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A novel needle trap device with single wall carbon nanotubes sol–gel sorbent packed for sampling and analysis of volatile organohalogen compounds in air

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ABSTRACT

This paper describes a new approach that combines needle trap devices (NTDs) with a newly synthesized silanated nano material as sorbent for sampling and analysis of HVOCs in air. The sol–gel technique was used for preparation of the single wall carbon nanotube (SWCNT)/silica composite as sorbent, packed inside a 21-gauge NTD. Application of this method as an exhaustive sampler device was investigated under different laboratory conditions in this study. Predetermined concentrations of each analyte were prepared in a home-made standard chamber, and the effects of experimental parameters, such as temperature, humidity, sampling air flow rate, breakthrough volume and storage time on NTD, and the sorbent performance were investigated. The proposed NTD was used in two different modes and two different injection methods, and an NTD with a side hole, a narrow neck glass liner and syringe pump assisted injection of carrier gas were applied. The NTD packed with SWCNTs/silica composite was compared to the NTD packed with PDMS and also SPME with CAR/PDMS. For four compounds, LOD was 0.001–0.01 ng mL^{-1}, LOQ was 0.007–0.03 ng mL^{-1}, and the relative standard division for repeatability of method was 2.5–6.7%. The results show that the incorporation of NTD and SWCNTs/silica composite is a reliable and effective approach for the sampling and analysis of HVOCs in air. Coupling this system to GC–MS make it more sensitive and powerful technique.

1. Introduction

Halogenated volatile organic compounds (HVOCs) are also known as volatile organohalogen compounds. According to European VOC solvent directive 1999/13/EC, organohalogen compounds are those which have at least one halogen (fluorine, chlorine, bromine, iodine) atom with vapor pressure of more than 10 Pa at 20 °C [1]. These are very significant environmental and occupational pollutants due to their widespread usage and high toxicity. HVOCs are widely used in industry as solvents, cleaning and degreasing agents, polymerization and blowing agents, and also as disinfecting agents. Because of high vapor pressure, these compounds can easily be released into the workplace, and workers health may be affected [2–5]. Most VOCs, particularly the halogenated hydrocarbon solvents, are known to be hazardous. HVOCs can enter the human body by inhalation, dermal contact or inadvertent ingestion via hand-to-mouth contact. These chemicals can then enter the bloodstream and may either be excreted or accumulate in different organs. Industrial indoor exposure to these solvents may cause cancer or mutagenic, or teratogenic effects and thus represents a direct health risk to workers [6].

Sampling and analysis of HVOCs are very important for accurate assessment of indoor and outdoor exposure. The U.S. Environment Protection Agency (EPA) has recommended method 8010B, and the U.S. National Institute of Occupational Health and Safety (NIOSH) offers method 1003 for the sampling and analysis of halogenated volatile hydrocarbons in water and air matrices. There are also some techniques for sample preparation, preconcentration, and separation of HVOCs. The most common technique for analyzing HVOCs in water is liquid–liquid extraction with an organic solvent (hexane or pentane) and a subsequent analysis of the extract via gas chromatography with electron-capture detection (LLE–GC–ECD) [7,8]. The LLE–GC–ECD technique has many qualitative and quantitative limitations, and it is not recommended for sampling and analysis of air. There are also some microextraction techniques for preparation, preconcentration, and analysis of HVOC samples, such as liquid phase microextraction (LPME) techniques. However, these techniques are not suitable for analysis of HVOCs found in air. The other techniques are the gas phase extraction technique and the direct aqueous injection technique (pure water samples), which are suitable for HVOCs. Solvent microextraction (SME), solid phase

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extraction (SPE) and membrane extraction (ME) techniques are most often used for semi-volatile organohalogen compounds. None of these techniques are universal and almost can be only used for water analysis [9].

Despite the fact that all of these techniques are based on solvent usage for sample preparation and extraction of HVOCs, there are some solvent-less and solvent-free sample preparation and introduction techniques for VOCs and HVOCs. Among all of these, NTD and solid phase microextraction (SPME) techniques have earned more interest and are in use today. SPME, first introduced by Pawliszyn et al. in 1990 [10], is a solvent-free extraction method that has been used to extract halogenated organic compounds from a variety of matrices (gas, liquid and solid) [11–23]. The NTD technique, first introduced by Pawliszyn and coworkers in 2001 [24], combines the concept of miniaturized exhaustive active sampling as well as passive diffusive sampling with newly created microextraction techniques. When compared with NTD, SPME has some drawbacks, such as fiber fragility, which can cause fiber breakage from mechanical stress during the sample taking and sample delivery stages, and limited sorption capacity. Extraction with SPME is based on the equilibrium partitioning of HVOCs between a sampled matrix and the stationary phase (coated on a fiber) and has less specification for air samples than NTDs. In the stationary phase of NTD, samples are placed inside a stainless steel needle, and this process makes this a robust technique [25]. Sample introduction and determination can be performed in a single step, which offers many advantages for sampling and analysis of a wide range of compounds in air. These capabilities make NTD a good technique for workplace surveys of occupational exposure to hazardous compounds.

