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Preparation of phenyl group-functionalized magnetic mesoporous silica microspheres for fast extraction and analysis of acetaldehyde in mainstream cigarette smoke by gas chromatography–mass spectrometry

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ABSTRACT

Acetaldehyde is regarded as a toxic mainstream cigarette smoke constituent, and measurement of acetaldehyde in complex real samples is difficult owing to its high volatility and reactivity. In this work, phenyl group-functionalized magnetic mesoporous microspheres were developed as the solid-phase extraction sorbents for enrichment and analysis of acetaldehyde in mainstream cigarette smoke. The functional magnetic microspheres were first synthesized through a facile one-pot co-condensation approach. The prepared nanomaterials possessed abundant silanol groups in the exterior surface and numerous phenyl groups in the interior pore-walls, as well as a large surface area (273.5 m^2/g), strong superparamagnetism and uniform mesopores (3.3 nm). Acetaldehyde in mainstream cigarette smoke was collected in water and derivatizated with O-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine. The formed acetaldehyde oximes were extracted and enriched by the prepared adsorbents via π–π interactions and subsequently analyzed using GC–MS. Extraction conditions such as amounts of sorbents, eluting solvent, adsorption and desorption time were investigated and optimized to achieve the best efficiency. Method validations including linearity, recovery, repeatability, and limit of detection were also studied. It was found that the suggested methodology provided low detection limit of 0.04 mg/mL, good recovery of 88–92%, intra-day and inter-day RSD values of 4.5% and 10.1%, and linear range of 0.25–4 mg/mL ($R^2 = 0.999$). The results indicated that the proposed method based on phenyl-functionalized magnetic mesoporous microspheres was rapid, efficient and convenient for the enrichment and analysis of acetaldehyde in tobacco.

1. Introduction

Acetaldehyde has been identified as a mainstream cigarette smoke constituent of concern. It is mainly derived from sugars and flavors added in tobacco processing [1,2]. In addition, acetaldehyde has been classified as a main toxic component of large amounts in mainstream smoke with significant potential biological activity [3,4]. Being a reactive carbonyl compound, acetaldehyde is associated with many cigarette smoking diseases including chronic pulmonary disorder and cancer [5,6]. Acetaldehyde is highly cytotoxic and genetoxic. It can directly react with proteins and bind covalently to nucleic acids, consequently causing biological complications [7]. Furthermore, acetaldehyde from tobacco smoke is also an important source of carbonyls to indoor air, where it may cause various diseases not only in smokers but also in non-smokers [8,9]. Therefore, the monitor of the amount of acetaldehyde in mainstream cigarette smoke is essential to estimate environmental exposure, and guide the development of potential risk-reduced tobacco products.

The determination of acetaldehyde in cigarette smoke sample has been carried out by high performance liquid chromatography (HPLC) as their 2,4-dinitrophenylhydrazine (DNPH) derivatives and gas chromatography (GC) as their benzyloxime or thiazolidine derivatives [10]. However, in highly complex cigarette smoke, the potential of interferences always appears. Moreover, certain carbonyl compounds are always present at trace levels. The direct measurement of acetaldehyde in cigarette smoke is very difficult [11]. To solve the above problems, it is quite desirable to develop a fast and efficient sample extraction and enrichment technique for the analysis of acetaldehyde in mainstream cigarette smoke.

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In this regard, magnetic mesoporous silica microspheres may be the key to this issue. Magnetic silica-based materials consisting of a magnetic core surrounded by a mesoporous silica shell have attracted considerable interests for drug delivery, controlled release, and bioseperation over the past decades [12,13]. They possess the excellent characteristics of strong magnetization, high surface areas, uniform mesopore distribution, tunable pore sizes, large pore volumes, thermal and mechanical stabilities, and extra adsorption capacity [14–20]. Considering the special advantages of high adsorption capacity of mesoporous silica and separation convenience of magnetic nanoparticles, the functionalized magnetic mesoporous silica materials are considered as promising adsorbents for enrichment and preconcentration of target pollutants from environmental samples [21–23]. By employing those as solid-phase extraction (SPE) sorbents, simplified extraction procedure and high anti-interference ability can be readily achieved. The anti-interference ability of functionalized magnetic mesoporous microspheres first lies in that the functional groups on the sorbents contribute to selective extraction of targeted analytes due to specific forces and interactions. Another factor is that the exterior shell of mesoporous silica can prevent macromolecules (e.g. humic acid, BSA) in matrices from entering into the interior pore-walls, thus aiming at enrichment of specific small molecules [24]. In our previous work, C18 groups functionalized magnetic mesoporous silica spheres had been successfully synthesized and then applied to the extraction and analysis of phthalates in water [25]. The satisfactory results inspired us to take further researches on the application of functionalized magnetic mesoporous materials to a complicated matrix.

In the present work, phenyl group-functionalized magnetic mesoporous ($Fe_3O_4@mSiO_2$) microspheres were prepared by a simple co-condensation approach. Acetaldehyde in mainstream cigarette smoke was collected and derivatizated in water, and then extracted by the synthesized sorbents followed by the analysis of gas chromatography–mass spectrograph (GC–MS). Quantitative analyses of acetaldehyde were performed by measurement of its oximes. SPE extraction conditions and the method validations were also studied.

