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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 (trichoroethylene, perchoroethylene, xylenes and trifluralin) has also been described [11]. Equilibrium times were relatively short (60–85 min) and the method provided moderate detection

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limits (0.2–4.4 mg L^{-1}). Teflon PFA, a perfluoroalkoxyethylene polymer, which lacks C–H bonds, was employed to determine the total organic compounds from gasoline in water [12]. The authors showed that this polymer provides a clear spectral window in the C–H stretching region (around 3000 cm^{-1}) for identification and quantification of the total petroleum hydrocarbons (TPH) in water. Since the equilibrium times for aviation gasoline, unleaded gasoline and lighter fuel were long (more than 3 h), an extraction period of 30 min was chosen. The detection limits for TPH, obtained by extracting the hydrocarbons from aqueous solutions of these three fuels in water, were in the 0.8–2.9 mg L^{-1} range.

Albuquerque et al. [9] used a PDMS sensing phase to determine aromatic hydrocarbons in water with detection in the NIR region. A transflectance probe with a 10 mm optical path was employed, into which a PDMS rod was placed. Measurements made in the 11,765–5556 cm^{-1} range 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. Recently, Lima et al. [13] described the use of a PDMS sensing phase to determine BTEX in water, based on transmittance measurements in the 12,820–4000 cm^{-1} range, including studies on the effects of the salinity of the aqueous solutions on the detectability of the proposed method. Limits of detection of 0.080, 0.12, 0.14 and 0.27 mg L^{-1} were obtained for benzene, toluene, ethylbenzene and xylene, respectively, for extractions performed in 2.0 mol L^{-1} NaCl, with a 5.0 mm long PDMS disk.

A polymeric film coating on the surface of an attenuated total reflection element has also been used for both extraction and concentration of different analytes. Various polymers have been investigated for this purpose, such as polyisobutylene (PIB) [2,3,14], low-density polyethylene (LDPE) [2,3,15], ethylene–propylene copolymer (E/Pco) [2–4], 1,2-polybutadiene [2], polypropylene and polystyrene [16].

Poly(vinylchloride)—PVC is one of the polymers eligible to act as an extracting film. Its properties depend on the nature and quantity of the plasticiser used in film preparation [17]. This polymer is rigid and compatible with a great variety of plasticisers and shows many bipolar interaction points along its chains. Introduction of a plasticiser separates the macromolecules and causes the creation of free spaces and free volume regions which increase the rate of diffusion of analytes into the polymeric film [18]. Regan et al. studied 10 plasticised PVC sensing films to determine benzene, toluene, etylbenzene and xylene (BTEX) in aqueous samples employing attenuated total reflectance (ATR) [17]. The main drawback of this approach is related to the detachment of the film from the ATR element, when it is immersed an aqueous sample for a long period of time, associated with the difficulty of recovering the ATR element. In order to reduce these problems, a gas stream was used to transfer the volatile analytes from the aqueous phase to the sensing film. The results indicated that, for the 10 plasticisers investigated, diisooctyl azelate worked most favourably. In addition, by increasing the plasticising concentration in the PVC film from 25 to 65%, an increase in the absorbance values for the BTEX compounds was obtained. In a recent work, McCue et al. [19] described the design, construction and testing of a modular MIR optical fibre sensor that employs evanescent wave sensing with an analyte-enriching polymer (PVC with 30%, w/w of diisoctyl azelate plasticiser). This sensor system can detect benzene down to 500 mg L^{-1} level.

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 based on transmittance measurements in the MIR region. The salting-out effect [13,20] was also explored in order to improve the detectability. The plasticiser (DOP) and the stabiliser (Tinuvin) were chosen because they are often used in commercial PVC formulations. The stabiliser had already been used in a previous study, as it contributes to both film reutilisation and the diffusion of the analyte in the PVC.

2. Experimental

2.1. Reagents and solutions

Benzene (Aldrich), toluene (Vetec), ethylbenzene (Aldrich), xylene (Merck), methanol (Vetec), THF (Vetec) and sodium chloride (F. Maia) were used as purchased. Distilled–deionised water was used to prepare the contaminated water samples. 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.

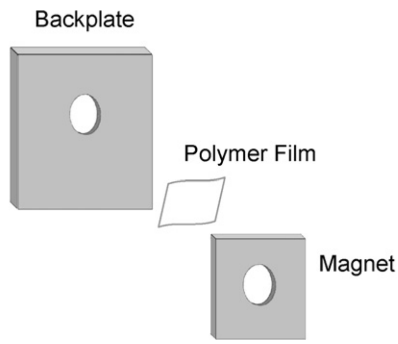

Fig. 1. Schematic diagram of SPME/IR holder.

