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DEVELOPMENT OF PLASTICISED PVC SENSING FILMS FOR THE DETERMINATION OF BTEX COMPOUNDS IN AQUEOUS SAMPLES

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A novel plasticised PVC polymer membrane as a sensing film for the determination of BTEX compounds using ATR-FTIR spectroscopy is demonstrated. A range of 10 plasticised PVC phases have been investigated using toluene and tetrachloroethylene as test analytes. Both analyte enrichment rates and infrared absorbance values were considered when choosing a suitable polymer for sensing. An enhancement in analyte absorbance at the characteristic IR absorption bands was noted as the plasticiser concentration in the film was increased. 2% PVC with 75% diisooctyl azelate was found to show promising results for simultaneous determination of the BTEX compounds. All BTEX analytes can be measured in less than 8 min. A study of a multicomponent sample demonstrated that analyte enrichment times were influenced by the presence of even one additional analyte component in the sample.

Keywords: Plasticiser; Sensing polymer films; Infrared spectroscopy; BTEX compounds

INTRODUCTION

Petroleum hydrocarbons pose a treat to the environment and to humans. Petroleum is composed of the aromatics BTEX (benzene, toluene, ethylbenzene, xylene isomers), naphthalene and the aliphatic alkanes, octane and decane [1]. The BTEX compounds are hazardous, carcinogenic and neurotoxic, and are classified as priority pollutants by the US Environmental Protection Agency (EPA), particularly benzene, which is a leukaemic agent in humans and has a very low maximum admissible concentration in drinking water of 5 µg/L. Underground tanks can leak due to internal or external corrosion of the metal. Leaks can occur through holes in the tanks or in associated piping and valves [2]. Underground tanks by the nature of their position pose a great monitoring challenge.

Consequently, a sensor, which could be placed in the subsurface environment, would alleviate the monitoring problems. Many laboratory-based methods are available for the

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determination of the BTEX compounds. These include gas chromatography (GC) [3], UV–Visible spectroscopy [4] near-infrared (NIR), infrared (IR) and raman spectroscopy [5,6] and solid phase micro-extraction methods (SPME) [7,8]. These techniques are laboratory based whereas an *in situ* method would be a more efficient, easier method, as samples would not have to be withdrawn and brought to the laboratory for analysis. Hauser and Popp [9] have utilised a mobile gas chromatographic device, originally designed for the analysis of the BTEX compounds in air and connected it to a flow cell for dynamic membrane extraction. Stellman *et al.* [10] evaluated a long-pathlength fiber-optic Raman ‘dip-stick’ for rapid *in situ* determination of BTEX in water. Limits of detection of 8–48 ppm for the BTEX analytes were calculated.

One approach, which is being investigated to increase the rate of diffusion of an analyte into a polymeric film, is the incorporation of a plasticiser into the polymer [11,12]. A plasticiser is a low-molecular weight compound that lowers the glass transition temperature (T_g) of the polymer. The wide range of plasticisers available affect the structure of PVC in various ways thus allowing more selective polymers to be designed. In a study by Borek and Osoba [13] dioctyl phthalate is used at concentrations ranging from 0–35% with PVC. It was found that the molecules of the plasticiser enter between tightly packed chains of PVC and they involve the separation of the chains. It causes the creation of the free space or a free volume region. According to free volume theory the penetrant molecule moves through the matrix of an amorphous polymer via random diffusional jumps through transient openings into a distribution of hole sizes, or free volume. Each penetrant molecule can jump through any opening equal to or larger than its effective size. At each step, the smallest molecules find the largest number of accessible sites into which to jump and therefore have the highest diffusion rate [14].

