Polymeric nanofilm-coated optical fibre sensor for speciation of aromatic compounds

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An optical fibre sensor has been shown to be suitable for monitoring of benzene, toluene and *o*-xylene (BTX) with both high selectivity and sensitivity. The sensing principle underlying this experimental device is based on the changes of the reflected optical power when BTX vapours are present in the analytical tube containing an optical fibre coated with a thin film of poly[methyl(3, 3, 3-trifluoropropyl)siloxane]. The interaction of organic vapour with the sensitive surface promotes a variation of the light power, proportional to the amount of adsorbed BTX vapour. A set of experiments concerning different operational conditions was performed in order to promote a higher analytical performance and the newly developed BTX sensor showed higher sensitivity and shorter analytical time than a method based on gas chromatography–flame ionisation detector. Furthermore, the proposed sensor also provides the basis for an inexpensive analytical technique with adequate specificity for measurements of BTX at trace levels with appropriate reversibility, repeatability, and reproducibility. Finally, the analytical performance of the developed sensor was also evaluated and found adequate for industrial air samples.

Keywords: BTX sensor; fluorosiloxane polymers; optical fibre sensor; confined environments monitoring

1. Introduction

The monitoring of aromatic hydrocarbons, such as benzene is extremely important from the environmental and public health points of view, since this compound is known to be carcinogenic [1] and included in a group of substances especially harmful to human health.

Benzene has been widely used as a solvent in chemical industries, in adhesives, in shoe making and printing industries. In recent years, the benzene utilisation has been reduced mainly after a wide awareness of its harmful effects, especially on human health. Nowadays, the potential and dangerous sources of benzene exposure are limited to some industrial uses, gasoline vapours and tobacco smoke [2].

Based on the ubiquity of benzene, toluene and *o*-xylene (BTX) on certain industrial environments and also on its carcinogenic potential there has been an increasing need to

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obtain reliable data on the levels of BTX in indoor and outdoor industrial atmospheres to prevent exceeding safety levels and assuring an acceptable air quality. From the analytical point of view and due to an increasing environmental awareness and pollution control strategies, accurate determination, *in situ* and real-time monitoring of BTX vapour becomes an important aim in environmental science as well as in sensor technology applied to environmental protection.

Optical fibre (OF) sensors show very appropriate analytical characteristics and attractive advantages, especially when compared to the traditional sensors used, for chemical sensing and monitoring. They show no electromagnetic interferences, high durability, small size, low maintenance cost, short analytical time and simple design [3–5]. Furthermore, OF sensors provide the possibility for fast, accurate, *in situ* and safe detection of toxic compounds besides showing high potential for remote measurements in inaccessible and harsh environments, in a continuous mode operation.

Many OF sensors have been developed for organic vapour detection, and the great majority of these sensors are based on polymeric film deposition on an uncladded optical fibre section. Basically, this type of sensor measures changes on polymer proprieties when a volatile organic compound (VOC) is absorbed. For example, researchers have used surface plasmon resonance (SPR) sensors for measuring refractive index changes on the polymeric film [6–8]. Ueno *et al.* [9] have also reported a portable system for BTX mixture analysis based on microfluidic device using mesoporous silicate adsorbent.

Thin films of polysiloxanes have been used as a sensitive sensor component with excellent results concerning organic compounds detection [10–15] and showing advantages, such as high thermostability, high chemical inertness and low dielectric constant when compared to more classical polymers [16,17]. Abdelghani *et al.* [6,7] developed a surface plasmon resonance (SPR) fibre sensor employing fluorosiloxane polymers as sensitive component for detection of vapours of chlorinated hydrocarbons and some aromatic compounds. However, low analytical selectivity and/or sensitivity constitutes analytical disadvantages, which are frequently attributed to these analytical devices. Furthermore, neither actual samples from field monitoring applications have been reported nor any comparative studies between OF sensors and a classical analytical methodology of reference have been carried out.

This work aimed at the development of a new and compact design for an OF sensor for monitoring of BTX. The sensor response was assessed and compared with gas chromatography–flame ionisation detector (GC–FID) in terms of BTX speciation with both high accuracy and sensitivity.

2. Experimental

2.1 *Development of an OF-based sensor*

2.1.1 *Optical fibre preparation*

The optical fibre (OF) chosen for this work was a single-mode optical fibre pigtail, core and cladding diameters of 4 and 125 μm, respectively. A directional 50 : 50 Y optical coupler (OC) was utilised. A small length of the OF in Port 3 was mechanically uncladded and then immersed in dichloromethane, in order to remove the protective cladding. The cleanness of the OF surface was checked by optical microscopy. The uncladded section was then cleaved on a length of 25 mm with a Cleaver V6 (from Future Instrument) precision fibre cleaver. On the cleaved OF end it was deposited, a thin polymeric film of

poly[methyl(3, 3, 3-trifluoropropyl)siloxane] (PMTFPS) with a refractive index of 1.383, Aldrich (481645).

2.1.2 *Polymeric film deposition and cure*

The sensitive film was achieved by coating the OF end with a solution of PMTFPS at 0.01% in dichloromethane (coating solution) by a spray technique. The coating solution was introduced into the aerographer reservoir and sprayed onto the optical surface. The deposition process was performed inside the home-made deposition chamber with an incorporate rotation system, allowing a uniform, constant, and circular movement of the cylindrical and uncladded OF surface. Finally, the OF was cured at 70.0°C during 24 h in order to produce a hard porous polymeric film. The temperature of polymeric film cure was previously determined in order to optimise the analytical performance of the OF sensor [18]. After the cure process the sensitised OF was introduced in a constant flow (10 mL min^{-1}) of nitrogen (N_2) for stabilisation, during 24 h. The film thickness affects the analytical signal of the OF sensor, and its control constitutes an important tool regarding sensors performance. Therefore, the developed sensor was tested for three different polymeric film thicknesses, in order to achieve an analytical performance (high analytical signal, sensitivity and response time) as advantageous as possible. The different polymeric film thicknesses were achieved by increasing the number of spray applications and estimated by Rutherford backscattering spectrometry (RBS).

