of HPLC-MS/MS analysis to eliminate the derivatization step and thus to simplify the sample processing. The original work [5], which was applied to simple matrices but did not show any chromatogram reported fairly high detection limits: 0.5–1 ng/mL for electrospray ionization (ESI) and 10–20 ng/mL for atmospheric pressure chemical ionization (APCI), respectively. The detection limits were considerably (about an order of magnitude) decreased by Serres-Pioles et al. [1] except for tFBA, for which hardly any improvement was observed. The maximum tolerated salt content of the samples allowed by the method was pretty low (1%) which required a considerable sample dilution (10–20 times) drastically limiting the scope of the method applications.

Although the reported selectivity of HPLC separation of a set of usually studied 20 tracers was generally high, the baseline separation of all of them was not achieved in any of the published works [3–9]. This caveat was compensated by the determination of the co-eluting compounds using different fragmentation

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reactions. On the other hand, the number of theoretical plates achieved in HPLC is important. Indeed, the poor specificity of fragmentation reactions (the loss of CO_2) used for the quantification, in combination with the unit resolution of a quadrupole filter and matrix rich in organic acids, may lead to the increase in baseline and false positives.

The above reasons spur the need for the development of methods allowing a considerable enrichment of FBAs with regard to salt and organic matrix. Solid phase extraction (SPE) is an attractive option for both matrix removal and preconcentration of analytes [10–12] prior to LC–MS/MS analysis of samples rich in salts. However, quantitative SPE of FBAs from reservoir waters is a difficult task because of the high polarity of the tracers. The problems result, on one hand, from the difficulty to trap quantitatively and simultaneously all the analytes while avoiding the retention of the matrix and, on the other hand, to release the trapped analytes quantitatively without substantial dilution. Another critical factor is the sample volume to be used for analysis as it determines the SPE time.

As a result of an extensive optimization study, Müller et al. reported fairly satisfactory recoveries (between 71% (2,5-dFBA) and 94% (3-FBA)) from tap water [7] but for reservoir waters the extraction efficiencies were generally low (down to 18% for 2,3,5,6-tetraFBA and 2,6-dFBA) and strongly compound-dependent [3]. Moreover, relatively large sample volumes (100 mL) processed [3,7] resulted in long analysis times. The recovery problems were (for six selected compounds) addressed by the use of custom synthesized deuterated internal standards [4] which were used in the analysis of reservoir and ground water [8].

The main goal of this work was the development of a rapid (small sample volume) quantitative SPE method allowing a direct multitracer (19 compounds) analysis in salt-rich (>20% salt) reservoir water samples with an objective to reach at least an order of magnitude in terms of detection limits over the direct injection procedure [1].

2. Experimental conditions

2.1. Samples collection

Reservoir water samples of different origins with different salt contents: Gabon (200 g/L), Qatar (220 g/L), Russia (170 g/L), Yemen (80 g/L) and Congo (250 g/L) were used for the method development. The salts components were primary sodium and calcium with minor contribution of potassium and magnesium [2]. The samples were collected in 5-L glass flasks and the aqueous and organic fractions were separated by gravitation. Sub-samples of 100 mL were transported in ambient temperature in glass flasks in containers preventing the exposure to light; the samples were acidified to pH 2–3 with formic acid and stored prior to analysis at 4 °C in dark; in these conditions they were stable at least 90 days.

2.2. Reagents and standards

Acetonitrile, acetic acid, tetrahydrofuran, ammonia aq. were purchased from Sigma–Aldrich (Saint-Quentin-Fallavier, France). Ultrapure water (18 MΩ cm) was obtained from a Milli-Q system (Millipore, Bedford, MA). The characteristics of the FBA standards used in this study are listed in Table 1. Deuterated 2,6-dFBA and 2,4,6-tFBA were a gift from Dr. K. Müller and Prof. Dr. A. Seubert (Faculty of Chemistry, Philipps-Universität, Marburg, Germany). 4-fluorobenzoic acid-α-^{13}C-2,3,5,6-d_4 was purchased from Sigma–Aldrich (Saint-Quentin-Fallavier, France).