The aim of this work is to investigate a variety of plasticised PVC phases for the determination of the BTEX compounds. These polymer films will be used in conjunction with ATR spectroscopy to develop a novel laboratory-based sensing system for the analytes. An air sparging sample delivery system is used in this study simply for transfer of analyte over the sensing film. Although polymeric films have their advantages, problems may arise when a polymer coated internal reflection element (IRE) is soaked in aqueous solution for a long period of time. Firstly, the film may lift off the surface of the IRE, as there is not a strong interaction between the polymer and the surface of the IRE. Secondly, water molecules may diffuse slowly into the polymer coating leading to spectral interference and also a change in refractive index of the coating layer. In order to reduce the above-mentioned problems a gas stream is used to transfer the volatile analytes from the aqueous phase to the IRE [15]. The authors will demonstrate the potential of some newly developed plasticised PVC films for the determination of the BTEX analytes using ATR-FTIR spectroscopy.

MATERIALS AND METHODS

Reagents

Benzene (99+%), toluene (99+%), ethylbenzene (99.8%), *o*-xylene (97%), *m*-xylene (99+%) and *p*-xylene (99+%) were all purchased from Lennox Laboratory Supplies, Dublin, Ireland. Poly (vinylchloride) (62 000 mw) was purchased from the Sigma Aldrich Chemical Company, Dublin, Ireland. The plasticisers (Table I) were purchased

TABLE I List of plasticisers tested, its number and abbreviation

<i>Plasticiser no.</i>	<i>Plasticiser name</i>	<i>Abbreviation</i>
1	Di(2-ethylhexyl) adipate	DEHA
2	Di(2-ethylhexyl) azelate	DEHAZ
3	Di(<i>n</i> -heptyl, <i>n</i> -nonyl) adipate	DHNA
4	Di(<i>n</i> -hexyl) azelate	DHA
5	Dicapryl adipate	DCA
6	Diisooctyl azelate	DIOA
7	Methyl laurate	ML
8	Butyl octyl phthalate	BOP
9	Di(2-ethylhexyl) sebacate	DEHS
10	Epoxidised soy bean oil	ESBO

from Scientific Polymer Products, USA. All chemicals were used without further purification. Zero-grade air was obtained from BOC Gases, Limerick, Ireland.

Materials and Equipment

The sparging system used for sample delivery consisted of tygon tubing, teflon tubing, teflon connections and a 3-way valve (AGB Scientific, Ireland) used for gas transfer from the sample to the sensing element. A rotameter, which was calibrated with a digital flow meter (Cole Parmer), was used to maintain equal gas flowrate. A Mattson 3000 FTIR spectrometer was supplied by Brennan and Company, Ireland. Winfirst software from Microsoft Windows was used to collect the data. A ZnSe ATR crystal ($6.2 \times 1.5 \times 0.7$ cm) with an angle of incidence of 45° was obtained from Brennan and Company, Dublin, Ireland. FTIR instrument conditions used were as follows: Velocity = 5 kHz; gain = 1; scan number = 64; resolution = 8.

PROCEDURES

Analyte Preparation

The analytes used for the initial investigations with the test plasticised PVC phases were tetrachloroethylene (TeCE) and toluene. 100 mg/L TeCE was prepared in 1 L of distilled water ($61.61 \mu\text{L}$ TeCE/L water) and stirred for 30 min. 100 mg/L Toluene ($115.60 \mu\text{L}/\text{L}$) was prepared in a similar manner to the latter. The analytes were added neat. While the analytes in the study are highly volatile and hydrophobic a solvent mediator (e.g. methanol) was not used, as it was not found to greatly improve measurement responses. The solutions were stirred constantly for 20 min before sparging was carried out. The analyte test solutions were kept at room temperature. A mixture containing 100 mg/L each of benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene was generated by adding the appropriate quantity of neat analyte to make up 1 L with distilled water. The compounds were also prepared individually in 1 L of distilled water to act as standards.

Measurement Protocol

Measurements of the analytes were carried out by purging zero grade air, (at a determined flow rate), through the aqueous samples, over the polymer-coated

ATR crystal. Quantitation of the specific analyte species was done by measuring the peak height of the characteristic IR absorption band for each analyte at a specific time. A measurement of a polymer coated ATR crystal purged with air was used as a reference.

