A PVC sensing phase for determination of BTEX in water employing mid-infrared spectroscopy

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Abstract

The evaluation of PVC films, cast with 2-(2-hydroxy-5-tert-octylphenyl)benzotriazol (Tinuvin) as stabiliser (0.3%) and di-2-ethylhexyl phthalate (DOP) as plasticiser (25 or 40%), for use as sensing phases for benzene, toluene, ethylbenzene and xylene (BTEX) determinations, based on transmittance measurements in the mid-infrared (MIR) region, is described. Measurements were carried out by inserting a PVC sensing phase into a vial, which was then completely filled with the hydrocarbon sample solution. Afterwards, the sensing phase was removed from the vial and placed in the optical path of a spectrophotometer for acquiring absorbance spectra from 12,800 to 650 cm⁻¹. Kinetic measurements showed that the films reached saturation within 180 min for all BTEX compounds. Analytical curves were constructed for BTEX compounds in the 0–80 mg L⁻¹ concentration range, showing, respectively, detection limits and sensitivities (expressed as the slope of the analytical curves) of 5.0 mg L⁻¹ and 2.6 × 10⁻⁵ L mg⁻¹ for benzene (measured at 688 cm⁻¹), 6.9 mg L⁻¹ and 3.6 × 10⁻⁵ L mg⁻¹ for toluene (at 728 cm⁻¹), 9.0 mg L⁻¹ and 4.7 × 10⁻⁵ L mg⁻¹ for ethylbenzene (at 695 cm⁻¹), and 4.0 mg L⁻¹ and 3.7 × 10⁻⁵ L mg⁻¹ for xylene (at 778 cm⁻¹), when PVC film with 25% plasticiser was employed. The sensitivity was increased when 40% of plasticiser was used in the film preparation. These results demonstrate the feasibility of using transmittance measurements in the mid-infrared region for determining BTEX compounds in water, after their extraction by a PVC film.

Keywords: PVC; Mid-infrared; BTEX; Optical sensor

1. Introduction

Nowadays it is common to use optical chemical sensors with detection systems in the mid-infrared (MIR) and near-infrared (NIR) regions to determine aromatic hydrocarbons in contaminated water samples. The advantages of using infrared spectroscopy over conventional chromatographic techniques are due to the less expensive and simpler instrumentation that allows field monitoring [1–7].

In IR-based methods, the hydrocarbons are extracted from water by an appropriate sensing phase which concentrates these compounds, avoiding the interference of water [8,9]. Some papers report the use of a polymer-clad silica fibre as a sensing phase, performing measurements based on the evanescent waves principle. Detection limits of 0.9 and 0.4 mg L⁻¹ for toluene and p-xylene, respectively, have been reported, when an 11-m long PDMS-clad optical fibre is used for measurement [10].

A method based on direct transmittance measurements of a polymeric sensing phase, after an extraction step, was developed by Tilotta and co-workers [8,11,12]. Low detection limits (66 μg L⁻¹–1.3 mg L⁻¹) were obtained to determine 10 volatile organic compounds in water, employing Parafilm M as the sensing phase and detection in the MIR region. However, intervals of time for obtaining the equilibrium state were relatively long, reaching up to 200 min. The use of poly(dimethylsiloxane) (PDMS) film for the determination of organic compounds of environmental concern (trichloroethylene, perchloroethylene, xylenes and trifluoracil) has also been described [11]. Equilibrium times were relatively short (60–85 min) and the method provided moderate detection...
The present work is aimed at evaluating PVC films cast from solutions containing 2-(2-hydroxy-5-tert-octylphenyl)benzotriazol (Tinuvin) as stabiliser and di-2-ethylhexyl phthalate (DOP) as plasticiser as sensing phases for BTEX determination. The main drawback of this approach has been explored in order to improve the detectability of the analyte. PVC powder was supplied by Tiletron, while DOP and Tinuvin (2-(2-hydroxy-5-tert-octylphenyl)benzotriazol) were supplied by Ciba-Geigy.

2.2. 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 of 0–80 mg L\(^{-1}\). The methanol concentration in all solutions, including the blank, was maintained at 1.0%.

2.3. Sensing phase preparation

Films were prepared from a mixture containing 0.3% (w/w) of stabiliser, 25% (w/w) or 40% (w/w) of plasticiser and enough PVC for obtaining a total mass of 2.0 g. This mixture was dissolved in 40 mL of THF and the solution was spread on a Petri dish (10 cm diameter) and dried for 24 h at ambient temperature (22 ± 2 °C), producing films with thicknesses of 150 ± 2 μm.