2. Material and methods

2.1. Chemicals and reagents

The standards of O-(2,3,4,5,6-pentafluorophenyl)hydroxylamine hydrochloride (PFBHA) and phenyl-triethoxysilane (PTES, Purity $> 95\%$) were purchased from Alfa Aesar (Tianjin, China). Acetaldehyde, iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ethylene glycol (EG), poly (ethylene glycol)-20000 (PEG-20000), hydrochloric acid, sodium hydroxide, trisodium citrate and sodium acetate anhydrous were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tetraethyl orthosilicate (TEOS) and cetyltrimethyl ammonium bromide (CTAB) were acquired from Qiangshun Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was purified by a Milli-Qsystem (Milford, MA, USA). Cigarette samples used as in the study were purchased from Shanghai Tobacco Monopoly store.

The standard stock solution of PFBHA was prepared by dissolving the required amounts in deionized water to acquire an initial concentration of 20 mg/mL. Standard stock solutions of acetaldehyde-PFBHA derivatives ranged 20–5000 μg/ml were prepared in deionized water. The chemical formula of the derivatization reaction was shown in Fig. S1. The derivatization of carbonyls with PFBHA can be performed under mild reaction conditions (ambient temperature and aqueous solution). The reaction is very fast and the corresponding oximes form in seconds [1]. The working standard solutions were stored under 4 °C and were found to be stable for three months.

2.2. Preparation of phenyl group-functionalized $Fe_3O_4@mSiO_2$ microspheres

Magnetic Fe_3O_4 microspheres with a mean diameter of 250 nm were synthesized according to a previously reported method [26]. The phenyl group-functionalized $Fe_3O_4@mSiO_2$ microspheres were prepared through a surfactant involved sol–gel process referring to the previous method with some modifications [27–29]. The prepared Fe_3O_4 magnetic particles and CTAB with a ratio of 50 mg/500 mg were dispersed in 50 mL deionized water and sonicated for 30 min. The resultant dispersion was mixed with 450 mL diluted NaOH aqueous solution and further sonicated for 5 min to form a stable mixture. The dispersion was then heated at 60 °C for 30 min. Afterwards, 2.5 mL TEOS/ethanol (v/v: 1/4) solution was added drop by drop under mechanical stirring, followed by heating at 60 °C for 30 min with stirring. Subsequently, 150 μL TEOS/PTES (v/v: 2/1) mixture was injected into the dispersion which was further heated at 60 °C for 12 h. The resulting products were collected by magnetic separation and refluxed in acetone at 60 °C to remove the CTAB templates thoroughly. Finally, the obtained phenyl-functionalized $Fe_3O_4@mSiO_2$ microspheres were dried at 50 °C for 24 h in vacuum for future use.

2.3. Instrument and chromatographic conditions

Scanning electronic microscopy (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operated at 20 kV. Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) performed at 200 kV. Fourier transform infrared (FT-IR) spectra were collected on Nicolet Nexus 470 Fourier spectrophotometer (USA) using KBr pellets. Nitrogen sorption isotherms, pore size distribution and BET surface area were measured at 77 K with a Micromeritcs Tristar 3000 analyzer (USA). Vibration in extraction procedure was performed by a Qilinbeier XW-80A vortex (Jiangsu, China) at 2800 rpm/min. The cigarette samples were smoked by a simple smoking machine that fulfilled the requirements recommended by the International Organization for Standardization (ISO), i.e. puffing parameters of 35 mL volume, 2 s duration and 60 s interval between puffs [1].

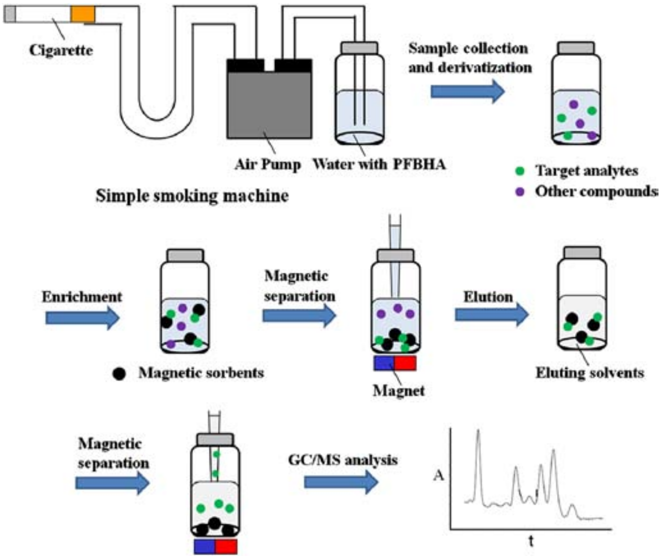
The GC–MS analyses were performed with a PerkinElmer Clarus 680 gas chromatograph (Waltham, MA, USA) connected to a Perkin Elmer Clarus SQ8T mass spectrometer (Waltham, MA, USA). Compounds were separated on an Elite-5 MS capillary column (30 m × 0.25 mm, 0.25 μm), and the samples were injected in splitless mode. The column oven temperature was programmed with an initial temperature of 40 °C for 2 min, raised to 80 °C with a ramping rate of 30 °C/min and held for 2 min, and then heated at 30 °C/min to 180 °C and kept for 9 min. Helium (99.999%) was used as the carrier gas at a flow rate of 1 mL/min. All samples were analyzed in scan mode in the range of 50–300 amu. The electron energy of MS is 70 eV, and the source temperature is set at 150 °C. The m/z ratio of quantitative ion for acetaldehyde oximes is 181, and m/z ratios of qualitative ions are 83, 209 and 85. TurboMass Ver 6.0.0 software was used for data acquisition.