Until now, NTD has been used with some commercial sorbents, such as polydimethylsiloxane (PDMS), divinylbenzene (DVB) and Carboxen1000 [26,27], Carbopack X and Tenax [28–30], and Porapak Q [31]. There are just a few studies related to the use of a needle trap device with carbon nanotubes (CNTs) as sorbent. CNTs, which have a high surface area, mechanical strength and chemical stability, were first discovered by Sumio Iijima in 1991 [32]. Because of the carbon atom layers in the wall of the nanotubes, CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). In recent years, MWCNTs and SWCNTs have been proven to possess great potential to be used as sorbent [33–35]. Potential characteristics of CNTs and the sol–gel technique can offer a great advantage for providing a sorbent for indoor and outdoor air pollution monitoring. The sol–gel technique can provide a useful approach for synthesis of different sorbent. With this technique, sorbent can be synthesized with better homogeneity and purity as well as lower temperature of preparation, strong mixing abilities for multi-component systems, control of particle size, shape and properties, and better thermal stability for higher thermal desorption [36].

Bagheri et al. used a NTD with sorbent, based on carbon nanotube-sol–gel for microextraction of PAHs from aquatic media [37]. Despite the authors' intensive literature review, no study combining SWCNTs with NTD as sorbent for sampling and analysis of HVOCs in air was identified.

In this paper, we prepared a needle trap device packed with silanated single wall carbon nanotubes and used it for sampling and analysis of some HVOCs in air. Performance of this device and also SWCNTs/silica composite as sorbent was investigated. Some of laboratory parameters, such as temperature, humidity, breakthrough volume, and GC parameters in analysis performance of HVOCs, were also investigated. A comparative study was carried out, and SWCNTs/silica composite was compared with the commercial sorbent (PDMS); also, an NTD technique was compared with the SPME technique.

2. Experimental

2.1. Reagents and standards

SWCNTs-COOH with purity higher than 90%, with 1–2 nm O.D., 0.8–1.6 nm I.D. and length of 5–30 μm and rate of surface carbon atom 8–10 mol%, were obtained from Chengdu Organic Chemicals (Chinese Academy of Sciences). The –COOH content of SWCNTs was 2.73 wt% and special surface area (SSA) was more than 380 $m^2\,g^{-1}$. Carbon tetrachloride (CTC), trichloroethylene (TCE), bis(chloromethyl)ether (BCME) and chloromethyl methyl ether (CMME) with highest purity available were purchased from Sigma-Aldrich (Germany). Nitric acid, sulfuric acid all in analytical grade were purchased from Merk (Germany). Ultrahigh purity helium was obtained from Raham (Tehran, Iran). Deionized water used for preparation of SWCNTs was obtained from a TKA (Germany) ultra water system. Trifluoroacetic acid (TFA), tetramethylorthosilicate (TMOS) and polymethyl hydrogensiloxane (PMHS) were supplied from Merck (Darmstadt, Germany). Sodium dodecylbanzenesulfunate (SDBS) was purchased from Fluka (Buchs, Switzerland).

2.2. Instrumentation

Chromatography was performed with Varian 3800 GC with a capillary column (VOCOL with 60 m × 0.25 mm × 0.25 μm) equipped with a Saturn 2200 MS system and a split-splitless injector. The column was initially set at 40 °C and held at this temperature for 4 min, then ramped at 6 $^\circ C\,min^{-1}$ to 160 °C, for a total run time of 24 min. For the separation of desorbed HVOCs from the NTD, injection was performed in splitless mode at an injection port temperature of 300 and 310 °C. The carrier gas was Helium (99.999%) at a flow rate of 1 $mL\,min^{-1}$. A home-made narrow neck glass liner with a 1.5 mm I.D. and a 0.5 mm neck diameter was used in GC injector for efficient delivery of analytes inside the needle to the GC column and for prevention of peak broadening. A home-made chamber was used for adjustment of concentration, temperature and humidity of sample matrix. A 21-gauge needle with 12 cm length and 700 μm I.D. was purchased from Kosan LTD (Japan). Two syringe pumps, JMS SP-510 (Hiroshima, Japan), were used for providing standard concentration and determined injection of the calculated amount of HVOCs into the sampling chamber and also for carrier gas injection into the GC injection port. A low volume sampling pump, SKC 222 series (PA, USA), with a sampling flow rate of 1–200 $mL\,min^{-1}$ was used for the performance evaluation of NTDs and accurate drawing of air inside the needles and through the sorbent bed.