Polymer Preparation

The investigation of plasticisers for use in PVC sensing films involved two stages.

- (I) Initially a range of 10 plasticisers were studied at two concentrations (25% and 65% w/w). From this study it was possible to select some potentially suitable plasticisers for enrichment of the target analytes. The plasticisers which have been investigated are listed in Table I. To prepare each PVC (2% w/v)-plasticiser (25% w/w) solution, 2 g of PVC (2%) was weighed out, combined with 0.6 g of the plasticiser and dissolved in 100 mL of tetrahydrofuran (THF). The mixture was stirred in a glass container until it was dissolved and of uniform consistency. To prepare 65% (w/w) plasticised film, 2 g of PVC was weighed out, mixed with 3.7 g of plasticiser and dissolved in 100 mL of THF.
- (II) For the second stage 2 plasticised PVC phases were selected. 2 g of PVC was weighed out with 6 g of plasticiser (giving 75% w/w) and dissolved in 100 mL of THF.

Coating Method

The polymer coatings were applied to the ATR crystal using a spin-coating technique. The crystal was held in position in the spin coating device under a vacuum. 250 μ L of polymer was dropped onto the crystal and the crystal was spun at 350 RPM for 18 s. Film thickness was measured using a profilometer (Dektak v 200-Si) e.g. the estimated thickness of a 2% PVC with 65% plasticiser (No. 6) was 0.5 μ m and with 75% plasticiser, 1 μ m.

Sparging Technique

A sparging system was used to deliver the sample. This involved flowing zero-grade air at 100 mL/min through an impinger containing a porous frit immersed in the aqueous sample. The analyte was purged from the aqueous phase into the gaseous phase and over the coated sensing element as shown in Fig. 1. For the initial characterisation of the films, measurements were carried out over a 30 min time period. For quantitation purposes measurements are taken at set time periods, usually at t_{90} . A strict time protocol was adhered to and this enabled good reproducibility of measurement (Table II).

Detection of the analyte took place as the analyte enriched into the polymer film where it interacted with the evanescent wave generated at the crystal surface. The selectivity was enhanced because the gas stream can only move volatile species out of the aqueous solution leading to less interference by the non-volatile compounds in the matrix. Spectral interference due to water was also eliminated.

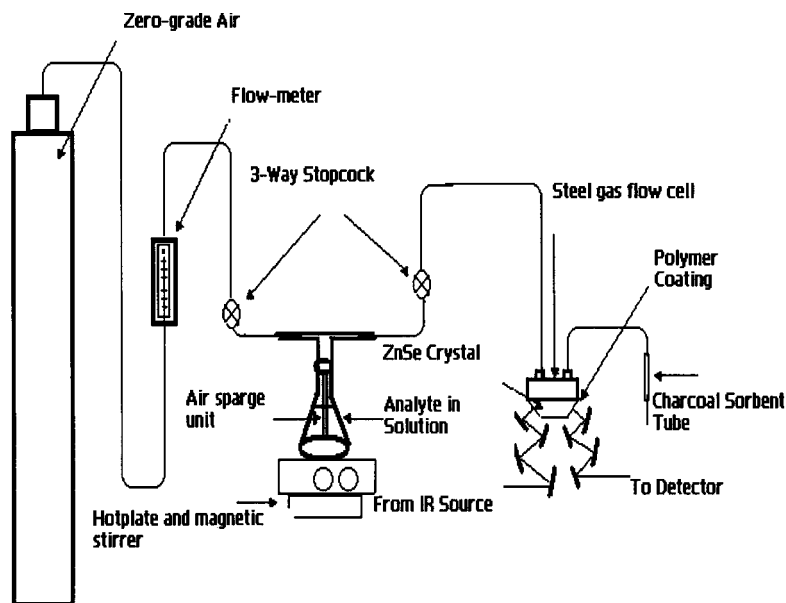


FIGURE 1 Schematic diagram of sparging set-up used to purge the analytes from the aqueous phase to the gaseous phase to the ATR-FTIR film-sensing device.