2.4. The micro solid-phase extraction procedure by phenyl group-functionalized $Fe_3O_4@mSiO_2$ microspheres

The schematic procedure of sample collection and enrichment process was shown in Scheme 1. For the optimization studies, the mainstream cigarette smoke was collected in 100 mL water containing 150 μL of 20 mg/mL PFBHA solution. Then, 10 mL sample solution (pH=7) was transferred to a vial with PTFE-silicone septum, followed by adding different amounts of phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres (5, 10, 15, 20, 30 mg) to extract the analytes with equable vibration by vortex for different time (5, 10, 15, 30 min) to achieve an effective mutual contact. The materials which had captured the targets were isolated by placing a magnet bar beside the vial and the supernatant solution was discarded. Subsequently, the analytes were eluted by 500 μL different solvents (acetone, methanol, chloroform) under continuous ultrasonic condition for different time (5, 10, 15, 20 min). Finally, 1 μL of the eluting solution was injected into the GC–MS system for analysis. The optimization conditions were determined by the amount of formed acetaldehyde oximes.

2.5. Analytical validations

The calibration curves were fabricated by plotting the peak area (y) of acetaldehyde derivatives versus corresponding concentration of the analyte (x) ranging from 20 to 5000 μg/ml. Concentrations of acetaldehyde in mainstream cigarette smoke were calculated from the resulting peak area ratio and the regression equations of the calibration curves.



Scheme 1. The schematic procedure of sample collection with simple smoking machine and enrichment process with functional magnetic mesoporous microspheres as adsorbents.

The limit of detection (LOD) was determined by analysis of the standard solution with a low concentration in spiked acetaldehyde-free samples on the basis of $S/N=3$. The limit of quantification (LOQ) was calculated on the basis of extrapolation to $S/N=10$.

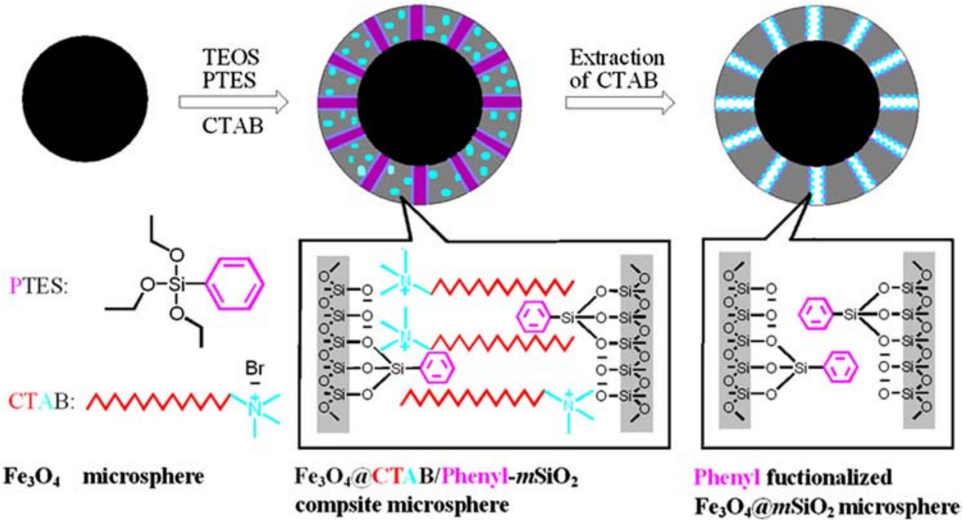
In addition, the system precision and accuracy were determined by five replicate analyses of the concentrations of extracted analytes in real samples under the optimized conditions in one single day and five consecutive days. The obtained peak areas were used for the calculation of the intra-day and inter-day relative standard deviations (RSDs) to demonstrate the extraction reproducibility. The recovery of the target compound was studied by extracting the spiked sample solution (0.5 and 1 mg/mL) containing known amounts of acetaldehyde under the optimized conditions for five times, and obtained by comparing real values of the added acetaldehyde with calculated values.

Moreover, in order to demonstrate the reproducibility of the synthesis process of the sorbents, five different batches of the prepared functionalized magnetic Fe_3O_4@$mSiO_2$ microspheres were employed in the SPE procedure under optimal extraction conditions. The resulting peak areas of extracted analytes in real samples were used to calculate the RSD value. All the above method validations were performed using the experimental data of the first acetaldehyde oxime compound.

2.6. Application of phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres to the analysis of cigarette samples

For each extraction procedure, one cigarette (0.8490 g) was smoked. Cigarette smoke was collected in 1000 mL water, and added with 1.5 mL of 20 mg/mL PHBHA solution for derivatization. The following micro SPE procedure by the functionalized magnetic Fe_3O_4@$mSiO_2$ microspheres was performed as described under the optimized conditions. Finally, 1 μL of the eluting solution of cigarette sample was injected into the GC–MS system and the chromatographic analysis was carried out. Reagent blank tests were also performed by the same micro SPE procedure without the presence of cigarette sample. The background of reagent blank was later subtracted from the smoke sample chromatograms.

To evaluate the reusability of the nano sorbents, adsorption of acetaldehyde and regeneration of targets-loaded phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres were performed in six



Scheme 2. The synthetic procedure of core–shell structured phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres.

consecutive cycles. In each cycle, regenerated adsorbents were washed thoroughly with chloroform before the next adsorption–desorption process.

3. Results and discussion

3.1. Preparation and characterization of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres

The synthetic protocol of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres was represented in Scheme 2. Briefly, by using the facile one-pot synthesis approach, phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres were synthesized through the co-condensation of TEOS and PTES in the presence of Fe_3O_4 microspheres as the seeds and CTAB as the template [29,30].