2.4. Apparatus

Absorbance spectra from 12,800 to 650 cm\(^{-1}\) were obtained with a Perkin-Elmer FTIR Spectrum GX spectrophotometer. Each spectrum was acquired with a resolution of 8 cm\(^{-1}\), by averaging eight scans, in a procedure that lasts about 30 s. Absorbance measurements were obtained directly on the polymeric film, with the aid of a home-made holder, as shown in Fig. 1.
2.5. Procedure

For all measurements, before the extraction procedure, the spectrum of the sensing phase was taken for reference, providing the $I_0$ intensities for absorbance calculations. Measurements were carried out by inserting a PVC sensing phase (a 54 mm$^2$ piece) and 3.0 g of NaCl into a 35-mL vial, which was then completely filled with an aqueous sample solution containing the hydrocarbons and kept under stirring for fixed time intervals. Afterwards, the sensing phase was removed from the vial, dried with a soft tissue and placed in the optical path of the spectrophotometer with the aid of the home-made holder.

Analytical curves were constructed for BTEX compounds in the 0–80 mg L$^{-1}$ concentration range, employing spectral data without pre-treatment, after baseline correction and after taking the first derivative (Savitzky-Golay filter with an 11-point window).

3. Results and discussion

3.1. Spectroscopic consideration

Infrared absorption spectra of 150 μm thick PVC films, containing DOP (25 and 40%) and stabiliser, are shown in Fig. 2. The peaks in the 775–667 cm$^{-1}$ region are due to C–Cl stretching, which have complex origins and are affected by both the polymer conformational structure and the spatial position of the atoms close to C–Cl bonds. The other peaks are due to different C–C and C–H vibrations [21]. The PVC main peaks are found at 2970 cm$^{-1}$ (C–H stretching of CHCl group); 2875 cm$^{-1}$ (C–H stretching of CH$_2$ group); 1737, 1468, 1435 cm$^{-1}$ (CH$_2$ bending); 1399–1227 cm$^{-1}$ region (C–H bending of CHCl group); 1128 and 1076 cm$^{-1}$ (C–C stretching) and 965 cm$^{-1}$ (CH$_2$ rotation).

DOP and stabiliser spectra are complex, presenting peaks that are superimposed on PVC peaks. The DOP spectrum presents peaks in the following regions: 1798–1646, 1316–1264 and 1167–1103 cm$^{-1}$. The principal stabiliser peaks are in the 1534–1494 cm$^{-1}$ region.

Fig. 3 shows the spectra obtained after immersing the film for 60 min in aqueous solutions containing 80 mg L$^{-1}$ of benzene, toluene, ethylbenzene and xylene, which were plotted after subtracting the spectrum of the respective sensing phase.

In the fingerprint region (900–650 cm$^{-1}$), small differences in the structure and constitution of the molecules results in significant changes in the distribution of the absorption peaks. The benzene spectrum presents a peak at 681 cm$^{-1}$; toluene at 734 and 696 cm$^{-1}$; ethylbenzene at 748 and 670 cm$^{-1}$ and...
xylens peaks are at 798, 773 and 693 cm\(^{-1}\). These intense bands are due to the bending out-of-plane of the aromatic ring C–H bonds. It is important to note that there are significant differences in this region and the peaks referring to each analyte do not overlap completely. The bands due to backbone vibrations are observed in the 1600–1585 and 1500–1400 cm\(^{-1}\) regions, involving axial deformation of the carbon–carbon bonds of the ring [22]. The aromatic C–H axial deformation bands occur between 3100 and 3000 cm\(^{-1}\). In these spectral regions the absorption bands of the sensing phase are not intense. Therefore, the spectrum subtraction procedure does not produce significant residuals in the resulting spectrum that would impair the identification of BTEX peaks and their determinations by this procedure.

Therefore, it can be noted that there are many peaks which provide analytical information about BTEX when PVC sensing phases are employed for measurements in the infrared region.

3.2. Equilibrium time

The contact time of the sensing phase with the sample must be precisely controlled in order to obtain reproducible data. A variety of parameters affect the equilibrium times of extraction, such as temperature, addition of an electrolyte, stirring and film thickness. Addition of a salt to the sample has proven successful in improving the extraction process. When the ionic strength is increased, the analyte solubility in the matrix decreases, which facilitates its extraction by the sensing phase [13,20]. The stirring efficiency is an important factor to determine the equilibrium time. When mechanical stirring is employed, it is fundamental to assure a constant velocity in order to obtain reproducible results [23,24]. The temperature also affects analyte solubility, therefore the partition coefficient between the two phases. In relation to the membrane dimensions, increasing the film thickness increases the extraction capacity, but a longer extraction time is required [9]. These effects have already been studied in solid phase micro-extraction associated with chromatography (SPME-GC) [23,24] and spectroscopy (SPME-IR) [2].