2.1.3 *Optical fibre sensor design for BTX detection*

A schematic diagram of the sensor configuration is shown in Figure 1. The light beam was emitted by a laser diode (L, $\lambda = 635$ and 650 nm) from Oz Optics that was connected to Port 1. The Port 3 with the sensitised OF was placed through a Teflon plug inside a 7.2 cm long glass tube (analytical tube). The complete OF sensor set-up includes a portable silicon photodiode (F, photodetector), also from Oz Optics (which was connected to Port 2) to

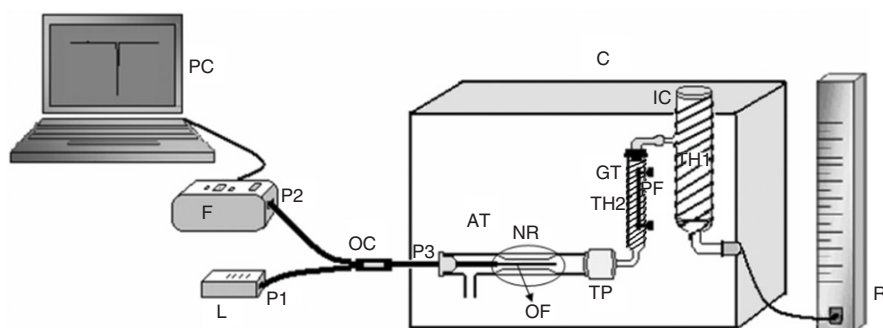Figure 1. Schematic configuration of the experimental layout (PC – laptop for data acquisition and processing, F – photodetector, L – laser diode, P1 – port 1, P2 – port 2, P3 – port 3, OC – optical coupler, AT – analytical tube, OF – optical fibre, NR – narrowed region, TP – Teflon plug, GT – glass tube, PF – PDMS fibre, C – dark chamber, IC – injection cell, TH1 and TH2 – tape heaters, R – flowmeter).

measure the modulated optical signal. The experiments were performed inside a dark chamber (C) to prevent possible environmental light interferences.

The analytical performance of the developed sensor system was also evaluated for measurements at the infrared spectral region. For this study some changes of the analytical system were performed, mostly of them related to the optical components of the OF sensor. The experimental set-up was constituted by an optical power meter with a detector of InGaAs, a laser diode set at 1310 and 1550 nm and an OF with core and cladding diameters of 9/125 μm, respectively.

The sensor behaviour was evaluated for different analytical tube (AT) designs in order to achieve an analytical performance of the OF sensor as high as possible. The same study was also performed regarding injection cell (IC) design. The schematic configuration of the different designs tested for both AT and IC are displayed in Figure 2. Four AT were home-made developed, one of them without narrowed region (ATWNR) and three ATs with a narrowed region of 6, 9 and 12 mm long (ATNR6 mm, ATNR9 mm, and ATNR12 mm). The length and diameter of the four analytical tubes tested were the same. The different designs of the injection cell consist on the inclusion of a bubble breaker (ICBB) and on ICs with a linear structure without bubble breaker of 6, 9 and 12 cm height (IC6cm, IC9cm, and IC12cm). All the ICs were the same diameter and home-made developed.

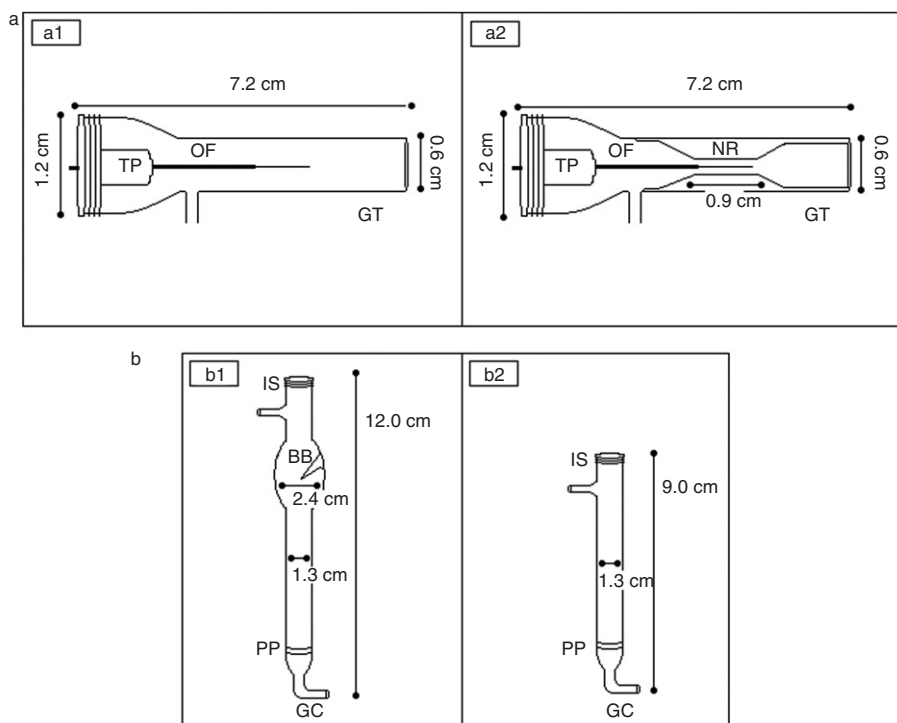Figure 2. Schematic configuration of the analytical tubes (a) and injection cells (b): a1 – analytical tube without narrowed region, a2 – analytical tube with narrowed region, b1 – injection cell with bubble breaker, b2 – injection cell without bubble breaker; TP – Teflon plug, OF – optical fibre, NR – narrowed region, GT – glass tube, IS – injection septum, BB – bubble breaker, PP – porous plate, GC – glass cell.