The size and morphology of the prepared magnetic mesoporous materials were investigated by TEM. A representative TEM image (Fig. 1b) revealed that the synthesized phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres exhibited a dark iron oxide center surrounded by a gray porous silica shell. According to the TEM image, the mean diameter and shell thickness of the microspheres were estimated to be about 220 and 60 nm, respectively. The SEM image (Fig. 1a) further indicated that the microspheres had a narrow size distribution and were well dispersed. Fig. 1b also implied that the dense pore channels in the shell were perpendicular to the microsphere's surface, which was favorable to the capacity of extraction as SPE absorbents.

The porosity of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres was studied by nitrogen adsorption–desorption measurement at 77 K. The N_2 adsorption–desorption isotherms (Fig. 2) showed IV curves of the representative type with a sharp capillary condensation step at a relative pressure of 0.2–0.4, indicative of a small cylindrical pore. The pore size distribution (Fig. 2 inset) derived from the adsorption branch using the Barrett–Joyner–Halenda (BJH) method indicated that the obtained materials had a pore size of about 3.3 nm with a narrow pore size distribution [31,32]. The BET surface area and the total pore volume were calculated to be 273.5 m^2/g and 0.22 cm^3/g, respectively, suggesting a high porosity.

FT-IR spectra (Fig. 3) also confirmed the presence of phenyl groups in phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres obtained by the co-condensation coating process. The peaks at 576 and 1074 cm^{-1} were attributed to the characteristic absorptions of Fe–O–Fe and Si–O–Si vibrations, respectively. The broad bands at 954 and 3388 cm^{-1} were from O–H stretching and Si–OH stretching. The absorption peaks at 1430 and 1663 cm^{-1} belonged to the skeleton vibrations of phenyl rings, indicating the successful synthesis of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres.

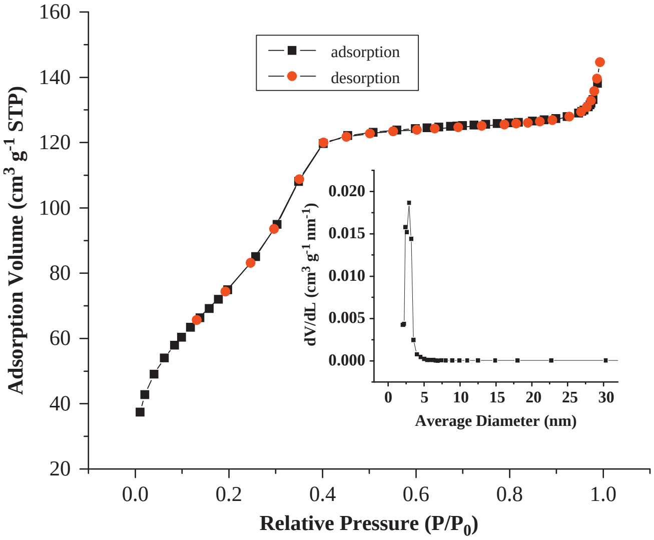


Fig. 2. Nitrogen adsorption–desorption isotherms and pore size distribution (inset) of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres recorded at 77 K.

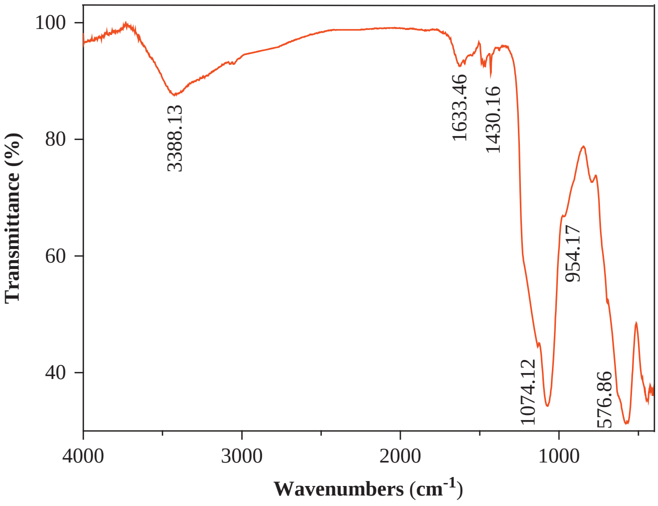


Fig. 3. FT-IR spectra of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres.

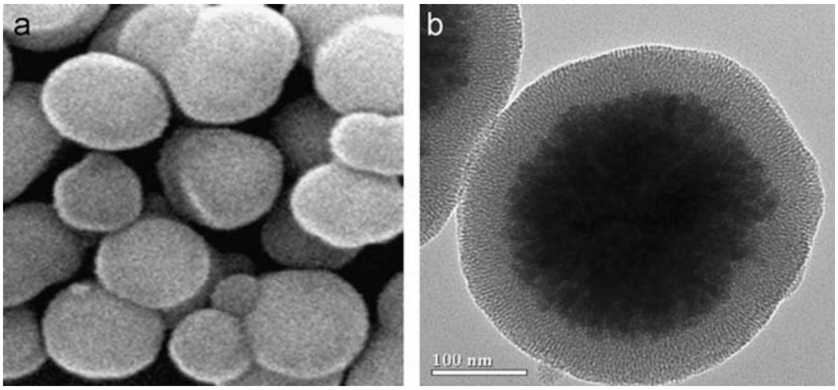


Fig. 1. (a) SEM images and (b) TEM images of phenyl group-functionalized Fe_3O_4@mSiO_2 microspheres.