![Fig. 4. First derivative signal of the absorbance spectra as a function of time for 80 mg L\(^{-1}\) aqueous solutions of toluene, benzene, ethylbenzene and xylens.](image)

Fig. 4 shows the signal profiles obtained as a function of time for measurements with 80 mg L\(^{-1}\) aqueous solutions of each analyte, in which different sensing phases were employed for each measurement.

The first derivative peaks, 688, 728, 695 and 778 cm\(^{-1}\), were selected because they show the highest absorbance for benzene, toluene, ethylbenzene and xylens, respectively. The saturation time was about 180 min for all BTEX compounds. In spite of the long time intervals necessary to reach steady-state signals, the intensities obtained after inserting the probe in contaminated water for 60 min were intense enough for the determination these compounds in water. Therefore, this shorter period of time was employed throughout the work.

3.3. Sensing phase regeneration

The reversibility of the sensing phase was evaluated by exposing it to air at ambient temperature (22 ± 2°C) after the extraction. The contact time of the sensing phase with the sample must be precisely controlled in order to obtain reproducible data. A variety of parameters affect the equilibrium times of extraction, such as temperature, addition of an electrolyte, stirring and film thickness. Addition of a salt to the sample has proven successful in improving the extraction process. When the ionic strength is increased, the analyte solubility in the matrix decreases, which facilitates its extraction by the sensing phase [13,20]. The stirring efficiency is an important factor to determine the equilibrium time. When mechanical stirring is employed, it is fundamental to assure a constant velocity in order to obtain reproducible results [23,24]. The temperature also affects analyte solubility, therefore the partition coefficient between the two phases. In relation to the membrane dimensions, increasing the film thickness increases the extraction capacity, but a longer extraction time is required [9]. These effects have already been studied in solid phase micro-extraction associated with chromatography (SPME-GC) [23,24] and spectroscopy (SPME-IR) [2].

![Fig. 5. Evaporative loss of xylens from PVC following a 60 min extraction (measurements at 778 cm\(^{-1}\)).](image)

Table 1

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Abs. bands (nm/cm(^{-1}))</th>
<th>Slope (AU/mg L(^{-1}))</th>
<th>R</th>
<th>LD (mg L(^{-1}))(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3284/3045</td>
<td>3.0 \times 10^{-5}</td>
<td>0.9911</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>6738/1484</td>
<td>2.8 \times 10^{-5}</td>
<td>0.9947</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>14,538/688</td>
<td>2.6 \times 10^{-5}</td>
<td>0.9818</td>
<td>5</td>
</tr>
<tr>
<td>T</td>
<td>3310/3021</td>
<td>7.3 \times 10^{-5}</td>
<td>0.9922</td>
<td>6</td>
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<tr>
<td></td>
<td>6672/1499</td>
<td>4.7 \times 10^{-5}</td>
<td>0.9930</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>13,740/728</td>
<td>3.6 \times 10^{-5}</td>
<td>0.9898</td>
<td>7</td>
</tr>
<tr>
<td>E</td>
<td>3310/3021</td>
<td>1.3 \times 10^{-4}</td>
<td>0.9907</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>6668/1499</td>
<td>8.7 \times 10^{-4}</td>
<td>0.9794</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>6706/1491</td>
<td>1.0 \times 10^{-4}</td>
<td>0.9825</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>14,386/695</td>
<td>4.7 \times 10^{-5}</td>
<td>0.9947</td>
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</tr>
<tr>
<td>X</td>
<td>6572/1522</td>
<td>6.9 \times 10^{-5}</td>
<td>0.9954</td>
<td>10</td>
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<tr>
<td></td>
<td>12,848/778</td>
<td>3.7 \times 10^{-5}</td>
<td>0.9968</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>14,360/696</td>
<td>2.5 \times 10^{-5}</td>
<td>0.9932</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>14,510/689</td>
<td>2.7 \times 10^{-5}</td>
<td>0.9982</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^a\) LD was estimated by 3Sb/Slope. Sb is the blank standard deviation (five extractions of a 1% methanol solution).
measurements. Fig. 5 depicts the response profile of the sensor as a function of time after measurements with \(80 \text{ mg L}^{-1}\) aqueous xylenes solution, taken as an example. A reversible response of the sensor under the experimental conditions employed may be observed, suggesting the possibility of its reutilisation. The same behaviour was observed when the sensing phase previously immersed in an aqueous toluene solution was immersed in pure water, although a longer time interval was necessary to recover the baseline signal.

