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Improving the detection limits of near infrared spectroscopy in the determination of aromatic hydrocarbons in water employing a silicone sensing phase

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Abstract

This work describes the use of a silicone sensing phase for the detection of aromatic hydrocarbons in water employing near infrared spectroscopy and the exploitation of the salting-out effect as a means of improving the limits of detection of the method. Sensing phases of polydimethylsiloxane (PDMS) were prepared from Silastic T2 (Dow Corning). Determinations were carried out by immersing a disk in a flask containing an aqueous solution of aromatic hydrocarbon (benzene, toluene, ethylbenzene and the xylenes, commonly called BTEX) and left under constant stirring. Afterwards, the disk was removed from the contaminated water, dried and placed in a home-made holder for absorbance measurements from 800 to 2500 nm, employing an MB 160 Bomem spectrophotometer. By employing a 2.0-mm height disk, measurements performed in water provided detection limits ($3s_{\text{blank}}$/sensitivity) of 1.1, 1.8, 1.1 and 1.1 mg L^{-1} for benzene, toluene, ethylbenzene and xylenes, respectively, while LOD values of 0.6, 0.7, 0.6 and 0.7 mg L^{-1} were obtained when sample solutions contained 2.0 mol L^{-1} sodium chloride. Detection limits of 0.080, 0.12, 0.14 and 0.27 mg L^{-1} were obtained with the use of a 5.0-mm height disk and 2.0 mol L^{-1} sodium chloride. Sodium chloride improves the limits of detection due to its salting out effect; however, headspace in the flask must be avoided during measurements, as the hydrocarbons are preferentially lost to the air. The precision of the proposed method was evaluated by constructing three analytical curves for toluene, providing average slopes and linear coefficients with relative standard deviations of 5.8 and 3.8%, respectively.

Keywords: BTEX; NIR spectroscopy; Optical sensor; NIR optode

1. Introduction

Near infrared (NIR) spectroscopy has proven to be a powerful analytical tool that has been applied in many fields, such as in the agriculture [1,2], food [3], pharmaceutical [4] and petroleum [5] industries and for environmental analyses [6]. The high acceptance of NIR spectroscopy and its widespread use relies on the fact that it can provide fast analytical methods, is non-destructive, does not need extensive sample pre-treatment and does not generate toxic residues, besides allowing simultaneous determinations with the aid of multivariate calibration chemometric techniques.

Most applications of NIR spectroscopy involve the determinations of species in organic matrices or non-aqueous solutions. In fact, water presents combination and overtone absorption bands due to the O–H bonds, which are very intense and broad, covering almost all the NIR region. These bands are stronger than the C–H absorption bands of the organic compounds, impairing direct determination of these species in water. Furthermore, non-polar organic compounds, such as benzene, toluene, ethylbenzene and the xylenes (BTEX), present low solubility in water, being found under the usual limits of detection of NIR spectroscopy, which is usually about 0.1%.

BTEX compounds are frequently determined in water by gas chromatography (GC), coupled to some pre-concentration technique, such as purge and trap [7,8] or solid phase micro-extraction (SPME) [9–12]. SPME is the most practical alternative to extract and pre-concentrate these aromatic compounds, performing a chromatographic analysis in two main

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steps. In the first, a silica fiber covered with a thin film of a suitable polymeric material (polydimethylsiloxane, polyacrylate, polystyrene–divinylbenzene) is immersed in the contaminated water or preferentially kept in its headspace for a period of time in order to reach equilibrium. This procedure allows extracting and pre-concentrating the hydrocarbons in the polymeric cladding of the fiber. Afterwards, the fiber is placed in the injection device of the chromatograph; the analytes are then thermally desorbed and carried towards the column and detection system. Although the SPME-chromatographic methods present high sensitivity, they are costly and bulky, offering difficulties for field monitoring.

Spectroscopic techniques have been proposed for determination of aromatic hydrocarbons in water samples. Although usually less sensitive, they provide simpler methods than the chromatographic ones. The direct determination of BTEX in water by UV spectroscopy has been proposed, presenting as its main disadvantage the interference due to the turbidity of the water samples [13]. This problem can be circumvented with the use of a liquid core waveguide based on Teflon AF, which is permeable to non-polar substances, and permits the construction of long optical path cell, improving the detectivity of the method [14].