The phenyl group-functionalized magnetic mesoporous silica microspheres obtained through one-pot synthesis displayed an excellent dispersibility in aqueous solution (Fig. S2), reflecting numerous silanol groups exposing on the exterior surface of the microspheres. The process of dispersion and separation required only 15 s from (a) to (b), indicating good magnetization of the synthesized materials. All the results mentioned above verified that the phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres with high magnetic responsivity and fine aqueous dispersion were successfully synthesized using the proposed approach.

3.2. Optimization of extraction conditions

Owing to the aromatic phenyl groups in the inner pore-walls, the phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres can be used to extract and enrich aromatic analytes by van der Waals and π–π interactions, and extraction conditions may contribute a lot to the mutual interaction. In order to obtain the maximum enrichment efficiency of targeted acetaldehyde derivatives, pH value of sample solution, the amounts of absorbents, eluting solvent, adsorption and desorption time were investigated. Both syn- and anti- acetaldehyde oximes were extracted by the phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres, and the quantitation of acetaldehyde should be done based on calibrations for both the two formed derivatives.

3.2.1. Optimization of sample solution pH

The pH value of sample solution plays an important role for the adsorption of target compounds by affecting the existing form of analytes, and the charge species and density on the sorbents surface. Thus, the sample solutions collected from cigarette smoke were adjusted by 0.01 mol/L HCl and NaOH solutions to form different pH values of 4, 7 and 10. The experimental results (Fig. 4) showed that the magnetic adsorbents gave the best performance in neutral solution. As a result, the sample solution was kept at its original pH value (pH=7) for the following micro solid-phase extractions.

3.2.2. Optimization of absorbent amount

The adsorbent amount added is known to be closely correlated with the quantity of the target analytes adsorbed. To obtain the maximum extraction efficiency, the optimization of the amount of phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres was performed by varying the adsorbents from 3 to 30 mg with the same enrichment procedure. Fig. 5 indicated that 20 mg sorbents was enough to achieve a satisfactory result because of the large surface area and high adsorption efficiency of the modified mesoporous nanosorbents. Furthermore, it was noticed that when the adsorbent amount increased to 30 mg, the extraction efficiency decreased instead. This could be interpreted as that 30 mg sorbents were too much for the eluting solvent to elute thoroughly, thus causing loss of enrichment efficiency. According to the above consequence, the optimal amount of the absorbents was decided to be 20 mg.

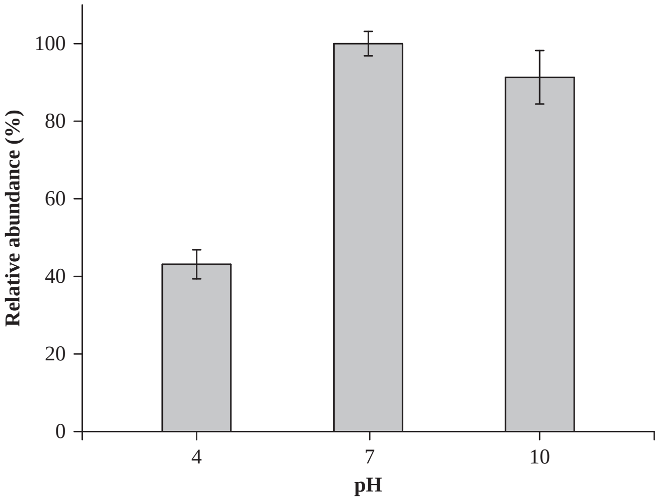


Fig. 4. The effect of different sample solution pH values (pH=4, 7, 10) (n=3 for each point). Absorbent amounts: 20 mg, extraction time: 15 min, eluting solvent: chloroform, desorption time: 10 min.

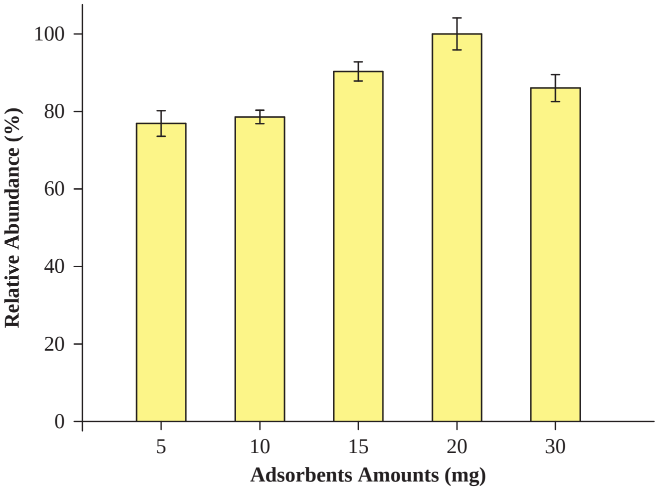


Fig. 5. The effect of different adsorbent amounts (5, 10, 15, 20, 30 mg) (n=3 for each point). Extraction time: 15 min, eluting solvent: chloroform, desorption time: 10 min.

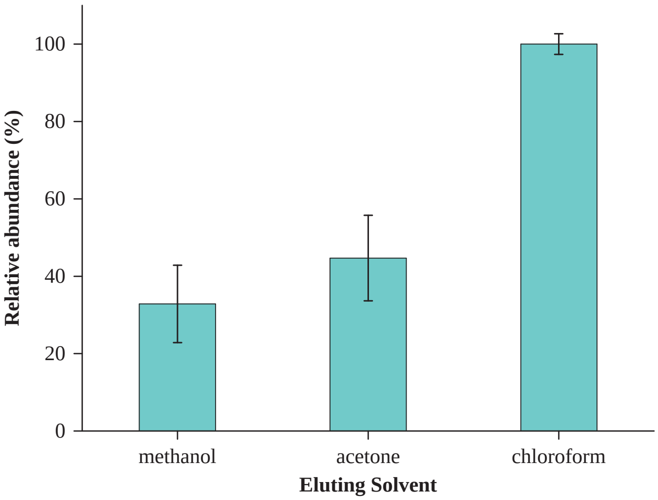


Fig. 6. The effect of different eluting solvents (methanol, acetone, chloroform) (n=3 for each point). Absorbent amounts: 20 mg, extraction time: 15 min, desorption time: 10 min.

