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Method for the determination of carboxylic acids in industrial effluents using dispersive liquid-liquid microextraction with injection port derivatization gas chromatography–mass spectrometry

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ABSTRACT

The paper presents a new method for the determination of 15 carboxylic acids in samples of postoxidative effluents from the production of petroleum bitumens using ion-pair dispersive liquid-liquid microextraction and gas chromatography coupled to mass spectrometry with injection port derivatization. Several parameters related to the extraction and derivatization efficiency were optimized. Under optimized experimental conditions, the obtained limit of detection and quantification ranged from 0.0069 to 1.12 μg/mL and 0.014 to 2.24 μg/mL, respectively. The precision (RSD ranged 1.29–6.42%) and recovery (69.43–125.79%) were satisfactory. Nine carboxylic acids at concentrations ranging from 0.10 μg/mL to 15.06 μg/mL were determined in the raw wastewater and in samples of effluents treated by various oxidation methods. The studies revealed a substantial increase of concentration of benzoic acids, in samples of wastewater after treatment, which confirms the need of carboxylic acids monitoring during industrial effluent treatment processes.

1. Introduction

Carboxylic acids, including fatty acids and benzoic acids, are often present in both municipal and industrial effluents [1–5]. A number of papers devoted to the most effective methods of degradation of the organic acids in wastewater have been recently published [2,6–9]. Also some analytical methods of control of the treatment efficiency of these group of compounds are available in the literature [10]. This particular interest on carboxylic acids results from their potential influence on the aquatic ecosystem, human health as well as odorous character of the most volatile compounds. The ever-growing restrictions concerning quality of wastewater, discharged from wastewater treatment plants is also an important driving force for studies on this group of compounds related to the environmental protection issues.

At present, the most common techniques for the determination of the organic acids are the chromatographic techniques, including liquid chromatography, and capillary electrophoresis [11]. However predominant role and leading in this field is gas chromatography [4,10]. Nevertheless, only a small fraction of carboxylic acids, including volatile fatty acids (C_1–C_{12}) can be determined, directly, using GC [12–14]. Those compounds that are not volatile and are characterized by high polarity and boiling point must be derivatized prior to the chromatographic analysis. To that point, compounds containing carboxyl group are subjected to various reactions, including esterification, silanization or alkylation. Among the available derivatization reagents, the most popular that block polar groups which are proton donors, are the alkylsilane reagents, such as *N*,*O*-*Bis*(trimethylsilyl)trifluoroacetamide, trimethylchlorosilane [15], *N*,*O*-*bis*(trimethylsilyl) acetamide, that introduce a trimethylsilane group into an acid molecule. Despite many advantages, silane derivatives are highly unstable and the sample analysis must be carried out within 12–24 h, which constraints the possibility of using this type of reagents in routine analyses [15]. Many compounds used in derivatization, such as dimethyl sulfate, diethyl sulfate [16], or diazomethane [17] are highly toxic. Despite their high reaction yield in a short time, such reagents are substituted with those more environmentally friendly ("green"), which in turn give lower reaction yield in much longer time *i.e.* pentafluorobenzyl bromide [18]. Another group of derivatization reagents are alkyl chloroformates. The reaction of carboxylic acids esterification using these reagents takes place in a few seconds, and alkyl esters could be easily extracted from water to non-toxic solvents [19].

In recent years reagents producing ion-pairs *i.e.* tetramethylammonium chloride (TBA-Cl), tetrabutylammonium hydrogen sulfate

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(TBA-HSO_4), tetrabutylammonium bromide (TBA-Br) or tetrabutylammonium iodide (TBA-I), tetramethylammonium acetate (TMAAc) [20] have been used for derivatization of carboxylic compounds. The short time of a single derivatization reaction is a considerable advantage of such procedure, because it limits only to addition of reagent and the buffer solution to the sample resulting in formation of ion-pairs. The main process of derivatization *i.e.* ion-pair transformation into ester derivatives takes place in a hot injector of gas chromatograph.

Additionally, to improve the sensitivity of the method, a proper extraction stage should be used. A preferred extraction technique is easy to use, allow the automation of procedure and is less time-consuming. Important criterion is also small consumption of organic solvents. Among popular extraction techniques *i.e.* liquid-liquid extraction [10,21], liquid-phase microextraction [3] solid phase extraction [22], solid phase microextraction [23], used for isolation and enrichment of the carboxylic compounds, a technique that meets all of the aforementioned requirements is dispersive liquid-liquid microextraction [24].

This paper describes a novel method for the determination of carboxylic acids in samples of postoxidative effluents from the production of petroleum bitumens using ion-pair dispersive liquid-liquid microextraction coupled to gas chromatography–mass spectrometry with injection port derivatization (IP-DLLME-GC–MS).