SPME has been also applied in conjunction with spectroscopic methods of analysis for the determination of aromatic hydrocarbons in water. As in the chromatographic methods, an appropriate polymer (often polydimethylsiloxane, PDMS) is used to extract and pre-concentrate the organic compounds before measuring the attenuation of radiation in the ultraviolet [15–17], infrared [18–20] or near infrared [21–25] regions of the electromagnetic spectrum. In fact, these contributions described in the literature can be related to research on optical sensors, as a sensing phase is used to interact with the analyte prior to measurement.

Tilotta and co-workers [15] proposed the use of a chip made of PDMS (OV-1 stationary phase), with dimensions of 10 mm × 2 mm × 4 mm (volume of 80 μL), for UV determination of BTEX in water. After extraction, a 10-mm optical path chip provided detection limits of 97, 10, 12 and 5.5 $\mu\text{g kg}^{-1}$ for benzene, toluene, ethylbenzene and *p*-xylene, respectively. The sensor was subsequently applied to the determination of fuel aromatics in water [16]. Merschman and Tilotta [17] used a PDMS-clad silica optical fiber cable for determination of BTEX by employing evanescent wave detection. Detection limits 18.2, 6.2, 3.6 and 3.0 mg L^{-1} for benzene, toluene, ethylbenzene and *p*-xylene, respectively, were obtained, with the use of a 10 cm long optical fiber and measurements at 254 nm.

Attenuated total reflectance spectroscopy with detection in the infrared region has been employed by Mizaikoff and co-workers [18] for determination of these aromatic hydrocarbons in water. A trapezoidal ZnSe ATR element was coated with ethylene/propylene copolymer film of 4.2 μm, providing detection limits of 45, 80 and 20 $\mu\text{g L}^{-1}$ (v/v) for benzene, toluene and *p*-xylene, which can be simultaneously determined by carrying out measurements in the fingerprint region (800–650 cm^{-1}). Parafilm M [19] and PDMS [20] films have been used by Tilotta and co-workers as sensing phases for extraction and pre-concentration of aromatic hydrocarbons, followed by detection in the infrared region. Detection limits of 182 and 66 $\mu\text{g L}^{-1}$ for benzene and *p*-xylene were obtained with the use of Parafilm M, while a value of 4400 $\mu\text{g L}^{-1}$ was achieved for *p*-xylene when PDMS was employed.

Evanescent wave optical sensors with near infrared detection have frequently been used for determination of hydrocarbons in water. Burck and co-workers extensively studied this approach [21–24], achieving limit of detections of 0.9 and 0.4 mg L^{-1} for toluene and *p*-xylene, respectively, with the use of an 11-m long PDMS-clad optical fiber [24].

Recently, Albuquerque et al. [25] proposed the use of a silicone sensing phase for detection of BTEX in water. A transflectance probe with an optical path of 10 mm was employed, in which a silicone rod was adapted, and measurements made from 850 to 1800 nm resulted in detection limits of 8.0, 7.0, 2.6 and 3.0 mg L^{-1} for benzene, toluene, ethylbenzene and *m*-xylene, respectively.

Although the contributions listed above are based on the concepts of solid phase micro-extraction, none of them employed the salting out effect in order to improve the limit of detection of the method, a procedure often employed in the headspace SPME procedure. This work describes the use of a PDMS phase for determination of BTEX in water based on transmittance measurements in the 780 to 2500 nm region and studies the effect of the salinity of the solution as a means of improving the detectivity of the proposed method.

2. Experimental

2.1. Reagents and solutions

Benzene, toluene, ethylbenzene and xylene were purchased from Merck and used without any purification. Methanol (spectroscopic grade, Merck) was used to prepare stock solutions of the BTEX compounds. Sodium chloride (Vetec) was used to adjust the salinity of the water samples. Silastic T2 and its curing agent were supplied by Dow Corning. Distilled-deionized water was used to prepare the contaminated water samples.

2.2. Sensing phase preparation

The PDMS polymer was prepared as recommended by the manufacturer and according to the procedure previously described [25]. The polymer was cast in PTFE templates and cut into small disks of 3.2 mm diameter with the aid of a cork borer. The heights of the disks were optimized for maximum sensitivity.

2.3. Reference solutions

Stock solutions of each BTEX compound were prepared in methanol (50,000 mg L^{-1} for benzene and toluene; 10,000 mg L^{-1} for ethylbenzene and xylene), which were then properly diluted to obtain aqueous reference solutions in the range from 0 to 80 mg L^{-1}. Aqueous toluene solutions from 0 to 400 mg L^{-1} were also prepared to perform the initial experiments. The