3.2.3. Optimization of eluting solvent

A proper eluting solvent is of great importance after the extraction of analytes by phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres to obtain reliable and reproducible analytical results. In this study, various organic solvents including methanol, acetone and chloroform were adopted to investigate the desorption effects. As shown in Fig. 6, chloroform as the eluting solvent attained the highest efficiency, while methanol had a relative low eluting ability for acetaldehyde oximes. It could be explained as that chloroform

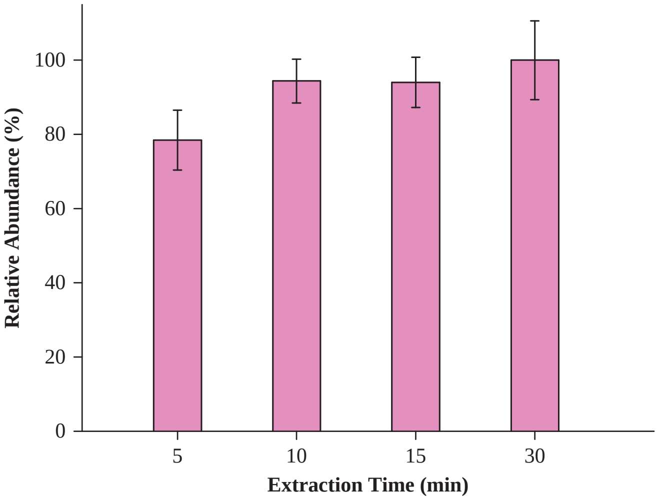


Fig. 7. The effect of different extraction time (5, 10, 15, 30 min) (n=3 for each point). Absorbent amounts: 20 mg, eluting solvent: chloroform, desorption time: 10 min.

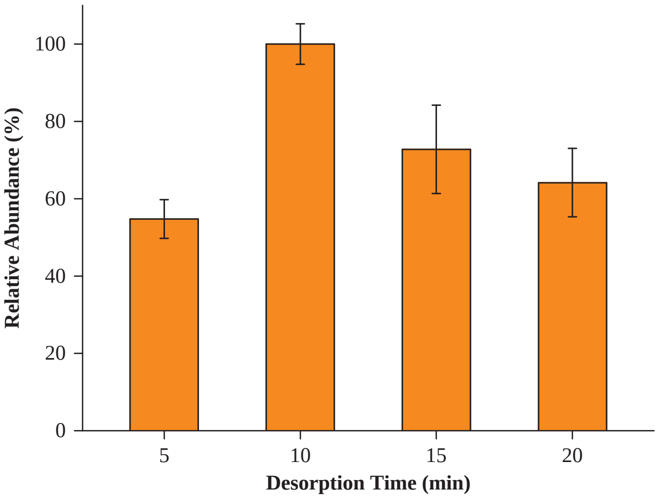


Fig. 8. The effect of different desorption time (5, 10, 15, 20 min) (n=3 for each point). Absorbent amounts: 20 mg, extraction time: 10 min, eluting solvent: chloroform.

had the similar polarity to the acetaldehyde-PFBHA derivatives, and the high content of fluorine in chloroform provided the availability of “like dissolves like”. On the other hand, the comparative strong polar solvent of methanol was not able to elute the targets from the sorbents easily. Therefore, chloroform was selected as the optimized eluting solvent in the following work.

3.2.4. Optimization of adsorption time

A certain adsorption time is required after the sorbents are dispersed into the solution in order to facilitate analyte–particle interaction. To enhance the extraction efficiency, different extraction time ranging from 5 to 30 min was studied. It could be concluded from Fig. 7 that the recoveries of the targeted compounds increased significantly with an extending time from 5 to 10 min. Once adjusted from 10 to 30 min, the adsorption amount had no remarkable improvement. It may be interpreted as that the distribution equilibrium between the analytes and phenyl group-functionalized $Fe_3O_4@mSiO_2$ microspheres was easily achieved in only 10 min due to strong π–π interaction, and a prolonged time did not contribute more enhancements to the enrichment efficiency. Hence, the best extraction time was determined to be 10 min.

3.2.5. Optimization of desorption time

Also, different desorption time (5, 10, 15 and 20 min) was investigated to receive the maximum elution results. Fig. 8 illuminated that 10 min was enough to elute the majority of adsorbed analytes under continuous sonication. But after 10 min, the extraction efficiency decreased instead with an increasing time. It was supposed that most analytes could be thoroughly eluted within 10 min, and extended sonication time may favor the readsorption of a small portion of acetaldehyde oximes because of their strong π–π interaction with phenyl group-functionalized $Fe_3O_4@mSiO_2$ microspheres. The above results pointed out that ultrasonication helped to disperse the magnetic mesoporous materials and increase the contact area between eluting solvent and targeted compounds, which accelerated the desorption course effectively.

Finally, the optimized extraction conditions including neutral sample solution, 20 mg sorbents added, chloroform as eluting solvent, adsorption time of 10 min, and desorption time of 10 min were selected for further study.