TABLE II Table showing (a) characteristic wavenumber used for measurements for BTEX compounds, (b) % RSD for t_{90} and absorbance measurements for analytes measured individually in solution (c) % RSD for t_{90} and absorbance measurements for analytes measured as part of a mixture of 6 species. Data points taken at 45 s intervals. Values for %RSD calculated for $n = 3$. Polymer film = 2% PVC/75% DIOA

BTEX analytes	(a)	(b)				(c)			
	Abs. bands (cm^{-1})	Measurement of individual analyte in solution				Measurement of a mixture of six analytes in solution			
		t_{90} (min)	%RSD t_{90}	Abs.	%RSD Abs.	t_{90} (min)	%RSD t_{90}	Abs.	%RSD Abs.
Benzene	677	2.7	0	0.12	9.4	2.4	25	0.19	6.7
Toluene	729	2.0	0	0.13	3.9	5.8	5.9	0.24	6.4
Ethylbenzene	696	4.5	8.6	0.16	3.4	10.7	3.2	0.29	8.3
<i>o</i> -xylene	742	7.4	0	0.27	7.0	20.4	18.8	0.42	5.6
<i>m</i> -xylene	768	7.4	0	0.18	1.2	17.8	27.3	0.25	5.3
<i>p</i> -xylene	795	5.4	7.2	0.15	0.3	18.4	19.3	0.25	10.5

RESULTS AND DISCUSSION

Plasticiser Selection Steps

An investigation of plasticised PVC phases was carried out using the BTEX compounds as target analytes. In stage 1 of the investigations 10 plasticised PVC films were tested using TeCE and toluene as the test analytes. A variety of plasticiser types were investigated including azelates, adipates, phthalates, sebacates and oils. By selecting a suitable plasticiser with the most suitable characteristics for the analyte in question e.g. polarity, enrichment capability and suitable spectral characteristics, a polymer

can be tailor made for the analytes of interest. A more rapid response can also be achieved when the analyte is compatible with the plasticiser. The aim of this broad study was to select a plasticiser, which gave the best compromise between t_{90} values for the analytes and absorbance values. The value t_{90} is used to represent the analyte enrichment rate. For this study the term t_{90} can be defined as, the time taken for the analyte to reach 90% of the maximum absorbance value at the characteristic analyte IR band. From this it was possible to select two plasticisers for stage 2 of the study i.e. investigation of multi-analyte effects.

Sparging for Sample Delivery

The aim of using this sample delivery technique is principally to remove interference of water from the film for initial polymer film characterisations. While state of the art may involve stabilising the polymer layers by covalently binding the polymer film to the transducer surface, this initial study does not involve such an adhesion process. The method of sparging the sample described here was found to be reproducible as demonstrated by the results shown in Table II.

Effect of Varying Plasticiser Concentration

Figure 2 is a bar chart representing the effect of plasticiser concentration on the enrichment of the test analytes, TeCE and toluene. 100 mg/L concentrations of TeCE and toluene were used with films of 2% PVC containing 25 and 65% plasticiser. Overall, the absorbance of the analyte TeCE (measured at 910 wavenumbers cm^{-1}) reached a higher maximum level with all plasticised PVC phases compared with the analyte toluene. This was probably due to a higher molar absorptivity for TeCE than toluene.

From the investigation a trend was observed that on going from the 25 to 65% concentration of plasticiser for both test analytes an enhanced maximum absorbance value was achieved. While the main goal for optimisation of a sensing film for analyte determination would be lower detection limits or high signal-to-noise ratio, these initial