2.1.4 *BTX measurements*

Standards and samples were injected with a gastight micro syringe (Hamilton) to the top of a glass cell (injection cell, IC). The temperature at the injection cell (IC) was controlled and maintained at 150°C by a coiled tape (TH1, Cole Parmer). The organic compounds were injected as liquids and after vaporisation the organic vapours were carried by a continuous stream (10 mL min^{-1}) of N_2 (N45 from Praxair), controlled with a flowmeter (Sigma), to the glass tube (GT) (adsorption/desorption sensor system) and finally to analytical tube (AT) (detection system component). The carrier gas flow rate affects the velocity and contact time of the organic vapour phase onto the polymeric film, and consequently the sensor performance as already reported elsewhere [18]. The adsorption/desorption sensor system component is constituted by a GT placed between the IC and the AT, which contains a fused silica fibre coated with a film of polydimethylsiloxane (PDMS). This component allows the BTX mixture separation, providing selectivity to the developed sensor system. The analyte molecules are thermally desorbed by increasing the temperature of the second tape heater (TH2), which surrounds the GT by a temperature program controlled with home-made software. The tape heater starts at 22°C, with a program rate of 15°C min^{-1} until 75°C and 30°C min^{-1} until 150°C. The temperature program rate used was previously selected taking into account the best results obtained during the study of the temperature program rate versus sensor analytical performance (sensitivity and selectivity). The constant flow of N_2 was maintained in the system between experiments and no IC cleaning was needed.

The light power guided through Port 3 is reflected at the fibre/polymer interface. The exposure of the fluorosiloxane polymer to vapour of aromatic compounds inside the analytical tube leads to changes in its refractive index and consequently on the reflected light power, which are measured in a photodetector and used as the analytical signal. Data acquisition was performed with a PC via software home-made.

2.2 *Application of a GC–FID methodology*

The GC–FID methodology was performed according to NIOSH methodology [19], in a Gow-Mac Series 600 with a capillary column (fused silica-Supelcowax, 30 m × 0.32 mm ID × 1.0 μm, 100% PEG, Cat no. 24211, Supelco, Spain). Column temperature starts at 40.0°C (10 min) rises up to 230°C with a program rate of 10.0°C min^{-1} and the carrier gas (helium) flow rate was 2.6 mL min^{-1}. The standards injected were aromatic volatiles standard mix solution of benzene, toluene, and *o*-xylene, 100 μg mL^{-1} of each compound in methanol, was analytical grade (Supelco Cat no. 47504). Injections were performed using different volumes of BTX standard solution.

2.3 *Sampling details*

Air samples were collected from a confined industrial environment of a Portuguese solvent industry and analysed by the OF sensor and the GC–FID method. This experiment aimed at the comparison of the analytical performance of the developed sensor against a methodology of reference recommended by NIOSH for aromatic hydrocarbons, regarding actual monitoring of industrial air samples. The sampling process was performed according to the NIOSH 1501 method [19] using coconut shell charcoal, 100 mg/50 mg (Supelco Cat no. 20267-U). The sampling flow rate was 0.2 L min^{-1}, with
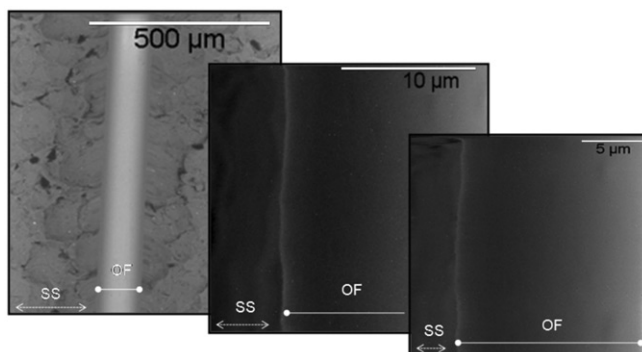
Figure 3. SEM images of an OF coated with a PMTFPS film: SS – SEM stage, OF – coated optical fibre.

a total sampling time and volume of 25 min and 5 L, respectively. Sample desorption was performed while adding 1 mL of carbon disulfide (CS_2) to each vial and allowed to stand 30 min with agitation.

3. Results and discussion

In order to ensure that the coating process provides a homogeneous layer at OF surface, images of Scanning Electron Microscopy (SEM) of the coating surface have been recorded and they are displayed in Figure 3. The OF surface coated with a thin film (2 nm) of PMTFPS by spray technique, shows a very homogeneous and regular texture, without any cracks or holes, proper for applications on OF sensors.

The performance of the developed sensor system was assessed for some operational conditions in order to achieve an analytical signal as high as possible. Firstly the analytical system was tested for three different polymeric film thicknesses, namely 2, 8 and 20 nm. The obtained results are displayed in Figure 4 and it can be observed that the film thickness strongly affects the OF sensor performance. As shown in Figure 4(a) the analytical signal obtained during the analysis of 0.05 μg of benzene (used as proxy for aromatic compounds) using an OF coated with a polymeric film of 2 nm (9.9 dB) was considerably higher than those obtained for a film thickness of 8 nm (7.4 dB) and 20 nm (2.1 dB). A slight increase in recovering time of the analytical signal, has been also observed when using an OF with a film thickness from 2 nm (4 s) to 20 nm (9 s). The analytical sensitivity (slope of the calibration curves) of the OF sensor also increases with the decrease of the polymeric film thickness ($\sim$627, $\sim$204, and $\sim$63 dB μg^{-1} for a film thickness of 2, 8 and 20 nm, respectively), as it can be observed in Figure 4(b).