3.3. Method validations

Method validations such as linearity, recovery, repeatability, and limit of detection were studied. The calibration curves were constructed by analyzing a series of standard solutions of acetaldehyde derivatives with different concentrations and by plotting concentration versus peak area. The calibration curves showed good linearity in the range of 0.25~4 mg/mL. The regression equations were y=260,659x−31,180 and y=264,751x−23,074 for the two acetaldehyde oximes. The corresponding values (R^2) were 0.9993 and 0.9978, respectively. The LOD was 40 μg/mL, calculated on the basis of S/N=3. And on the basis of S/N=10, the LOQ of acetaldehyde oximes was 133.3 μg/mL. Precision of the adopted method was assessed by the intra-day and inter-day RSDs of SPE procedure and the values were determined to be 4.5% and 10.1% respectively, which indicated a satisfactory repeatability. The recovery of the analytes was studied by extracting the spiked sample solution (0.5 and 1 mg/mL) containing different known amounts of acetaldehyde, and the value was calculated to be 92.0% and 88.0%. Besides, the RSD value for the reproducibility of the synthesized microspheres was determined to be 9.4% by studying the extraction performance of five different batches of the prepared adsorbents.

Table 1 summarized the main analytical figures of the comparable methods reported for the analysis of acetaldehyde in mainstream cigarette smoke. Compared with the earlier systems [1,4], our synthesis of phenyl group-functionalized magnetic mesoporous silica microspheres provided an effective sample pretreatment process and largely reduced the interfering background of the complex matrices. Meanwhile, it should be highlighted that the

Table 1
Comparison of the proposed method with previous reported alternatives for the determination of acetaldehyde in cigarette smoke.

Method	Linear range (μg/mL)	RSD (%)	LOD (μg/mL)	Recovery (%)
MSPE-GC–MS[a]	250–4000	4.5	40	88
SPME-GC-μFID[b], [1]	71.6–716	6.7	48	85
HPLC-UVD[c], [4]	370–1150	5.0	50	/[d]

[a] MSPE, magnetic solid-phase extraction.
[b] μFID, micro flame ionization detector.
[c] UVD, ultraviolet detector.
[d] /, data not provided.

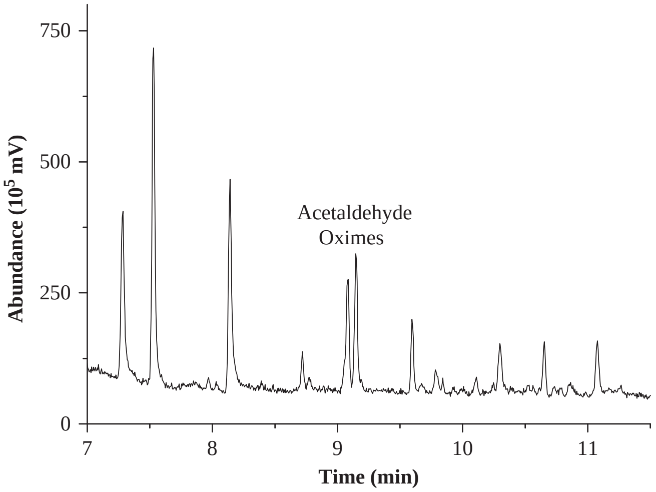


Fig. 9. The representative chromatogram of mainstream cigarette smoke by the proposed method (scan mode, quantitative ion *m*/*z* ratio 181, qualitative ion *m*/*z* ratios 83, 209, 85).

present method offered lower RSD and LOD, wider linear range, and higher recovery, which entitled the analysis approach to achieve satisfactory results due to its comparable advantages. These data disclosed that the proposed method based on magnetic micro SPE technique was reliable for the analysis of acetaldehyde in real samples.

3.4. *Determination of acetaldehyde in mainstream cigarette smoke*

Inspired by the satisfying enrichment results above, the phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres were applied to the extraction and enrichment of acetaldehyde in cigarette samples ($n=3$). Under the optimal conditions, mainstream cigarette smoke from two brands of cigarettes was analyzed. A representative chromatogram of a cigarette sample by magnetic SPE and GC–MS was depicted in Fig. 9. Although the cigarette sample was an extremely complex matrix, the component of acetaldehyde which was not of the largest amount could still be detected using the suggested technique. Acetaldehyde oximes formed two derivatives, and were quantitatively analyzed using external standard method. Table 2 summarized the calculated concentrations of acetaldehyde in cigarette samples of different brands. Higher acetaldehyde concentration is likely to be more carcinogenic and harmful.

Due to the high stability of the phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres, the enrichment procedure was repeated for six cycles to study the reusability of the adsorbents. The adsorption efficiency of the regenerated material was shown in Fig. S3. The regenerated adsorbent shows a slight decrease in the subsequent cycles. However, the analytes uptake capacity can still reach about 85% and 75% of the original capacity for the two oximes after the sixth cycle. Overall, this material shows excellent regeneration for the application to real samples.

In the proposed method, the synthesized phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres were successfully applied as adsorbents to determine acetaldehyde in mainstream cigarette smoke. Moreover, it proved the suitability of this technique to assess the presence of target aromatic compounds in complicated real samples.

4. Conclusions

In this study, phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres were successfully synthesized through a facile one-pot co-condensation approach, and developed as magnetic SPE sorbents for the enrichment and determination of acetaldehyde in mainstream cigarette smoke. Due to the abundant silanol groups on the exterior surface and functional phenyl groups on the interior surface, the prepared core–shell nanomaterials displayed good dispersibility and promising extraction capacity for aromatic compounds in complex real samples. Moreover, the optimal method had attained satisfactory analysis results with a little amount of adsorbents within a short period of time. To summarize, the biggest advantages of the suggested technique are simple collection and fast derivatization of sample, selective extraction and concentration with magnetic SPE, and fast analysis by GC–MS. Therefore, the proposed method based on phenyl group-functionalized Fe_3O_4@$mSiO_2$ microspheres is proved to be a rapid, efficient and authentic method for the determination of acetaldehyde in cigarette. It is a potential tool for quality control of tobacco and is recommended for the assessments of toxic substances in other fields such as air, water, food and so on.