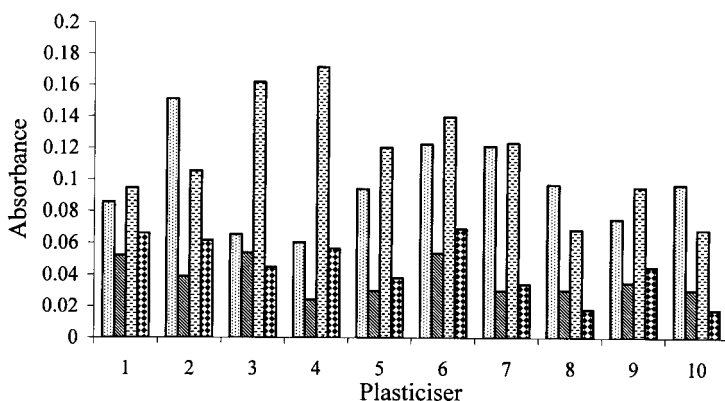


FIGURE 2 Bar chart representing the effect of plasticiser concentration on the enrichment of TeCE and toluene [100 mg/L]. Analytes were sparged at a flow-rate of 100 mL/min. 2% PVC with 25 and 65% concentrations of plasticiser were used. The plasticisers are listed in Table I. Maximum absorbance values are shown (%RSD < 10 for $n=3$ repeat measurements). TeCE in 25%; Toluene in 25%; TeCE in 65%; Toluene in 65%.

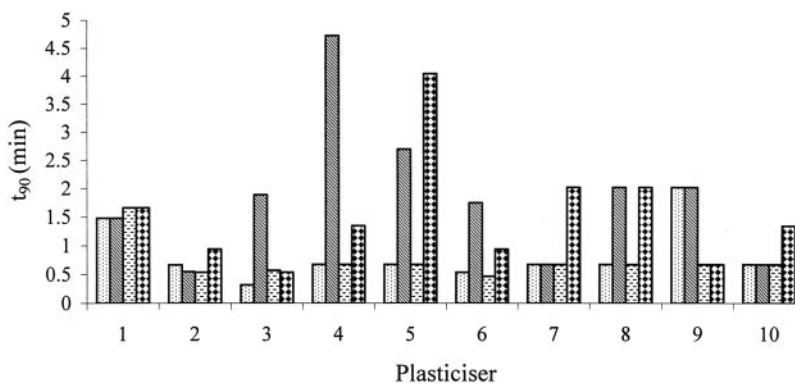



FIGURE 3 Bar chart representing enrichment time *versus* plasticiser type. Test analytes are TeCE and toluene at [100 mg/L]. Analytes were sparged at a flow-rate of 100 mL/min. 2% PVC with 25 and 65% concentrations of plasticiser. The plasticisers are listed in Table I ($n=3$ repeat measurements). 

observations on absorbance provided information for comparison purposes. The increase in plasticiser concentration made the PVC more amorphous thus facilitating enrichment of more analyte within it.

The t_{90} value was also taken into consideration for selection of a suitable plasticiser for the sensing film. Figure 3 represents the effects of plasticiser concentration on the t_{90} values of TeCE and toluene. For the analyte TeCE t_{90} values of less than 1 min were observed for the majority of the films tested with the exception of plasticiser No. 1 (DEHA). No change in t_{90} was noted on going from the 25 to 65% concentration of plasticiser for TeCE. The latter is due to the limitations of the instrument as measurements could only be taken every 45 s. By taking data more frequently it would be possible to determine a more accurate t_{90} for rapidly enriching analytes like TeCE. The important thing to note from this study was that all plasticisers allowed the smaller molecule to enrich rapidly, while the enrichment rate of the larger molecule (toluene), was determined by the % plasticiser in the PVC film.

t_{90} values of up to 6 min were observed for toluene at the 25% concentration of plasticiser. However, at the higher concentration (65%) plasticiser a reduction in t_{90} was observed. This was noted with plasticiser Nos. 3, 4, 6 and 9. This trend was also noted in the literature [15] and is a significant factor in measurement of these analytes in real time situations where interfering compounds might be eliminated based on enrichment rates.

Toluene, an aromatic hydrocarbon is larger and bulkier in size than TeCE, an aliphatic hydrocarbon, thereby explaining the longer enrichment rates observed.