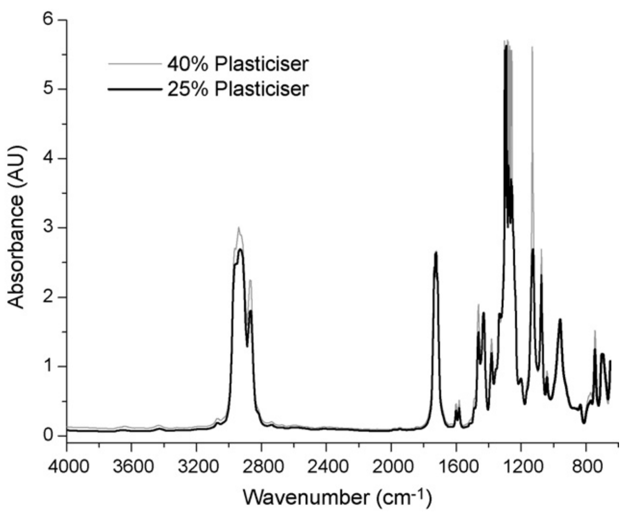

Fig. 2. Infrared absorption spectrum of 150 μm thick poly(vinyl chloride) film with 40% (gray) and 25% (black) of the stabiliser.

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

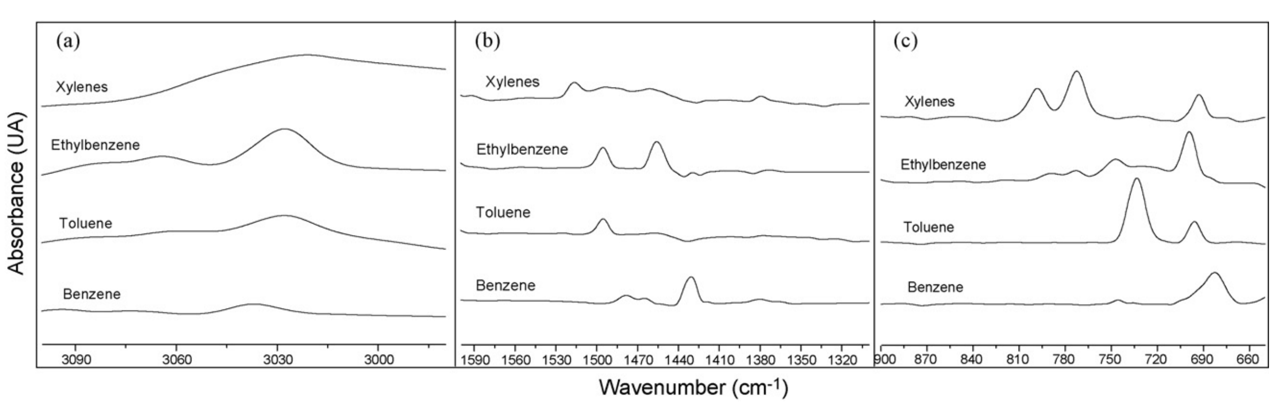

Fig. 3. Infrared spectra obtained in PVC following a 60 min extraction of a water solution containing 80 mg L^{-1} each of benzene, toluene, ethylbenzene and xylene: (a) 2985–3115 cm^{-1} region, (b) 1310–1600 cm^{-1} region, (c) 650–900 cm^{-1} region.

xylenes 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].

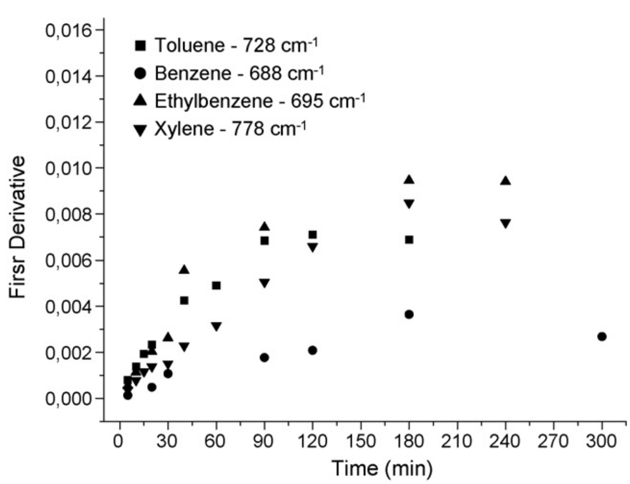

Fig. 4. First derivative signal of the absorbance spectra as a function of time for 80 mg L^{-1} aqueous solutions of toluene, benzene, ethylbenzene and xylenes.

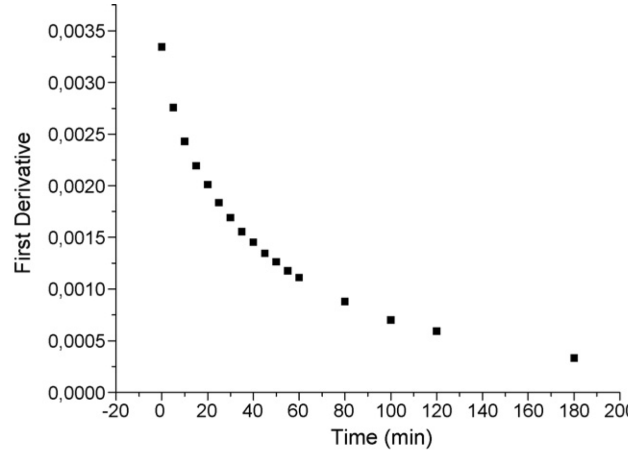

Fig. 5. Evaporative loss of xylenes from PVC following a 60 min extraction (measurements at 778 cm^{-1}).

