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Rapid determination of pyridine derivatives by dispersive liquid–liquid microextraction coupled with gas chromatography/gas sensor based on nanostructured conducting polypyrrole

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ABSTRACT

Polypyrrole (PPy) gas sensor has been prepared by polymerization of pyrrole on surfaces of commercial polymer fibers in the presence of an oxidizing agent. The sensing behavior of PPy gas sensor was investigated in the presence of pyridine derivatives. The resistive responses of the PPy gas sensor to pyridine derivatives were in the order of quinoline > pyridine > 4-methyl pyridine and 2-methyl pyridine. The PPy gas sensor was used as gas chromatography (GC) detector and exhibited linear responses to pyridine derivatives in the ranges 40–4000 ng. Dispersive liquid–liquid microextraction (DLLME) combined with GC/PPy gas sensor has been developed for simultaneous determination of pyridine derivatives and quinoline. The purposed method was used for determination of pyridine derivatives from cigarette smoke. The GC runs were completed in 4 min. The reproducibility of this method is suitable and good standard deviations were obtained. RSD value is less than 10% for all analytes.

1. Introduction

Pyridine and substituted pyridines play an important role in the sensory properties of cigarette smoke [1]. These chemicals are important industrial starting materials with an unpleasant smell and high toxicity. Pyridine is frequently found in indoor air and in volatile components of certain foodstuffs [2]. These toxic compounds are well absorbed in the gastrointestinal tract of mammals and undergo extensive metabolism by C- and N-oxidation and N-methylation. Acute pyridine intoxication affects the central nervous system in the human body [2]. Pyridine, substituted pyridines and quinoline also possess adverse human health effects on respiratory organs and reproduction [3–5]. According to the American Lung Association, 20–30% of low-weight babies, up to 14% of preterm deliveries and about 10% of all infant mortality are due to smoking during pregnancy [6], so measurement of known toxins in tobacco smoke is important.

Literature cited methods for detection and quantification of pyridines include electrostatic precipitation [7], GC [8,9], liquid chromatography–mass spectrometry (LC–MS) [10], and GC–MS [11–14]. Since these compounds are volatile, collection of cigarette smoke plays an important role in the determination procedure. Solvent trap was found to be a better device for collection of cigarette smoke rather than a Cambridge filter pad in order to reduce the loss of analyte in collected samples [10].

Chemical sensors such as conductive polymer sensors [15], surface acoustic wave (SAW) sensors [16,17] have important applications in the area of environmental monitoring, public security, automotive application, and medical diagnosis. Over the past few decades, researchers and engineers have dedicated their effort to develop conductive polymer sensors with the characteristics of high sensitivity, good selectivity, and reliability [18–22]. Application of conducting polymers including polypyrrole (PPy) towards sensors for chemicals and biological is of considerable interest. In this aspect, PPy remains to be distinct from others by possessing unique structural characteristics and the consequent redox behavior, interlinked with the degree of doping and protonation [23]. Many studies have so far been conducted and devoted to the development of chemical sensors [22–28]. Recently, conducting polypyrrole nanomaterials have received considerable attention in sensors because of remarkable physical and chemical characteristics originating from their small dimensions and high surface area [29–36]. Hernandez et al. [30] fabricated a gas sensor based on single PPy nanowire. Reports also showed the sensitivity, to a certain extent, was dependent on the diameter of the one-dimension nanomaterial [31,32]. However, the diameter of the PPy nanowire used as gas sensor is often over hundreds of nanometers. Small diameter and high density PPy nanowire arrays will present a significantly

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high surface-to-volume ratio which will result in high sensitivity [33,34]. Jang and co-workers [31] reported sensing behaviors of polypyrrole nanotubes prepared in reverse microemulsions and the effects of transducer size and transduction mechanism, the electrical response of PPy nanotubes to analyte (NH_3 vapor) was strongly dependent on their diameters. The PPy nanotube sensors showed conspicuously enhanced responses compared with conventional PPy. Currently, the focus is on the development of sensors for various organic pollutant vapors/gaseous molecules [35].

The present work is a continuation of our earlier studies on the development of gas sensors based on conducting polymer films [36], and is devoted to investigate the gas-sensing behaviors of chemically prepared conducting polypyrrole gas sensor exposed to pyridines compounds. With regarding to the sensing potential and fast response time of conducting polymer films gas sensors, a polypyrrole gas sensor coupled to a GC for detection of the pyridine derivatives. The dispersive liquid–liquid microextraction (DLLME) method was used for sample preparation at room temperature. DLLME is a very simple and rapid method for extraction and preconcentration of organic compounds from water samples [37–40].

