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## Sample preparation procedure using extraction and derivatization of carboxylic acids from aqueous samples by means of deep eutectic solvents for gas chromatographic-mass spectrometric analysis

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### ABSTRACT

The paper presents a new procedure for the determination of organic acids in a complex aqueous matrix using ultrasound-assisted dispersive liquid–liquid microextraction followed by injection port derivatization and GC–MS analysis. A deep eutectic solvent (choline chloride: 4-methylphenol in a 1:2 mol ratio) was used both as an extracting solvent and as a derivatizing agent to yield ion pairs which were next converted to methyl esters of organic acids in a hot GC injection port. The procedure was optimized in terms of selection of a deep eutectic solvent, disperser solvent, and the ratio of their volumes, pH, salting out effect, extraction time, injection port temperature and time of opening the split valve. The developed procedure is characterized by low LOD (1.7–8.3 µg/L) and LOQ (5.1–25 µg/L) values, good repeatability (RSD ranging from 4.0 to 6.7%), good recoveries for most of the studied analyte (81.5–106%) and a wide linear range. The procedure was used for the determination of carboxylic acids in real effluents from the production of petroleum bitumens. A total of ten analytes at concentrations ranging from 0.33 to 43.3 µg/mL were identified and determined in the effluents before and after chemical treatment. The study revealed that in effluents treated by hydrodynamic cavitation an increase in concentration of benzoic acid and related compounds was observed.

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### 1. Introduction

Carboxylic acids, such as volatile fatty acids, benzoic and hydroxybenzoic acids occur commonly in municipal wastewater [1,2], and also at relatively high concentrations in industrial effluents, including paper [3,4], pharmaceutical [5], textile, tanning [6], or petroleum industries [7]. As a result of malodorous nature of the most volatile acids, potential toxicity of individual compounds and a negative impact on the aqueous environment, carboxylic acids have been the subject of numerous studies concerning the technology of their removal [8–10], and the development of procedures for their determination at low concentration levels.

At present, the determination of carboxylic acids in samples with aqueous matrices involves chromatographic techniques, pri-

marily gas chromatography. However, due to specific properties of carboxylic acids, *i.e.* high polarity, high boiling point and low volatility of a large number of the acids, only a small fraction of them (including volatile fatty acids from C<sub>1</sub> to C<sub>12</sub>) can be subjected to direct GC analysis [11,12]. Hence, it is often necessary to derivatize analytes through esterification, alkylation or silylation. The majority of available derivatization procedures is based on application of alkylsilane derivatizing agents which form unstable derivatives and the time of reaction can be as long as 24 h [13]. Other commonly used derivatization methods require strongly toxic reagents [14,15] or reagents characterized by a low derivatization yield [16]. Among the available procedures, only a few can be considered environmentally friendly and free from the above shortcomings. Examples include the use of alkylchloroformates in esterification [17] or, recently popular, derivatization resulting in formation of ion pairs making use of nontoxic quaternary ammonium salts, such as tetramethylammonium chloride (TMA-Cl), tetramethylammonium acetate (TMAAc), tetrabutylammonium hydrogensulfate (TBA-HSO<sub>4</sub>), tetrabutylammonium chloride (TBA-Cl), tetrabutyl-

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lammonium bromide (TBA-Br) or tetrabutylammonium iodide (TBA-I) [7,18]. The latter procedure has a number of advantages due to its simplicity of derivatization, which involves addition of derivatizing agent and a buffer solution. Thus formed ion pairs are converted to esters in the hot GC injection port.

Determination of low concentrations of organic acids in wastewater samples requires an appropriate extraction technique which, in accordance with principles of green chemistry, should be simple, rapid, automatable and using only small volumes of organic solvents. One of the sample preparation techniques meeting the above criteria is dispersive liquid–liquid microextraction (DLLME) introduced in 2006 [19]. However, since the inception of this technique it was pointed out that it makes use of mostly hazardous chlorinated organic solvents with a density higher than water, which facilitates separation of phases and transfer of the extract to the GC injection port or to autosampler vials. Solvents having density lower than water can also be used but collection of the extract is more difficult as it requires an additional step of solidification of organic drop or the use of special vials which are not yet available commercially [20–22].

An alternative to toxic chlorinated solvents are deep eutectic solvents (DESs). These are liquids which are formed upon mixing two solids (at ambient temperature), typically quaternary ammonium salts being hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD), whose melting points are much lower than those of individual components [23]. In addition, DESs have physico-chemical properties similar to ionic liquids; however, the synthesis of DESs is much simpler and cheaper and they are less toxic and easier to biodegrade than ionic liquids [24]. The majority of papers refer to synthesis and use of hydrophilic DESs [23,25–27], and only a few mention hydrophobic DESs which can be potentially used as extracting solvents for samples with an aqueous matrix [28–33].

The paper describes a new procedure for the determination of carboxylic acids in aqueous samples which was used for the analysis of effluents from the production of bitumens. The procedure is based on ultrasound-assisted dispersive liquid–liquid microextraction combined with GC injection port derivatization and mass spectrometric detection (IP-USA-DLLME-GC-MS), in which the same deep eutectic solvent is used as an extracting solvent and a reagent for the formation of ion pairs (IPR).