Secondly the sensor response was evaluated for different working wavelengths, two of them at the visible spectral region (635 and 650 nm) and two at the infrared spectral region (1310 nm and 1550 nm). The results obtained in this set of experiments are displayed in Figure 5, which shows that the intensity and hence the sensitivity of the analytical signal obtained during benzene detection increases in the following order: $635 < 650 < 1310 < 1550$ nm. This increase of analytical signal with increasing wavelengths may be due to the effect also observed by Bariáin *et al.* [4] during studies of OF organic compounds sensor response at three different working wavelengths: an increase of
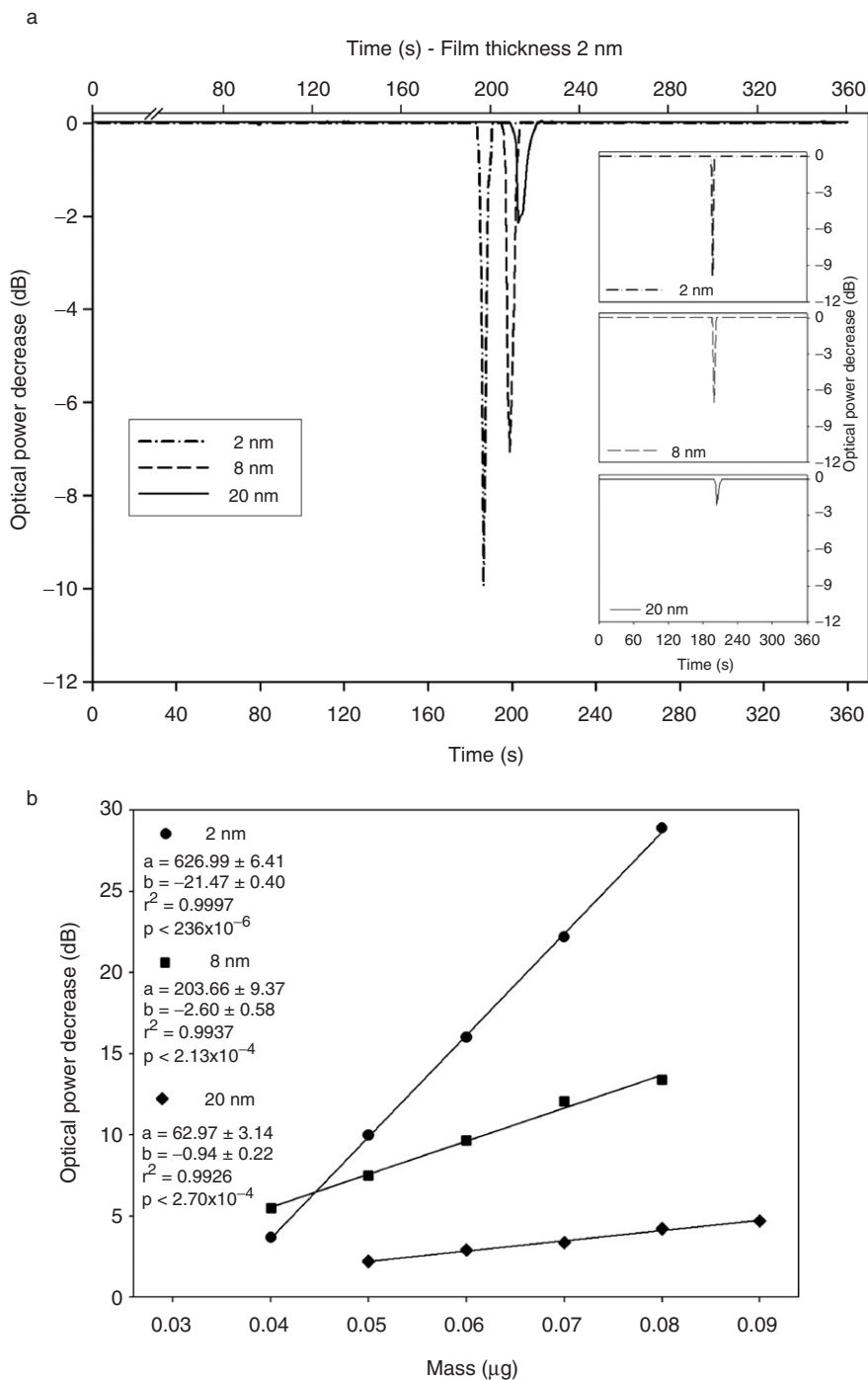
Figure 4. Study of the influence of the polymeric film thickness on the OF sensor response. (a) Example of the sensor response profile obtained for an OF coated with a polymeric film thickness of 2, 8, and 20 nm. (b) Calibration of the OF sensor with different amounts of benzene using an OF coated with different polymeric film thickness (2, 8 and 20 nm).
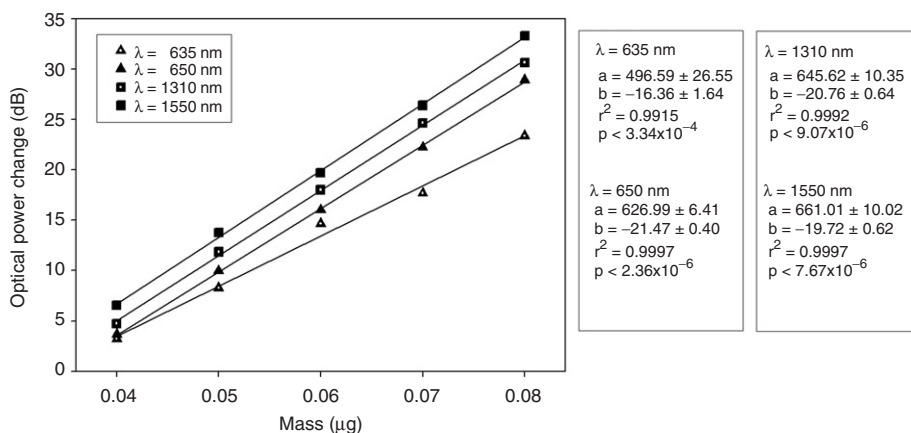
Figure 5. Response of the OF sensor to different amounts of benzene using an optical source set at 635, 650, 1310 and 1550 nm. Estimates of the slope and the interception for each of the linear responses also have their associated SD.