2. Experimental

2.1. Chemicals

Pyrrole (Fluka, Switzerland) was distilled and stored in a refrigerator in dark prior to use. Ferric chloride ($FeCl_3$) was used as oxidant from Aldrich. All organic compounds used for sensitivity tests and extraction procedure were purchased from Merck.

2.2. Fabrication of PPy gas sensor

The PPy polymer was synthesized by chemical polymerization at 0 °C under atmospheric condition. Pyrrole of $0.1\,\mathrm{mol\,L^{-1}}$ as monomer and $FeCl_3$ of $0.2\,\mathrm{mol\,L^{-1}}$ as oxidant was added to this solution for the purpose of initiation of polymerization. This solution was maintained for 2 h at 0 °C. PPy layer was prepared on the polyester substrate by using the dip coating method. After the polymerization and coating, the substrate was taken from the reaction solution and abundantly washed with deionized water for 5 min, and finally dried for 1 h at 70 °C in oven. We re-used a technique that has been designed in our previous work for fabrication of gas sensors [36].

2.3. Apparatus

The PPy gas sensor consisted of a fiber in 20 mm length having a diameter of ca. 0.5 mm was put in a copper tube of 4 mm inner diameter. The resistance change of PPy due to the exposure of pyridine compounds were monitored every 0.5 s with Escort 3145 Multimeter and an automatic data acquisition system. The normalized electrical resistance change was calculated by $(R - R_o)/R_o$, where R_o and R denote the initial resistance and real-time resistance (resistance of the sensor when it was exposed to analyte gas). The gas sensors were tested with pyridine derivatives using a gas chromatography (Shimadzu GC-4C) system. The column for the GC analysis of mixture compounds was made of a steel tube (3.2 mm i.d., 1 m length) packed with OV-17 (Shimadzu). A sensor was directly connected to the outlet of the column, and the whole part was placed in a copper tube. Sensor and the column temperature are regulated by a thermistor and temperature control circuit. The carrier gas was nitrogen (purity level 99.99%) with flow rate of $80\,\mathrm{mL\,min^{-1}}$ and passed through a 13× molecular sieves (Fluka) trap to remove water vapor and other possible contaminations before entering into the sensor system. The identification of each chemical was established by chromatographic retention times. The scanning electron micrographs (SEM) of the fiber surface were obtained using a Philips XL30 scanning electron microscopy (Holland).

2.4. Dispersive liquid–liquid microextraction procedure

A 5 mL of distilled water was placed in a 10 mL screw cap glass test tube with conic bottom and spiked at the level of different concentrations of pyridines, 1.5 mL of acetone (as disperser solvent) containing 30 μL CS_2 (as extraction solvent) was injected into a sample solution rapidly and then the mixture was gently shaken. A cloudy solution (water, acetone, and carbon disulfide) was formed in a test tube (the cloudy state was stable for a long time). Then the mixture was centrifuged for 2 min at 5000 rpm. Accordingly, the dispersed fine particles of extraction phase were sedimented in the bottom of conical test tube. The 4 μL of sedimented phase was removed using a 10 μL microsyringe (Hamilton) and injected into GC. The volume of the sedimented phase was determined using a 100 μL microsyringe which was about 10 μL.

2.5. Calculation of enrichment factor, extraction recovery and relative recovery

The enrichment factor (EF) was defined as the ratio between the analyte concentration in the sedimented phase (C_{sed}) and the initial concentration of analyte (C_0) within the sample:

$$\mathrm{EF} = \frac{C_{sed}}{C_0} \tag{1}$$

The C_{sed} was obtained from calibration graph of direct injection of pyridines standard solution in the CS_2. The extraction recovery (ER) was defined as the percentage of the total analyte amount (n_0) which was extracted to the sedimented phase (n_{sed}).

$$\mathrm{ER} = \left(\frac{n_{sed}}{n_0}\right) \times 100 = \left(\frac{C_{sed}}{C_0}\right) \times \left(\frac{V_{sed}}{V_{aq}}\right) \times 100 \tag{2}$$

$$\mathrm{ER} = \left(\frac{V_{sed}}{V_{aq}}\right) \mathrm{EF} \times 100 \tag{3}$$

where V_{sed} and V_{aq} are the volumes of sedimented phase and sample solution, respectively.