## 2. Experimental

### 2.1. Reagents

Solvents (purity >99.9%), including isopropanol (IPA), methanol (MeOH), and acetone (AC) were purchased from POCH (Poland). Choline chloride (ChCl), 4-chlorophenol (4CPh), 4-ethylphenol (4EtPh), phenol (Ph), 2-methylphenol (2MPh), 3-methylphenol (3MPh), 4-methylphenol (4MPh), and 2,6-dimethylphenol (2,6DMPh) were obtained from Sigma-Aldrich (USA), while sodium chloride (NaCl), sodium hydroxide (NaOH) and hydrochloric acid 35–38% were purchased from POCH (Poland). High-purity standards (benzoic acid, 2-methylbenzoic acid, 4-methylbenzoic acid, 2,4-dimethylbenzoic acid, 4-butylbenzoic-*tert*-butylbenzoic acid, 2-hydroxybenzoic acid, octanoic acid, nonanoic acid, decanoic acid, 10-undecylenic acid, dodecanoic acid) and internal standard: 2-chlorobenzoic acid were obtained from Merck (Germany). Compressed gases: hydrogen (purity N 5.5) generated by a PGXH2 500 Hydrogen Generator (PerkinElmer, USA), air (purity N 5.0) generated by a DK50 compressor with a membrane dryer (Ekkom, Poland) and further purified by a GC3000 zero air generator (PerkinElmer, USA), and nitrogen (purity N 5.0) (Linde Gas, Poland).

### 2.2. Real samples

Effluents from the production of bitumen 20/30 from vacuum bottom of crude oil Rebco:Kirkuk 65:35 m/m (mixture of Russian and Iraqi crude oils) were collected behind a plate separator which separated condensed organic phase from aqueous phase. The aqueous phase of raw effluents was investigated along with the effluents subjected to various chemical treatments, including hydrodynamic cavitation (HC) as well as hydrodynamic cavitation combined with oxidation by hydrogen peroxide (HC/H<sub>2</sub>O<sub>2</sub>). A detailed characteristic of the effluents was provided in previous papers [34–36]. In the study, 300 mL of raw effluents and effluents after treatment were collected in 350-mL glass bottles.

### 2.3. Apparatus

A model QP2010 GC–MS SE gas chromatograph-mass spectrometer (Shimadzu, Japan) equipped with a combi-PAL AOC 5000 autosampler (Shimadzu, Japan) and an HP-5 MS (30 m × 0.25 mm × .25 μm) capillary column (Agilent, USA) were used in the investigations. A PerkinElmer Autosystem XL gas chromatograph with flame ionization detector (PerkinElmer, USA) and an HP-1 (30 m × 0.53 mm × 1.5 μm) capillary column (Agilent, USA) were employed in optimization of operational parameters. LabSolutions software (Shimadzu, Japan) with NIST 14 mass spectra library and TurboChrom 6.1 (PerkinElmer, USA) were used for data management. An RK 156 BH ultrasonic bath (BANDELIN electronic GmbH & Co. KG, Germany) was used for extraction and an EBA 8S centrifuge (Hettich, Germany) was used for the separation of extracts from samples. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer (Bruker, USA) with an ATR (diamond plate) accessory and OPUS software (Bruker, USA).

### 2.4. Synthesis and characteristics of deep eutectic solvents

Deep eutectic solvents were synthesized as follows: 1.39 g ChCl (HBA) and an appropriate amount of HBD (including Ph, 2MPh, 3MPh, 4MPh, 2,6DMPh, 4EtPh, and 4CPh) so as to obtain mixtures with a mole ratio (HBA: HBD) of 1:0.5, 1:1, 1:2, 1:3, 1:4 and 1:5 were added to a 20-mL beaker. The mixture was stirred magnetically at 50 °C until a homogeneous liquid was obtained.

### 2.5. Derivatization and extraction procedure

A sample of effluent (9 mL) was transferred to a 12-mL vial followed by addition of 5 μL of a 5000 μg/mL solution of an internal standard (2-chlorobenzoic acid). Next, the solution pH was adjusted using a 7% HCl solution. 1.0 mL of a mixture consisting of DES (ChCl: 4MPh (1: 2)) serving as an extracting solvent/derivatizing agent and MeOH as a disperser solvent in a 1:1 vol ratio was then added to the vial. The vial was closed tightly and placed in an ultrasonic bath at room temperature (25 °C) (RT) for 10 min, followed by centrifugation for 5 min at 4000 rpm. Subsequently, 200 μL of the organic phase was collected with an autopipette and transferred to 2-mL vials equipped with 300-μL micro-inserts. The volume of the extract subjected to GC–MS analysis was 0.5 μL.

### 2.6. Chromatographic conditions

Temperature program: 50 °C (5 min) – ramped at 5 °C/min to 250 °C (5 min); injection port temperature 300 °C; purge off time 2 min (splitless mode); 1 μL of the extract was injected into the GC system; detector temperature 300 °C; ion source temperature (EI,

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