wavelength can cause an increase in the index of refraction of the sensitive film and therefore an increase in the reflected optical power (i.e. the analytical signal). As also shown in Figure 5 the higher analytical sensitivity ($661 \pm 10\,dB\,\mu g^{-1}$) was obtained for a system with a working wavelength set at 1550 nm and the lower system variability (estimated from the coefficient of variation as 1%) was obtained for measurements performed at 650 nm. An estimation of the limit of detection was found to be 5.1, 1.0, 1.5 and 1.4 ng during benzene detection with an OF sensor with a working wavelength set at 635, 650, 1310 and 1550 nm, respectively. The detection limits were calculated using $y = y_B + 3SB$, where SB is the SD of the blank signal estimated as s_{y}/x, the residual SD taken from the calibration line, and y_B is the blank signal estimated from the intercept taken also from the calibration line [20]. However, this criterion for the detection limit calculation is not adequate in this case, since the analytical signal obtained with the OF sensor has been found not linear for concentrations lower than the smallest concentration value of the calibration curve. Therefore, the detection limit for OF sensor was re-calculated based on the 95% confidence interval of the first point of the calibration curve using $x_o \pm ts_{xo}$, $(n-2)$ degrees of freedom, where s_{xo} is given by [20]

$$s_{xo} = \frac{s_{y/x}}{b}\left\{1 + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}\right\}^{1/2}.$$

The detection limit for benzene calculated by the above referred criterion was found to be 39 ± 7, 40 ± 1, 40 ± 2 and 40 ± 2 ng using an OF sensor with a working wavelength set at 635, 650, 1310, and 1550 nm, respectively. These values suggest that the analytical performance of the sensor system working at both visible and infrared spectral region are very similar in terms of the order of magnitude of their detection limits, and therefore they cannot be differentiated in terms of this figure of merit.

Figure 6 reports the evaluation of the influence of the AT design on the analytical performance of the sensor system during benzene detection. In this set of experiments four ATs, containing the sensitised OF, with different designs were used in order to improve the analytical signal. This study was performed using the experimental set-up displayed in
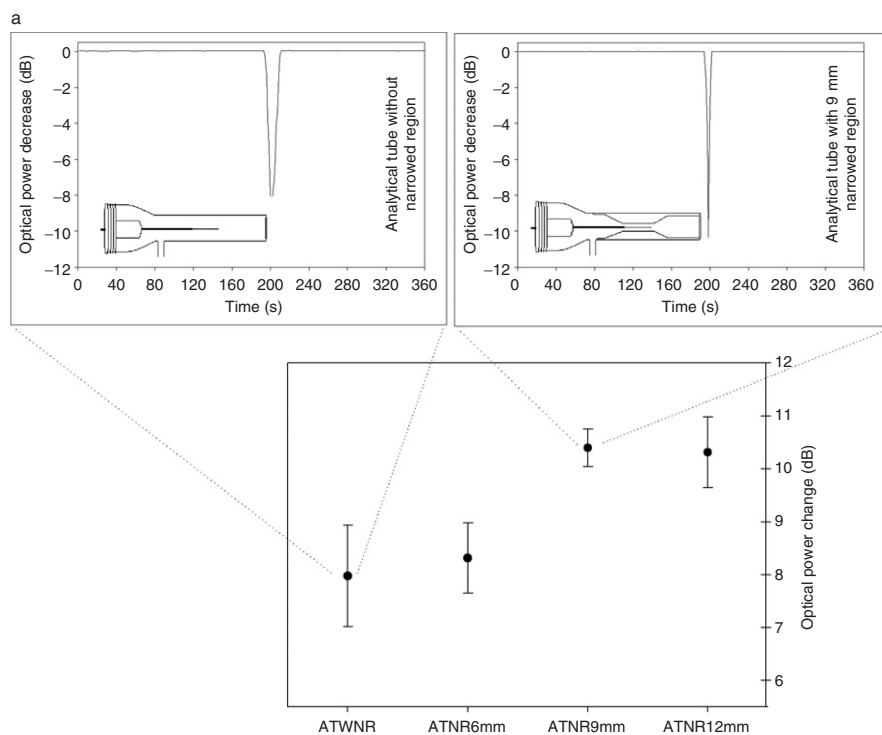
Figure 6. Response sensor during the study of the influence of the analytical tube design (ATWNR – Analytical tube without narrowed region; ATNR6 mm, ATNR9 mm, and ATNR12 mm – Analytical tube with narrowed regions of 6, 9 and 12 mm long, respectively): (a) typical analytical responses; (b) comparison of the optical power change (mean and SD) for ATWNR and ATNR.