Multi-component Effects

From the initial study of a range of plasticisers, it was possible to select two suitable films for the target analytes. The plasticisers chosen were di(2-ethylhexyl) azelate (DEHA) and diisooctyl azelate (DIOA). In designing a sensing film it is important that measurements can be obtained rapidly and reproducibly. These plasticisers gave the best compromise between analyte enrichment rate and absorbance for the target analytes. The 6 BTEX analytes were measured simultaneously. Figure 4 shows the

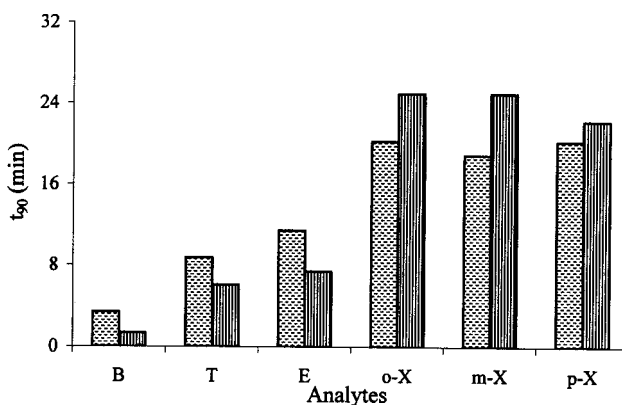




FIGURE 4 Effect of analyte measured as part of a mixture on enrichment rate. Bar chart representing enrichment rates (t_{90}) of BTEX compounds [100 mg/L] as part of a mixture with 2 plasticised PVC phases. 2% PVC with 75% concentrations of plasticiser were used. Analytes sparged at a flow-rate of 100 mL/min. Abbreviations for analytes: B = Benzene; T = Toluene; E = Ethylbenzene; o-X = o-Xylene; m-X = m-Xylene; p-X = p-Xylene.  = DEHA;  = DIOA.

enrichment rates (t_{90}) for the BTEX compounds with the 2 plasticised films selected. The xylene isomers require the longest time to enrich into the films. These analytes have a bulkier structure than the other BTEX compounds therefore the available free volume may inhibit their ingress. Free volume as developed by Cohen and Turnbull [14] predicts that transport occurs when a diffusing species encounters a space that exists with a volume greater than an analyte volume. In this theory a geometrical factor relating to the transported species is also taken into account. The smallest molecules find the largest number of accessible sites into which to jump and therefore have the fastest enrichment rate [14]. However, special polymer and penetrant interactions may also occur in addition to macromolecular variations.

Simultaneous Analysis

The simultaneous determination of BTEX compounds was carried out by measuring their associated IR bands and the results are shown in Table II. A study was carried out to observe the effects of the analytes present in a mixture, on the measurement of a particular single analyte. In order to do this the diffusion behaviour of a mixture of BTEX compounds and individual BTEX compounds was monitored using a DIOA-PVC film. It was observed that when the analytes are investigated individually (i.e. the sample is a single component in deionised water) they have t_{90} values below 7.5 min. In comparison, when the analytes were studied as a mixture (i.e. the sample contained all 6 BTEX compounds in water) the t_{90} values increased dramatically for each analyte, especially for the xylene isomers. When the analytes are studied individually there is no competition for enrichment and so they enter the polymer membrane with ease. However, when other analytes are present in a mixture there is competition. Benzene was found to have the lowest t_{90} (2.4 min) followed by toluene (5.8 min), ethylbenzene (10.7 min) and lastly the xylene isomers (18–20 min). This trend was observed with the majority of plasticisers studied. This observation can be linked to the size and shape of the analyte molecules [11]. The overall trend as summarised in

Table II was that the time taken for analytes to enrich from the mixture exceeded that of analytes when measured individually. The %RSD values shown indicate that from these initial studies, the reproducibility of measuring components in a mixture is poorer than when the components are in solution alone. This may be attributed to a mutual increase in analyte solubility, hence lowering the vapour pressure, leading to variability in the gas phase concentration under the experimental conditions used.