2.6. Sample preparation

For preparation of cigarette sample, 10 cigarettes smoke was passed through trap containing 50 mL distilled water with 5% hydrochloric acid (Scheme 1). After completion of the smoking, the volume of water was molten in a 250 mL separatory funnel and 50 mL methylene chloride was added to that. The mixture was vigorously shaken for 10 min and allowed the phases to separate. The organic phase was discarded and upper aqueous phase was transferred to a clean test tube. A 5 mL of the aqueous extract was transferred to a 10 mL screw cap glass test tube with conic bottom and sodium hydroxide solution added to it. The resulting neutralized solution was extracted by DLLME procedure described as above.

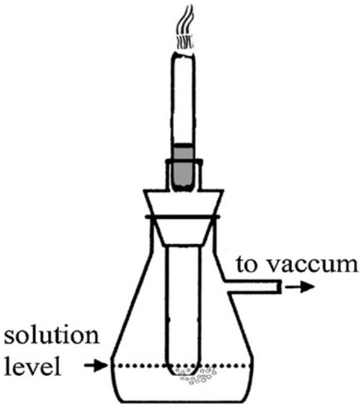
3. Results and discussion

3.1. Response behavior of PPy gas sensor

Table 1 gives the response behaviors (detection limit, linear ranges, calibration sensitivity, and correlation coefficients) of PPy gas sensor. The theoretical detection limit of the PPy gas sensor, which was calculated as the amount, gives a reading equal to three times the standard deviation of a series of the procedural blank

Table 1
Figure of merits of PPy gas sensor for pyridines at 100 °C.

Compound	Detection limit (ng)	Linear range (ng)	Sensitivity (1/ng)	R^2
Pyridine	8	40–4000	7.3×10^{-7}	0.992
2-Methyl pyridine	20	40–4000	6.3×10^{-7}	0.995
4-Methyl pyridine	20	40–4000	6.3×10^{-7}	0.991
Quinoline	2	40–4000	9.5×10^{-7}	0.993



Scheme 1. The solvent trap method for the collection of cigarette smoke.

or background signals (response of the sensor, measured in the absence of compound), can be estimated as follows:

$$\mathrm{DL} = \frac{3\sigma_b}{(\text{calibration} \quad \text{sensitivity})} \qquad (4)$$

The detection limits for the selected pyridines were between 2 and 20 ng and calibration graphs were linear in the range of 40–4000 ng. The sensitivity of PPy gas sensor is defined as the normalized electrical resistance change per unit amount (ng) of analyte species, which can be obtained from slope of the calibration curves, $(R - R_o)/R_o$ vs pyridines standard solution in the CS_2. As shown in Table 1 the sensitivity of the PPy gas sensor for these compounds, apparently in the following order: quinoline > pyridine > 4-methyl pyridine and 2-methyl pyridine. The response time of sensor was less than 1 s.

Morphology of the polypyrrole conducting film on the surface of the fibers was examined by SEM. Fig. 1 show the SEM micrograph of the PPy film at 30,000 folds magnification. One clearly observes that the deposited polymers are in spherical shape. The nanostructure PPy films look more porous.

The PPy gas sensor was also applied as a gas chromatographic detector for determination of some pyridine compounds. The pyridines mixture samples were extracted by DLLME method. There are different factors that affect the extraction process. Some of them are selection of suitable extraction solvent, selection of suitable disperser solvent, volume of extraction solvent, volume of disperser solvent, and extraction time. It is very important to optimize them in order to obtain the good recovery strategy forms.

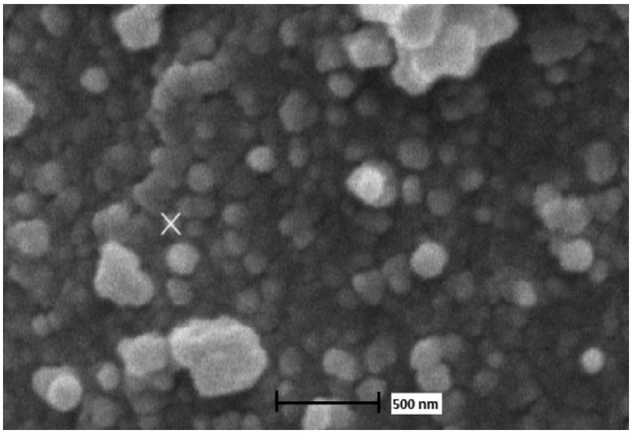


Fig. 1. SEM images of the fiber surfaces of PPy sensor.