Figure 1 with a light source set at 650 nm, focusing the study of the sensor behaviour at the visible spectral region. This operational choice was performed taking into account that the variability of the measurements performed at 650 nm was slightly lower than the one obtained for the other working wavelengths evaluated. From the results displayed in Figure 6(b) it is possible to verify that the mean of the optical power variation slightly increases from an AT without narrowed region (ATWNR) to an AT with a narrowed region (NR) of 6 mm (ATNR6 mm) and further considerably increases for an AT with a NR of 9 mm long, reaching a plateau for an AT with a NR longer than 9 mm. The comparison of the SD obtained for ATWNR and ATNR6 mm, performing an *F*-test, showed that there are no significant difference ($p = 0.245$) between the two variances. However, the variance of the data obtained with an AT with a NR of 9 mm is significantly lower ($p < 0.041$) than the one obtained with an AT without a NR, which suggests that the results obtained using an ATNR9 mm are more precise. These results may be due to the fact that the 9 mm long NR in the analytical tube could provide more contact time, with higher probability of interactions between the organic vapour and the polymeric film, especially when the amounts of analyte to be detected are very low. Furthermore, this analytical tube design minimises the gas flow dispersion. Finally, the *F*-test between the 9 and 12 mm NR indicated that there are not significant differences ($p = 0.127$) between the two associated variances.
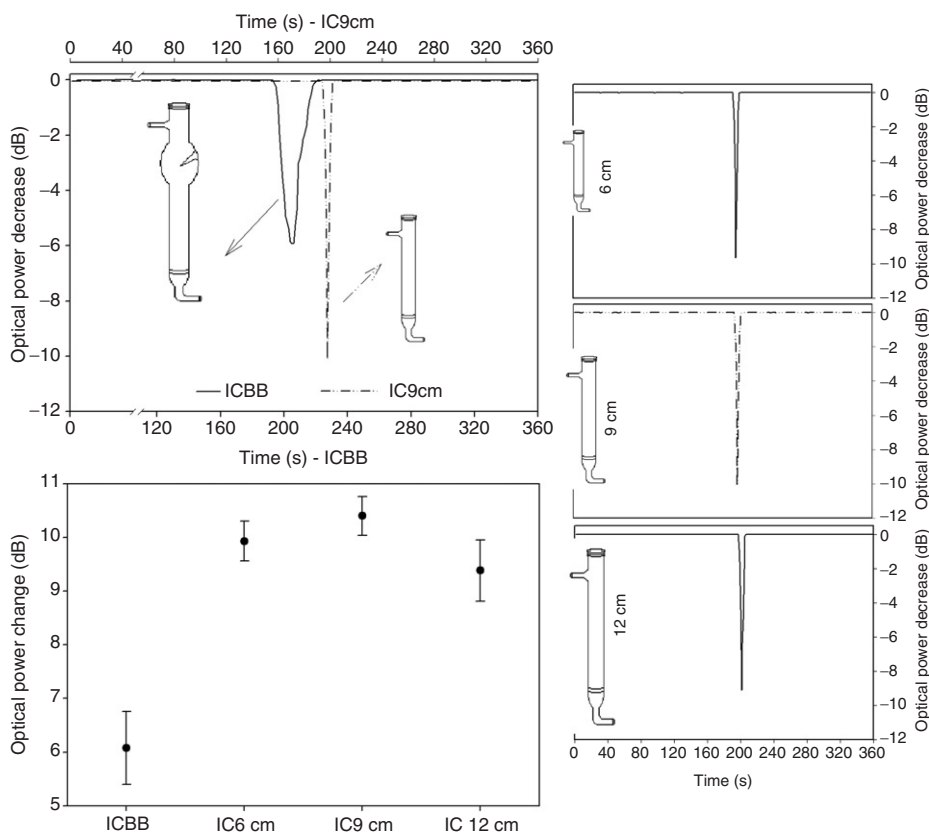
Figure 7. Response sensor during the study of the influence of injection cell design (ICBB – injection cell with bubble breaker; IC 6cm, IC 9cm and IC 12cm – injection cell without bubble breaker of 6, 9 and 12 cm height).

Figure 7 shows the results obtained in the study of the influence of the injection cell (IC) design on the analytical performance of the developed sensor. Improvements on the analytical sensor performance were achieved using ICs with linear structure and without bubble breaker. Such a design may provide for a plug type of flow without a significant mixing area and consequently a smooth Gaussian peak without distortions. The highest optical power variation, meaning the difference between the optical power before injection and the lower value obtained after injection, was achieved for an IC with linear structure without bubble breaker, namely for an IC of 9 cm height (IC9cm). The comparison between the variances obtained for the IC9cm and IC6cm showed that there are no significant difference ($p = 0.433$) of the two variances and there are also no significant difference ($p = 0.273$) between the variances obtained for IC9cm and IC12cm.

In conclusion, and taking into consideration all the above experiments, an improvement of the analytical performance of the sensor can be attained by choosing the following operational parameters: wavelength at 650 nm, utilisation of an analytical tube with a 9 mm narrowed region and IC of 9 cm height with a linear design.

Figure 8 reports the sensor response obtained with increasing injection amounts of BTX, showing that this sensor system shows a high statistical degree of linearity for
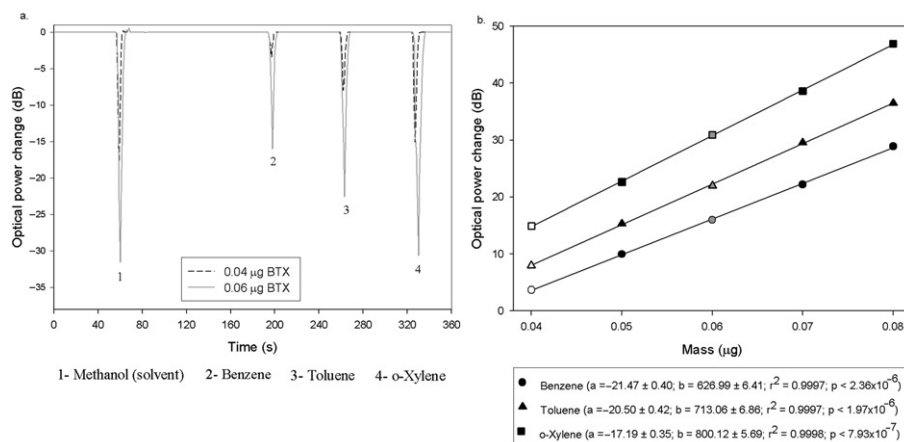
Figure 8. Sensor response for different amounts of BTX: (a) examples of sensor response profile obtained when 0.04 and 0.06 μg of BTX were injected; (b) calibration of OF sensor with amounts of BTX in a range between 0.04 and 0.08 μg.