2. Materials and methods

2.1. Materials

Except for carbon disulfide purchased from Sigma Aldrich (USA), all solvents (dichloromethane (DCM), chlorobenzene (CB), chloroform (CF), carbon disulfide (CDS) isopropanol (IPA), methanol (MeOH), acetone (AC)) were purchased from POCH (Poland). Purity of all solvents was greater 99.9%. Sodium chloride (NaCl) and sodium hydroxide (NaOH) were from POCH (Poland), TBA-HSO_4 from Sigma-Aldrich (USA).

All high quality standards (benzoic acid, 2-methylbenzoic acid, 4-methylbenzoic acid, 2,4-dimethylbenzoic acid, 4-*tert*-butylbenzoic acid, 2-hydroxybenzoic acid, propanoic acid, butyric acid, 2-ethylhexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, 10-undecylenic acid, dodecanoic acid) and internal standard: 2-chlorobenzoic acid were obtained from Merck (Germany).

2.2. Real samples

Samples of postoxidative effluents from the production of petroleum bitumen 20/30 from the vacuum residue of REBCO:Kirkuk (88:12 w/w), a blend of Russian and Iraqi crude mixture, were collected from a plate separator which separated the condensed organic phase from the aqueous phase. The investigated samples were the aqueous phase of raw wastewater, as well as chemically treated wastewater through oxidation. The studied advanced oxidation processes (AOPs) were: titanium dioxide in combination with ozone and UV radiation (TiO_2/O_3/UV); titanium dioxide in combination with ozone, hydrogen peroxide and UV radiation ($TiO_2/O_3/H_2O_2$/UV); hydrodynamic cavitation in combination with the ozone (HC/O_3) and Sonocavitation in combination with the ozone (SC/O_3). Detailed information on the characteristics of the postoxidative effluents and phenomena occurring during the bitumen oxidation were described in our previous papers [25–27].

2.3. Apparatus

Separation was performed on GC instrument coupled with Mass Spectrometer model QP2010 GC–MS SE (Shimadzu, Japan) equipped with an autosampler combi-PAL AOC 5000 and auto injector (Shimadzu, Japan), and a Clarus 580 gas chromatograph (Perkin Elmer, USA) with a flame ionization detector (FID). The capillary columns used were Rxi-624Sil MS (60 m × 0.25 mm × 1.40 μm) (Restek, USA) and DB-624 (60 m × 0.32 mm × 1.80 μm) (Agilent, Santa Clara, CA, USA). Data were processed using LabSolutions software (Shimadzu, Japan) with NIST 14 mass spectra library; TurboChrom 6.1 software (Perkin Elmer, USA) and an EBA 8S centrifuge (Hettich, Germany).

2.4. Procedures

2.4.1. Sample preparation

The samples of aqueous phase of the raw effluent (9 mL) was removed to a 12-mL vials and spiked with 10 μL of a 5% solution of internal standard, 2-chlorobenzoic acid, in AC and derivatized by adding 0.61 g TBA-HSO_4 (final concentration of TBA-HSO_4 was 0.2 M). The pH was adjusted to 7.0 using 5 M NaOH. Subsequently, 300 μL of the extraction solvent–CF and 900 μL of disperser solvent–IPA was added. The sample was vigorously shaken for 60 s, followed by centrifugation at 4000 rpm for 5 min at room temperature. A volume of 250 μL of the sedimented organic phase was removed and analyzed by GC–MS.

2.4.2. Chromatographic conditions

The following conditions were used in the investigations: oven temperature program: 60 °C (5 min) – ramped at 7 °C/min to 260 °C (20 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, 70 eV) 200 °C; GC/MS transfer line temperature 300 °C; the carrier gas was hydrogen (1 mL/min). Column: Rxi-624Sil MS (60 m × 0.25 mm × 1.40 μm) (Restek, USA).

2.4.3. Method validation

The limit of detection (LOD) was calculated from Eq. (1):

$$\mathrm{LOD} = \frac{3.3 \cdot \mathrm{Sa}}{\mathrm{b}} \qquad (1)$$

where: Sa – standard deviation of the intercept of calibration curve, b – the slope of calibration curve.

The limit of quantitation (LOQ) was calculated from Eq. (2):

$$\mathrm{LOQ} = 2\mathrm{LOD} \qquad (2)$$

Linear range: The linearity of calibration curve carried out using an internal standard calibration was estimated using the correlation coefficient (r). In order to confirm an appropriate selection of the linear range, a standard residual analysis was performed [28].

Recovery (R) was calculated from Eq. (3).

$$R\,[\%] = \frac{C_{quant} - C_0}{C_{expect}} \cdot 100\% \qquad (3)$$

where: $C_{quant.}$– found analyte concentration in spiked sample [μg/mL], $C_{expect.}$ – analyte concentration added as spike [μg/mL], C_0 – found analyte concentration in non-spiked samples [μg/mL].