Competitive Effects of Analytes

A study was carried out to investigate the effect on the target analyte measurement when one other species is present. Figure 5 shows diffusion curves for the analyte ethylbenzene when measured individually and in the presence of the other BTEX compounds. Similar studies were carried out for each analyte. It can be seen that benzene and toluene had the effect of slightly decreasing the maximum absorbance value for ethylbenzene. The observations relating to absorbance changes may be due to macroscopic changes in the polymer with other compounds entering the sensing film. The polymer structure may become altered thereby affecting the polymer refractive index and thus the absorbance measurement by ATR in the evanescent field technique. Further studies are needed to confirm this.

The xylene isomers were found to inhibit ethylbenzene from entering the film to a greater degree. These compounds also had the effect of increasing the t_{90} values for

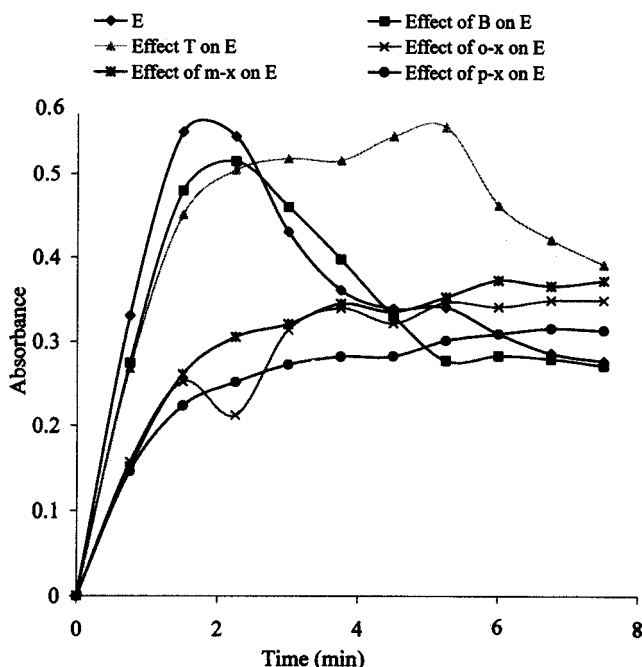


FIGURE 5 Diffusion profiles showing the effect of benzene, toluene and xylene isomers on the diffusion of ethylbenzene into 2% PVC with diisooctyl azelate. 100 ppm concentrations of the BTEX compounds were investigated in. Abbreviations for analytes: B = Benzene; T = Toluene; E = Ethylbenzene; *o*-X = *o*-Xylene; *m*-X = *m*-Xylene; *p*-X = *p*-Xylene.

ethyl benzene enrichment. This study showed that in a real sample where many components are present simultaneously, other analytes present will affect the sensor response significantly.

CONCLUSIONS

The preliminary results presented here show that novel plasticised PVC phases show promise as sensing films for determination of BTEX compounds using ATR-FTIR spectroscopy. Of the 10 plasticisers investigated in this initial study diisooctyl azelate performed most favourably for the determination of BTEX compounds as a group and was selected for investigation of enrichment effects. Other plasticisers also showed promise. The authors have shown that simultaneous determination of a BTEX mixture is possible providing useful qualitative information. Further work is needed in order to realise quantitation due to the competitive effects, which were observed. The results have shown that by modifying the PVC film (increasing plasticiser concentration) led to a reduction in enrichment time (t_{90}) and improvements in absorbance values for the mixture of BTEX compounds.

In order to assess the selectivity of the films towards the BTEX compounds the enrichment of TeCE and toluene was compared. By comparing the t_{90} values it was possible to select plasticisers that readily allowed or inhibited enrichment of toluene. Further work on polymer and method selectivity is required. Reproducibility of enrichment measurements for the plasticised film (2% PVC with 75% diisooctyl azelate) was found to be < 10% RSD ($n = 3$, t_{90} and absorbance) for determination of BTEX compounds when measured individually. Further studies are on-going to address the issue of sensor film robustness, selectivity and plasticiser-leaching effects.

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