the calibration model used for the three aromatic compounds analysed. The response of the OF sensor for the three aromatic compounds tested shows different analytical sensitivities, measured as the slope of the calibration curve (dB μg^{-1}) and which increases in the following order: 627 for benzene <713 for toluene <800 for *o*-xylene. The analytical signal depends on the chemical interactions, which can take place between the sensitive cladding (polymeric film) and the analyte molecules, modifying the refractive index of the polymeric film and consequently the reflected optical power. These interactions are strongly affected or determined by both the analyte molecules and sensitive cladding properties. In this way, the different analytes properties, such as the boiling temperature and vapour pressure are sufficiently different to explain the significant differences of sensitivities observed for each organic compound analysed. As it can be inferred from Figure 8 the optical power variation (Figure 8(a)) and the analytical sensitivity (Figure 8(b)) increase with increasing boiling temperatures of the analytes (80.1°C for benzene <110.6°C for toluene <144.4°C for *o*-xylene) and decrease of the vapour pressure in mmHg at 25°C (95.2 for benzene > 28.4 for toluene > 6.7 for *o*-xylene), which is in a good agreement with the results obtained by Abdelmalek *et al.* [10] and Silva *et al.* [18,21] during qualitative measurements of organic volatile compounds by optical fibre analysers sensitised with polymeric films. Furthermore it is important to highlight that the mixture was completely separated into its analyte composition. The analytical response time for each detected compound is very short, $\sim$7 s, which is in good agreement with the nanometric structure obtained for the sensitive film. The total analytical time was found to be around 6 min for all four well-separated compounds detected. The detection limits based on three times the residual SD [20], obtained for the three aromatic compounds analysed by OF sensor and GC–FID method were found to be 1.0 and 1.6 ng for benzene, 0.9 and 1.5 ng for toluene and 0.7 and 1.2 ng for *o*-xylene, respectively. However as already referred this criterion is not adequate for the OF sensor case and its calculation based on the 95% confidence interval of the first point of the calibration curve was found to be 40.1 ± 1.3, 39.9 ± 1.2 and 40.1 ± 0.9 ng for benzene, toluene and *o*-xylene, respectively. The obtained values show the high potential of this

Table 1. Optical power changes obtained in consecutive weeks, with five injections of 0.05 µg of benzene, for the same sensor.

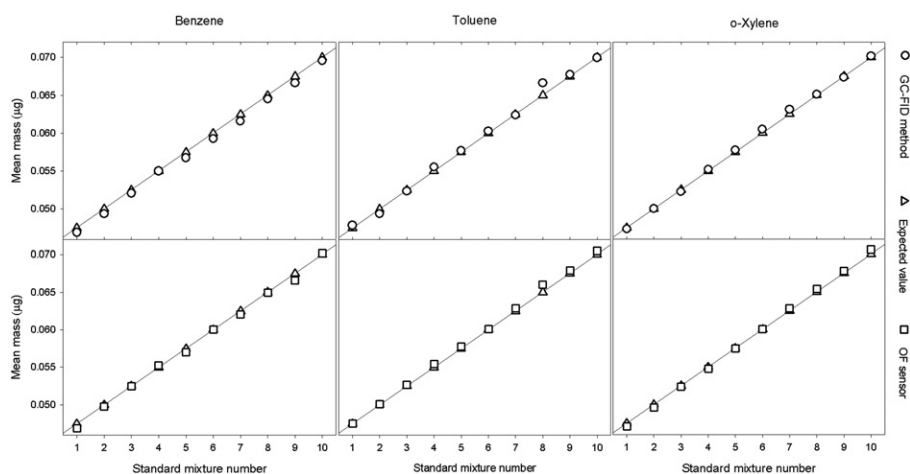| Benzene (µg)	ΔdB			
	1st week	2nd week	3rd week	4th week
0.05	9.950	10.223	10.111	9.956
	10.333	10.123	10.041	10.177
	9.730	9.997	10.045	9.800
	9.843	9.866	9.630	9.954
	10.021	9.656	10.055	9.863
Mean	9.975	9.973	9.977	9.972
SD	0.228	0.222	0.196	0.155

Figure 9. Comparison of the results obtained for 10 standard mixtures of BTX using the GC–FID method and the proposed OF sensor.

sensor system for measuring trace amounts of BTX and they are approximately 10 times lower than the detection limits reported on method 1501 by NIOSH for benzene, toluene and *o*-xylene.

Table 1 shows the optical power variation obtained with injections 0.05 µg of benzene with the same sensor, on consecutive weeks. Between experiments the sensor was kept under nitrogen. The repeatability of the analytical sensor [22], r, was estimated as 5.5×10^{-1} dB, using $r = 1.96 \times \sqrt{2} \times s_w$, where s_w is the residual SD of the sets of five sequential experiments. The reproducibility [22] calculated as $R = 1.96 \times \sqrt{2} \times \sqrt{(s_w^2 + s_b^2)}$, where s_b^2 is the between-weeks variance, is in this case coincident with the repeatability since between weeks variability is not significant ($p = 0.996$).

The analytical performance of the OF sensor was also compared with GC–FID method: 10 different concentrations of BTX were injected, five times each, using both methods in order to test the performance of the developed sensor against the GC–FID method. The obtained results are displayed in Figure 9. The ANOVA of the

Table 2. Comparison of the results obtained with the GC–FID and the proposed OF sensor for five air samples from a solvent Portuguese industry.