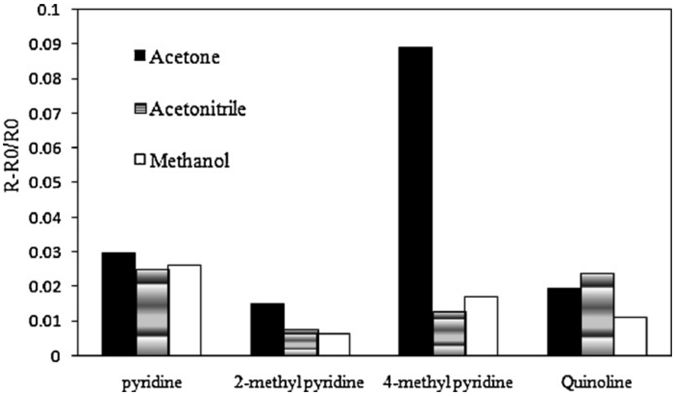


Fig. 2. Effect of the disperser solvent type on the DLLME of pyridine derivatives that calculated by using PPy gas sensor response. Extraction conditions: water sample volume, 5 mL; disperser solvent (acetone, acetonitrile, methanol) volume, 1.5 mL; amount of each analyte, 10 μg.

3.2. *Effect of extraction conditions*

Organic solvents are selected on the basis of higher density rather than water, extraction capability of interested compounds, and good gas chromatography behavior. We could use CS_2, carbon tetrachloride, and tetrachloroethylene as extraction solvent but carbon tetrachloride, and tetrachloroethylene do not have good chromatography behavior in this work therefore, CS_2 was selected as the extraction solvent. Miscibility of disperser solvent in organic phase (extraction solvent) and aqueous phase is the main point for

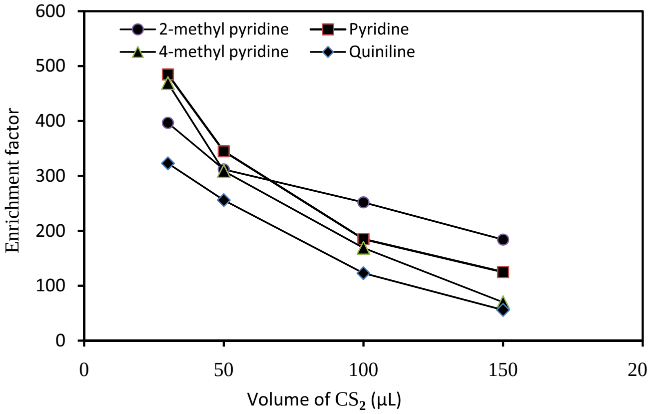


Fig. 3. Effect of the volume of CS_2 on the enrichment factor of pyridine derivatives obtained from DLLME by using PPy sensor response. Extraction conditions, water sample volume, 5 mL; disperser solvent (acetone) volume, 1.5 mL; room temperature; amount of each analyte, 10 μg.

Table 2
Quantitative results of DLLME of pyridine derivatives and GC–PPy gas sensor for water sample. Extraction conditions: water sample volume, 5 mL; disperser solvent (acetone) volume, 1.5 mL; extraction solvent (CS_2) volume, 30 µL at room temperature.

Compound	Detection limit (ng)	Sensitivity (1/ng)	Linear range (ng)	RSD (%)	R^2
Pyridine	36	1.0×10^{-6}	50–10,000	7.6	0.992
2-Methyl pyridine	50	7.6×10^{-7}	50–10,000	7.2	0.993
4-Methyl pyridine	45	0.8×10^{-6}	50–10,000	7.2	0.993
Quinoline	5	2.2×10^{-6}	50–10,000	6.3	0.991