During the measurements, the evaporative loss is accelerated by the IR radiation. Although the increase of scans co-addition improves the S/N ratio, this procedure decreases the signal intensity due to evaporative loss. In this study, eight scans were employed, which corresponds to 30 s to acquire the spectra, in accordance with Heglund and Tilotta [8].

Spectra were pre-processed by employing the first derivative (Savitzky-Golay algorithm employing a 11-point window), and baseline correction techniques. The best results, in relation to sensibility (\(s\), slope of the analytical curve), correlation coefficient (\(R\)) and detection limits (LD), were obtained with this first derivative technique. Table 1 summarises the results obtained for BTEX compounds.

Table 2
Detection limits estimated by 3Sb/Slope (LD\(_\text{table 1}\) and as suggested by Stahl and Tilotta [12])

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>LD(_\text{table 1})</th>
<th>LD(_{S-T})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>688</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Toluene</td>
<td>728</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>695</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Xylene</td>
<td>778</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 3
Polymeric sensing phases used to determine BTEX concentrations using infrared spectrometry

<table>
<thead>
<tr>
<th>Sensing phases</th>
<th>Method</th>
<th>Extraction time (min/LD mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>T</td>
</tr>
<tr>
<td>PIB(^{25})</td>
<td>ATR</td>
<td>–</td>
</tr>
<tr>
<td>EP/Co(^{7})</td>
<td>ATR</td>
<td>20/0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parafilm M(^{11})</td>
<td>Transmittance</td>
<td>90/0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDMS(^{9})</td>
<td>Transflectance</td>
<td>90/8.0</td>
</tr>
<tr>
<td>PDMS(^{13})</td>
<td>Transmittance</td>
<td>60/0.08</td>
</tr>
<tr>
<td>PVC (this work, 25% plasticiser)</td>
<td>Transmittance</td>
<td>60/5</td>
</tr>
</tbody>
</table>

Fig. 6. Effect of increasing the plasticiser concentration from 25 to 40% on the 80 mg L\(^{-1}\) toluene solution (extraction time of 60 min) (a) spectra and (b) slope of the analytical curves (728 cm\(^{-1}\)).
the International Union of Pure and Applied Chemistry (IUPAC), suggested a simpler way of estimating LD directly from the spectral information. The procedure assumes that the noise of the baseline around the analytical band is equivalent to the white noise in the absorbance region of the substance being analysed. Using this definition, the detection limits were also estimated based on the noise within 50 points of the absorption peak of a single spectrum, as shown in Table 2.

It may be observed that, in general, the LD values estimated according to Stahl and Tilotta [12] are slightly lower, although within the same range as those obtained by the conventional method.

Fig. 6 shows the effect of increasing the plasticiser concentration in the sensing phase. When 40% of plasticiser was used in film preparation, the sensitivity of the analytical curves was increased, indicating higher extraction factors, due to the increase of the diffusion coefficients and/or solubility of the analyte in the polymeric matrix.

A comparison with other polymers employed as sensing phases for BTEX determination using infrared spectrometry is shown in Table 3. Compared to ATR methods [7,25], the PVC sensing phase provides higher LD and extraction times and the acquisition technique (transmittance) is much simpler. The LD obtained with Parafilm M [11] are lower than PVC, although extraction times for benzene and xylenes are higher than those employed in the measurements with PVC. Although equivalent LD were obtained with a PDMS rod adapted in a transflectance probe with detection in the NIR range [9], the PVC requires shorter extraction times. Compared to a PDMS sensing phase with transmittance measurements in the NIR range using the salting-out effect [13], PVC demonstrated detection limits 10 times higher with the same extraction times. However, it is necessary to emphasise that the present method is able to determine the BTEX compounds by performing measurements in the fingerprint region, circumventing the need of a wide set of samples used in multivariate calibration for NIR.

4. Conclusions

The results obtained in the present work demonstrate the feasibility of using transmittance measurements in the mid-infrared region of the electromagnetic spectrum as a means of determining BTEX compounds in water, after their extraction by a plasticised PVC film. The proposed method is simpler than those already described in the literature, providing limits of detection of similar magnitude.

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References