Table 2
Acetaldehyde concentration in cigarette samples ($n=3$).

Cigarette samples	Acetaldehyde (mg/cigarette)
Brand 1	2.31 ± 0.05
Brand 2	1.26 ± 0.03

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.05.068.

References

[1] H.Q. Lin, Q. Ye, C.H. Deng, X.M. Zhang, J. Chromatogr. A 1198–1199 (2008) 34.
[2] J.I. Seeman, M. Dixon, H.J. Haussmann, Chem. Res. Toxicol. 15 (2002) 1331.
[3] K.L. Ou, C.C. Yu, Y.C. Liu, K.H. Yang, C.C. Wang, Q.Y. Chen, Mater. Res. Bull. 46 (2011) 2333.
[4] P.R. Houlgate, K.S. Dhingra, S.J. Nash, W.H. Evans, Analyst 114 (1989) 355.
[5] M. Al Rashidi, A. Shihadeh, N.A. Saliba, Food Chem. Toxicol. 46 (2008) 3546.
[6] P.J. Branton, K.G. McAdam, D.B. Winter, C. Liu, M.G Duke, C.J. Proctor, Chem. Cent. J. 5 (2011) 15.
[7] T. Miyake, T. Shibamoto, J. Chromatogr. A 693 (1995) 376.
[8] X.B. Pang, A.C. Lewis, Sci. Total Environ. 409 (2011) 5000.
[9] L. Annovazzi, V. Cattaneo, S. Viglio, E. Perani, C. Zanone, C. Rota, F. Pecora, G. Cetta, M. Silvestri, P. Iadarola, Electrophoresis 25 (2004) 1255.
[10] H. Kataoka, A. Sumida, M. Makita, Chromatographia 44 (1997) 491.
[11] J.Z. Dong, S.C. Moldoveanu, J. Chromatogr. A 1027 (2004) 25.
[12] S.S. Huang, C.X. Li, Z.Y. Cheng, Y. Fan, P.P. Yang, C.M. Zhang, K.Y. Yang, J. Lin, J. Colloid Interf. Sci. 376 (2012) 312.
[13] A. Mehrani, K. Mehrani, J. Inorg. Organomet. Polym. 22 (2012) 1419.
[14] J.H. Wang, S.R. Zheng, Y. Shao, J.L. Liu, Z.Y. Xu, D.Q. Zhu, J Colloid Interf. Sci. 349 (2010) 293.
[15] K.M. Ponvel, Y.H. Kim, C.H. Lee, Mater. Chem. Phys. 122 (2010) 397.
[16] Z.A. Alothmana, A.W. Apblett, Chem. Eng. J. 155 (2009) 916.
[17] B.Y. Song, Y.J. Eom, T.G. Lee, Appl. Surf. Sci. 257 (2011) 4754.
[18] V.V. Oliveira, C. Airoldi, J. Solid State Chem. 196 (2012) 293.

[19] C.F. Wang, G.W. Zhou, Y.J. Li, N. Lu, H.B. Song, L. Zhang, Colloids Surfaces A, Physicochem. Eng. Aspects 406 (2012) 75.
[20] X.H Zhang, X.W. He, L.X. Chen, Y.K. Zhang, J. Mater. Chem. 22 (2012) 16520.
[21] X.C. Fu, X. Chen, J. Wang, J.H. Liu, Microporous Mesoporous Mater. 139 (2011) 8.
[22] S.Y. Tao, C. Wang, W. Ma, S. Wu, C.G. Meng, Microporous Mesoporous Mater. 147 (2012) 295.
[23] X.D. Xin, Q. Wei, J. Yang, L.G. Yan, R. Feng, G.D. Chen, B. Du, H. Li, Chem. Eng. J. 184 (2012) 132.
[24] X.L. Zhang, H.Y. Niu, W.H. Li, Y.L. Shi, Y.Q. Cai, Chem. Commun. 47 (2011) 4454.
[25] Z.B. Li, D.N. Huang, C.F. Fu, B.W. Wei, W.J. Yu, C.H. Deng, X.M. Zhang, J. Chromatogr. A 1218 (2011) 6232.
[26] H. Deng, X.L. Li, Q. Peng, X. Wang, J.P. Chen, Y.D. Li, Angew. Chem. Int. Ed. 44 (2005) 2782.
[27] K.L. Ding, B.J. Hu, G.M. An, R.T. Tao, H.Y. Zhang, Z.M. Liu, J. Mater. Chem. 19 (2009) 3725.
[28] Y.H. Deng, D.W. Qi, C.H. Deng, X.M. Zhang, D.Y. Zhao, J. Am. Chem. Soc. 130 (2008) 28.
[29] W.R. Zhao, J.L. Gu, L.X. Zhang, H.R. Chen, J.L. Shi, J. Am. Chem. Soc. 127 (2005) 8916.
[30] L. Wang, J. Bao, L. Wang, F. Zhang, Chem. Eur. J. 12 (2006) 6341.
[31] L.D. Gelb, K.E. Gubbins, Langmuir 15 (1999) 305.
[32] M. Kruk, M. Jaroniec, J.M. Kim, R. Ryoo, Langmuir 15 (1999) 5279.