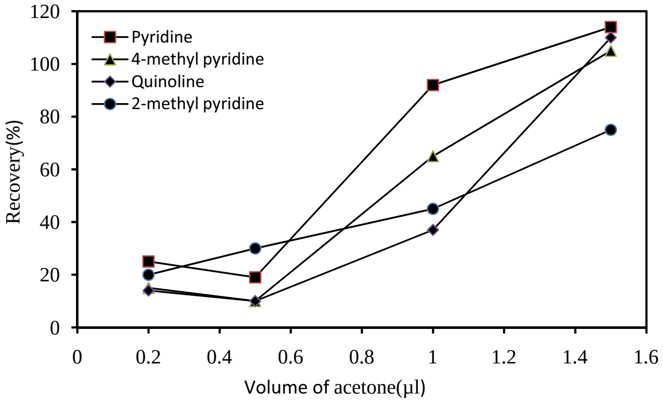


Fig. 4. Effect of the volume of acetone on the recovery of pyridine derivatives obtained from DLLME by using PPy sensor response. Extraction conditions: water sample volume, 5 mL; sedimented phase volume, 10 µL; amount of each analyte, 10 µg.

selection of disperser solvent. Therefore, acetone, acetonitrile, and methanol are selected for this purpose. The pyridines solution was studied by using 1.5 mL of each disperser solvent containing 30 µL CS_2 (as extraction solvent). The relative response of PPy gas sensor to the pyridines in the cases acetone, acetonitrile, and methanol as disperser solvents were calculated and results were illustrated in Fig. 2. According to these results, acetone is the best disperser, thus, acetone is selected as disperser solvent.

To examine the effect of extraction solvent volume, solutions containing different volumes of CS_2 were subjected to the same DLLME procedures. The experimental conditions were fixed and included the use of 1.5 mL acetone containing different volumes of CS_2 (30, 50, 100 and 150 µL). By increasing the volume of CS_2 from 30 to 150 µL, the volume of the sedimented phase increases from 10 to 100 µL. The extraction recoveries of analyte is increasing for each analyte by increasing the volume of CS_2 and were in the ranges 30–95. However, as the volume of the sedimented phase increases, enrichment factor decreases with increasing the volume of CS_2 as shown in Fig. 3. Subsequently, at low volume of extraction solvent, high enrichment factor and good recovery are obtained. Thereby, the gain in sensitivity was achieved by using 30 µL volume of CS_2. Variation of the volume of acetone (as disperser solvent) causes change in the volume of sedimented phase; hence, it is impossible to consider the influence of the volume of acetone on the extraction efficiency. To avoid this matter and in order to achieve a constant volume of sedimented phase, the volume of acetone and CS_2 were changed spontaneously. The experimental conditions were fixed and included the use of different volumes of acetone 0.5, 1, 1.5, and 2 mL containing 24, 27, 30, and 35 µL of CS_2, respectively. Under these conditions, the volume of the sedimented phase was constant (10 ± 0.5 µL). The results are shown in Fig. 4. According to these results, at the acetone volume > 1 mL extraction efficiency increases and then decreases by increasing the volume of acetone. A 1.5 mL of acetone was chosen as optimum volume of disperser solvent. Extraction time is one of the most important factors in most of the extraction procedures. In DLLME extraction, time is defined as an interval time between injection of mixture of disperser solvent (acetone) and extraction solvent (CS_2), and before starting to centrifuge. Because of that our previous work results showed that time has no influence on extraction efficiency and extraction procedure is fast ($\leq$2 min) so that extraction time of 2 min was selected at room temperature.

Fig. 5a illustrates typical chromatogram of pyridines in water sample by using DLLME. The results show the ability of PPy gas sensor to be used as detector in coupled with DLLME–GC for analysis of pyridines in water samples. The analytes 2-methyl pyridine and 4-methyl pyridine showed the same peak with the same retention time so that for 2-methyl pyridine separate analysis was done to calculate figure of merit. Variation of temperature and flow rate of carrier gas have effect on separation, resolution or peak shape, so, temperature and gas flow rate optimized and work was done in 100 °C column temperature and 80 mL min^{-1} flow rate. The characteristic of calibration curves shown in Table 2 was obtained under optimized conditions. The linear calibration curve was obtained for each analyte by plotting the relative resistance changes against the amount of the analyte. The range of the 6-point calibration curve was varied from 50 to 10,000 ng for pyridine derivatives. All calibration curves showed good linearity with typical correlation coefficient (R^2) $\geq$ 0.99. The detection limit was calculated as three times of the standard deviation of lowest calibration standard, were in the range of 5–50 ng. Three replicate measurements were performed for each analyte and standard deviations were calculated. Precision of this method was determined by calculating the relative standard deviations (RSD) of the replicate measurements. All the analytes have RSD values less than 8% (Table 2).