2.3. Materials

The SPE disposable cartridges (C_{18}, 500 mg, 3 mL) were supplied by Sigma–Aldrich (Saint-Quentin-Fallavier, France). Separations were carried out using an Acquity UPLC BEH C_{18} column (150 mm × 2.1 mm × 1.7 μm) with a matching precolumn Acquity UPLC BEH C_{18} VanGuard (130 Å, 1.7 μm, 2.1 mm × 5 mm; Waters, Guyancourt, France).

2.4. Instrumentation

SPE was carried out using a Supelco VisiPrep 24DL (supplied by Sigma–Aldrich). Eluates were evaporated to dryness using an Eppendorf Concentrator Plus (Eppendorf France SAS, Montesson). An Acquity UPLC system (Waters) including a binary solvent pump, a cooled autosampler and a column oven were used. The detector was a XevoTQ (quadrupole-T-wave-quadrupole) MS with an orthogonal Z-spray-electrospray interface (Waters).

Table 1
Standard compounds used in this study.

Name	Abbreviation	Formula	Purity (%)	Supplier	Mass	pK_a	log P
2-Fluorobenzoic acid	2-FBA	$C_7H_5O_2F$	99	Across Organics*	140.11	3.23	1.77
3-Fluorobenzoic acid	3-FBA	$C_7H_5O_2F$	99	Across Organics	140.11	3.67	1.77
4-Fluorobenzoic acid	4-FBA	$C_7H_5O_2F$	98	Sigma–Aldrich**	140.11	3.79	1.77
2,6-Difluorobenzoic acid	2,6-dFBA	$C_7H_4O_2F_2$	98	Across Organics	158.10	2.42	1.92
2,5-Difluorobenzoic acid	2,5-dFBA	$C_7H_4O_2F_2$	98	Across Organics	158.10	2.87	1.92
2,3-Difluorobenzoic acid	2,3-dFBA	$C_7H_4O_2F_2$	98	Sigma–Aldrich	158.10	2.87	1.92
2,4-difluorobenzoic acid	2,4-dFBA	$C_7H_4O_2F_2$	99	Across Organics	158.10	3.00	1.92
3,5-Difluorobenzoic acid	3,5-dFBA	$C_7H_4O_2F_2$	97	Sigma–Aldrich	158.10	3.31	1.92
3,4-Difluorobenzoic acid	3,4-dFBA	$C_7H_4O_2F_2$	99	Across Organics	158.10	3.43	1.92
2,3,6-Trifluorobenzoic acid	2,3,6-tFBA	$C_7H_3O_2F_3$	99	Sigma–Aldrich	176.10	2.06	2.06
2,4,6-Trifluorobenzoic acid	2,4,6-tFBA	$C_7H_3O_2F_3$	98	Sigma–Aldrich	176.10	2.19	2.06
2,4,5-Trifluorobenzoic acid	2,4,5-tFBA	$C_7H_3O_2F_3$	99.5	Across Organics	176.10	2.64	2.06
2,3,4-Trifluorobenzoic acid	2,3,4-tFBA	$C_7H_3O_2F_3$	98	Sigma–Aldrich	176.10	2.64	2.06
3,4,5-Trifluorobenzoic acid	3,4,5-tFBA	$C_7H_3O_2F_3$	98	Sigma–Aldrich	176.10	3.07	2.06
2-Trifluoromethylbenzoic acid	2-tFmBA	$C_9H_5O_2F_3$	98	Across Organics	190.12	3.17	2.51
3-Trifluoromethylbenzoic acid	3-tFmBA	$C_9H_5O_2F_3$	99	Sigma–Aldrich	190.12	3.50	2.51
4-Trifluoromethylbenzoic acid	4-tFmBA	$C_9H_5O_2F_3$	98	Sigma–Aldrich	190.12	3.69	2.51
2,3,4,5-Tetrafluorobenzoic acid	2,3,4,5-tetraFBA	$C_7H_2O_2F_4$	99	Sigma–Aldrich	194.08	2.27	2.20
3, 5-bis-Trifluoromethylbenzoic acid	3,5-bisFmBA	$C_9H_4O_2F_6$	98	Sigma–Aldrich	258.12	2.97	3.39

* Across Organics supplied by Fisher Scientific SAS (Illkirch, France).
** Sigma–Aldrich (Saint-Quentin-Fallavier, France).