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 xylenes, 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

Table 1
Principal analytical first derivative peaks for the BTEX compounds extracted by PVC sensing phase (25% of DOP) employing an extraction time of 60 min, with 2.4 mol L^{-1} NaCl

Analyte	Abs. bands (nm/cm^{-1})	Slope (AU/mg L^{-1})	R	LD (mg L^{-1})[a]
B	3284/3045	3.0×10^{-5}	0.9911	11
	6738/1484	2.8×10^{-5}	0.9947	10
	14,538/688	2.6×10^{-5}	0.9818	**5**
T	3310/3021	7.3×10^{-5}	0.9922	6
	6672/1499	4.7×10^{-5}	0.9930	7
	13,740/728	3.6×10^{-5}	0.9898	**7**
E	3310/3021	1.3×10^{-4}	0.9907	3
	6668/1499	8.7×10^{-4}	0.9794	3
	6706/1491	1.0×10^{-4}	0.9825	7
	14,386/695	4.7×10^{-5}	0.9947	9
X	6572/1522	6.9×10^{-5}	0.9954	10
	12,848/778	3.7×10^{-5}	0.9968	4
	14,360/696	2.5×10^{-5}	0.9932	24
	14,510/689	2.7×10^{-5}	0.9982	12

[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 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 ($LD_{table\ 1}$ and as suggested by Stahl and Tilotta [12] (LD_{S-T}) for PVC with 25% plasticiser

Analyte	Wavenumber (cm^{-1})	$LD_{table\ 1}$	LD_{S-T}
Benzene	688	5	3
Toluene	728	7	1
Ethylbenzene	695	9	3
Xylene	778	4	4

The relative standard deviations (R.S.D.) were estimated using measurements of five authentic replicates (different extractions with different films) of a 40 mg L^{-1} aqueous solution of each analyte, providing values of 5.4% for toluene (at 728 cm^{-1}), 12.4% for ethylbenzene (at 695 cm^{-1}), 8.3% for xylene (778 cm^{-1}) and 20.3% for benzene (at 688 cm^{-1}). These values are of acceptable magnitude for volatile compounds [12].

The recommended procedure for determining the detection limit of a method, such as those listed in Table 1, is difficult and time-consuming. Stahl and Tilotta [12] estimated the detection limit based on a concentration that produces an absorbance value twice the noise of the baseline. This criterion, reported by

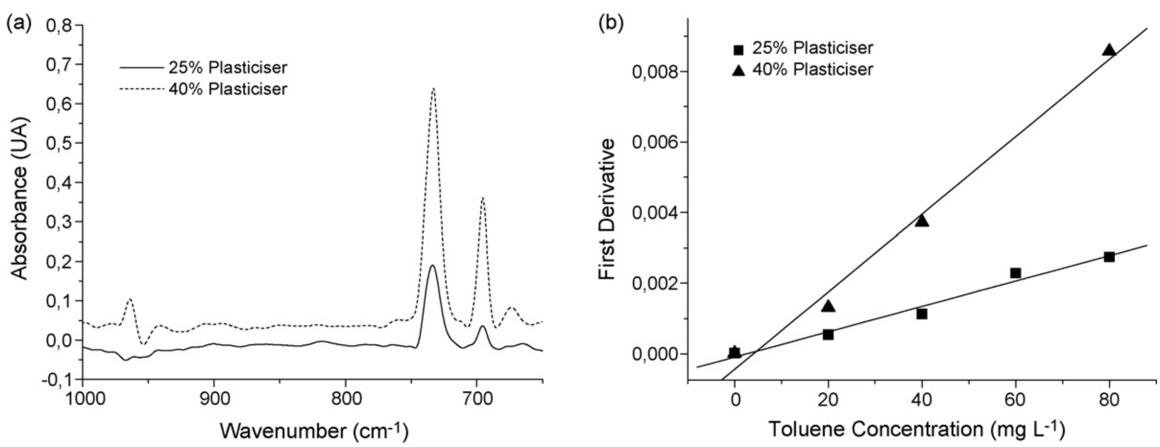

Fig. 6. Effect of increasing the plasticiser concentration from 25 to 40% on the 80 mg L^{-1} toluene solution (extraction time of 60 min) (a) spectra and (b) slope of the analytical curves (728 cm^{-1}).

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

Sensing phases	Method	Extraction time (min/LD mg L^{-1})			
		B	T	E	X
PIB[25]	ATR	–	20/0.29	–	–
EP/Co[7]	ATR	20/0.04	20/0. 08	–	Ortho 10/0.01 Meta 20/0.02 Para 20/0.02
Parafilm M[11]	Transmittance	90/0.18	30/0.75	60/0.18	Ortho 165/0.10 Meta 165/0.08 Para 200/0.07
PDMS[9]	Transflectance	90/8.0	180/7.0	360/2.6	405/3.0
PDMS[13]	Transmittance	60/0.08	60/0.12	60/0.14	60/0.27
PVC (this work, 25% plasticiser)	Transmittance	60/5	60/7	60/9	60/4

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 in 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.

Acknowledgments

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