3.3. Practical application

Three commercially filtered cigarettes (85 mm and 120 mm length) were analyzed for determination of pyridine derivatives from cigarette smoke by using the purposed method. The solvent trap method was used for the collection of cigarette smoke. The initial target was to develop and optimize a DLLME technique.

Table 3
Levels of pyridine derivatives and quinoline in different brands of cigarettes[a] in intraday and interday analyses.

Cigarette	Pyridine (µg/cig)		2-Methyl pyridine + 4-methyl pyridine (µg/cig)		Quinoline (µg/cig)	
	Intraday	Interday	Intraday	Interday	Intraday	Interday
Sample 1	4.9 ± 0.2	5.2 ± 0.2	6.2 ± 0.1	5.8 ± 0.2	8.2 ± 0.3	7.9 ± 0.3
Sample 2	5.3 ± 0.5	5.0 ± 0.5	8.6 ± 0.9	8.7 ± 0.9	4.6 ± 0.8	4.5 ± 0.8
Sample 3	4.4 ± 0.7	4.8 ± 0.7	7.3 ± 0.8	7.0 ± 0.8	3.3 ± 0.6	3.5 ± 0.6

[a] The CS_2 was used as internal standard.

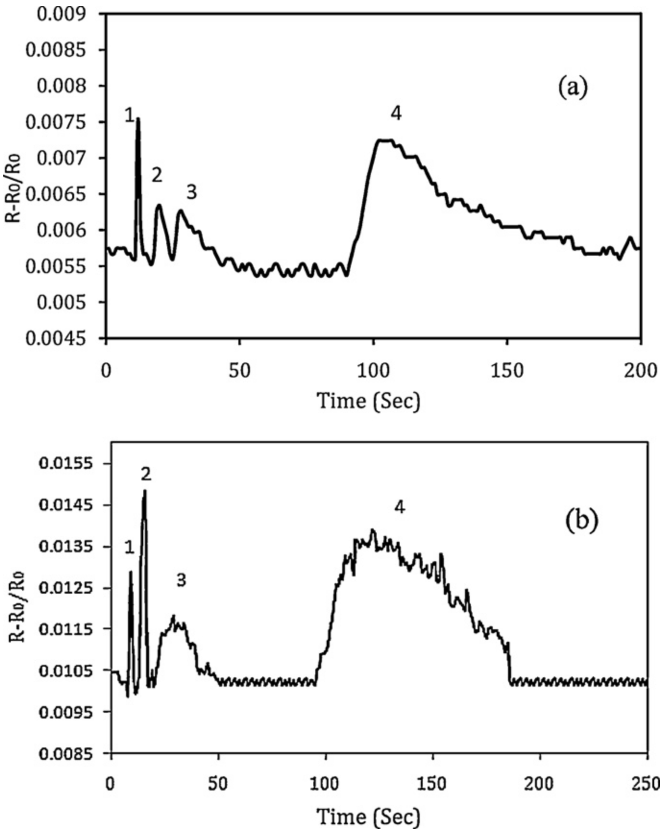


Fig. 5. Gas chromatogram coupled to PPy gas sensor as detector for analysis of pyridine derivatives in water sample by DLLME. Extraction conditions: water sample volume, 5 mL; disperser solvent (acetone) volume, 1.5 mL; extraction solvent (CS_2) volume, 30 μL; amount of each analyte, 500 ng (a); from cigarette smoke (b); peak identification: (1) CS_2, (2) pyridine, (3) 2-methyl pyridine + 4-methyl pyridine, (4) quinoline.

With the combination of smoke trap and DLLME technique, the interferences and matrix effects were minimized and the targeted analytes were clearly determined by retention time. Fig. 5b shows a typical chromatogram obtained from cigarette smoke sample. The level of pyridines and quinoline that determined by this technique has been presented in Table 3.

4. Conclusion

Polypyrrole was polymerized chemically and was doped with $FeCl_3$ resulting in a conductive material, suitable for application in chemiresistor sensor. The sensor are easy to make, response was fast, reversible and reproducible. The PPy gas sensor is applied as a highly sensitive detector for gas chromatographic detection of pyridine compounds. The DLLME/GC/PPy gas sensor method described facilitates fast, quantitative and qualitative determination of pyridine derivatives and quinoline from the mainstream cigarette smoke extract. The GC runs were completed in 4 min. Three commercially available cigarettes were analyzed by using DLLME/GC/PPy gas sensor. The proposed method can also be applied for the determination of pyridine derivatives in other sources where they are present in trace quantities.

Acknowledgments

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