Samples	OF sensor	GC–FID	Significant difference
	Benzene concentration (ng L^{-1})		
1	8.41 ± 0.07	8.37 ± 0.36	$p = 0.802$
2	8.31 ± 0.08	8.39 ± 0.42	$p = 0.652$
3	8.15 ± 0.09	8.19 ± 0.25	$p = 0.740$
4	8.30 ± 0.07	8.28 ± 0.24	$p = 0.814$
5	8.27 ± 0.11	8.23 ± 0.57	$p = 0.864$
	Toluene concentration (ng L^{-1})		
1	19.01 ± 0.09	19.12 ± 0.16	$p = 0.247$
2	19.16 ± 0.06	19.24 ± 0.18	$p = 0.344$
3	19.03 ± 0.16	18.95 ± 0.34	$p = 0.660$
4	18.92 ± 0.09	19.04 ± 0.42	$p = 0.567$
5	19.06 ± 0.20	19.18 ± 0.44	$p = 0.590$
	o-Xylene concentration (ng L^{-1})		
1	11.38 ± 0.12	11.28 ± 0.17	$p = 0.321$
2	11.39 ± 0.13	11.47 ± 0.25	$p = 0.572$
3	11.33 ± 0.04	11.24 ± 0.22	$p = 0.413$
4	11.41 ± 0.12	11.42 ± 0.25	$p = 0.934$
5	11.31 ± 0.14	11.40 ± 0.65	$p = 0.781$

results showed that there is no statistically significant difference ($p = 0.106, 0.798$ and 0.718 for benzene, toluene and *o*-xylene, respectively) for the effects of differences between the two methods. Although there is a statistically significance ($p < 0.01$) for the effects of the different levels of the expected concentrations, the results obtained by the two methods do not depend ($p = 0.985, 0.949$, and 0.755 for benzene, toluene and *o*-xylene, respectively) on what level the expected concentration is present. The analytical error, measured as the residual SD of both methods, varied between 8×10^{-4} and $1 \times 10^{-3} \mu$g.

The BTX analysis by OF sensor was performed in total analytical time of 6 min and for GC–FID the BTX analysis delayed 7 min; however, it must be considered the different analysers instrumentation and operational conditions, namely different chromatographic component, different temperatures program and carrier gas flow rate.

Both analytical methods were also applied to five actual samples of a Portuguese solvent industry, the obtained results are displayed in Table 2 and they are much lower than the occupational exposure limits recommended for benzene (3.19 mg m^{-3}), toluene (3.77 mg m^{-3}) and *o*-xylene (4.34 mg m^{-3}) by NIOSH [19].

The OF sensor was also tested for ether (ethyl ether), ketone (propanone), halogenated hydrocarbon (chloroform) and alcohol (ethanol), which could be considered interfering compounds referred on the Method 1501 from NIOSH [19]. Figure 10 shows the sensor response for a mixture of 0.05 μg of ethyl ether, propanone, chloroform and ethanol. Each of the evaluated compounds produced a peak, but at a different analytical time, none of them coincident with any aromatic compounds peak. Therefore the analysed compounds cannot be considered as interfering with BTX monitoring, as shown in Figure 10. The sensor response for CS$_2$, as this compound was used as eluent, was also tested but no significant analytical signal was obtained, suggesting that there are not interactions
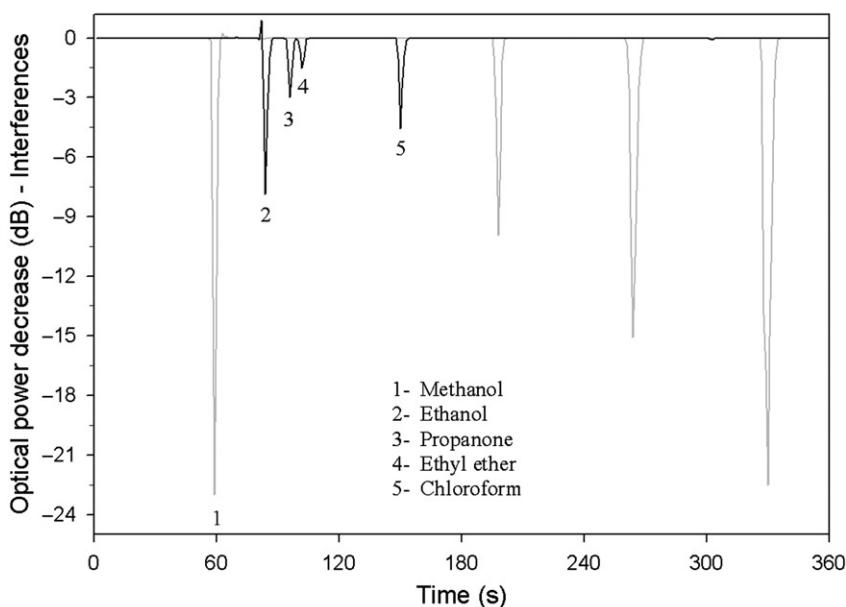
Figure 10. Optical power decrease obtained for a mixture of 0.05 μg of ethanol, propanone, ethyl ether and chloroform (black line). The grey line reports the typical analytical response for a BTX mixture (0.05 μg).

between this inorganic carbon compound and the sensitive cladding, and therefore CS_2 do not interfere with BTX analysis.

4. Conclusions

An OF sensor was developed for analysis of BTX with high specificity and high sensitivity. The use of an OF coated with a film thickness of 2 nm shows important analytical advantages over thicker films regarding the development of OF sensors for organic vapours monitoring. Changes of up to 14 dB in the reflected optical power were detected during 0.04 μg of BTX mixture at 650 nm, evidencing the high analytical sensing potential of the proposed method for BTX monitoring. The new and compact design of the developed sensor has obvious analytical advantages, showed high potential for miniaturisation and for *in situ* operation, which makes this sensor an excellent alternative for accurate BTX monitoring in actual industrial environments. Furthermore, the analytical apparatus is much less expensive than others methods for BTX detection, such as GC–FID, although it keeps the analytical performance at the same level for actual samples.

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