2.3. SWCNTs silanation with sol–gel technique

For preparation of SWCNTs/silica sol solution, 2 mg of SWCNTs with –COOH group was dispersed in 50 μL of SDBS solution (5% w/v) as a surfactant in an Eppendorf vial. The obtained suspension was agitated by ultrasonic bath for 15 min and then 400 μL TMOS and 50 μL PMHS were added and the mixture was sonicated for 30 min. Afterward, 50 μL of TFA was added, and the total solution was sonicated in an ultrasonic bath for 15 min. To remove the non-reacted material, the resulting mixture was refluxed in dichloromethane and ethanol solution (2:1 v/v) for 1 h. Finally, the mixture was centrifuged at 4000 RPM for 10 min, and then the obtained solid sorbent was dried in an oven with a temperature of 120 °C for 2 h, and after weighing the produced SWCNTs/silica meshed over the range of 53–63 μm.

2.4. Preparation of NTD

As illustrated in Fig. 1, the needle size was 21-gauge with 12 cm length and 700 μm I.D. If a larger needle was used, poor resolution was often observed and GC chromatogram showed broad peak. If it was smaller, blockage of the needle was inevitable. The distance between the sorbent and the tip of the needle varied according to its application. If the NTD was prepared for passive TWA sampling, the distance could not be zero. For exhaustive sampling, the sorbent could be packed exactly from the tip of the needle. According to the morphology and temperature gradient of the GC injector, a side hole (~0.4 mm I.D.) was drilled 3 cm from the blunt end tip of needle. For sorbent packing inside the needle, a metal wire was used to indicate the position inside the needle where the sorbent would be packed. First, 3 mm of glass wool was packed, and then 1.5 cm length of needle was packed with SWCNTs/silica composite as sorbent, and finally another 3 mm glass wool was used. The purpose of glass wool packing before and after the SWCNTs sorbent was for holding the sorbent firmly without bleeding and for fixing its position. After packing, the prepared NTD was conditioned in a GC injector at 290 °C for 3 h with drawing Helium as carrier gas in order to remove impurities. After all of these processes, the NTD was ready to use.

2.5. Sampling by NTD

For NTD sampling, a home-made chamber was prepared (Fig. 2). In this chamber, a dynamic standard concentration of a predetermined amount of CTC, TCE, BCME and CMME was prepared with adjusted injection of each analyte using a syringe pump into a flow direction line connected to the sampling chamber. With this system, a different range of concentrations from 0.001–250 ng mL^{-1} for each analyte was achieved. The sampling temperature was at three levels (10, 25 and 35 °C) using a thermostated plate and a visible light radiation lamp inside an additional chamber, located upstream of the sampling chamber. The temperature inside the chamber was successfully adjusted in a defined range using this temperature controller system. For adjusting relative humidity inside the chamber, a humidifier and a hygrometer system was used, and relative humidity was also successfully adjusted in two levels of 20% and 80%. For the sampling and adsorption of analytes, the side hole of the needle was sealed by a septum cap, and the tip of the needle was inserted into the sampling chamber for taking the samples. Using a low volume-sampling pump, air was drawn inside the needle. After taking the samples analysis was performed by GC/MS system.

2.6. Desorption in GC injection port

Two methods for desorption in the GC injection port were investigated in this study. In the first desorption mode, a home-made narrow neck glass liner was used for efficient directing of carrier gas inside the needle via side hole (Fig. 3). For proper sealing of the NTD and neck part of the liner, the tip of the needle should be well squared and fit the glass liner of the GC injection port. In this desorption mode of the NTD, the hub of the needle was sealed and the septum was removed to open the side hole. The needle was inserted into to the liner of the GC injector. The carrier gas entered the needle through the side hole, passed through the sorbent, and aided the delivery of the desorbed analytes into the GC column. Following desorption, the NTD was removed from the injector, and the system was then ready for another sampling. In the second injection mode, a syringe pump was used for force drawing of pure carrier gas inside a syringe through the needle as another desorption option in the injector. With this desorption system, a needle was used without a side hole, and a steady state flow rate of 1 mL min^{-1} of pure helium was drawn through the needle.

2.7. Method validation

For method validation, three different numbers of sampling cycles were used. For determination of the normal calibration curve, different concentration levels in the range of 0.01–250 ng mL^{-1} for CTC, TCE, BCME and CMME were analyzed. For determining the effect of temperature in three levels (10, 25 and 35 °C) and humidity in two levels of 20% and 80% on sampling efficiency, five sampling

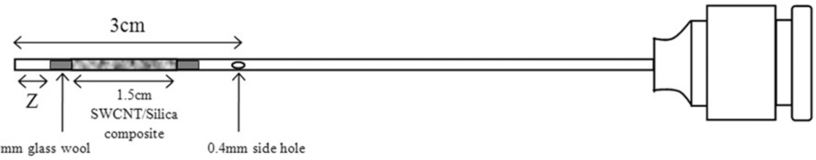

Fig. 1. Schematic of needle trap device with side hole, glass wool and SWCNTs/silica composite as sorbent.

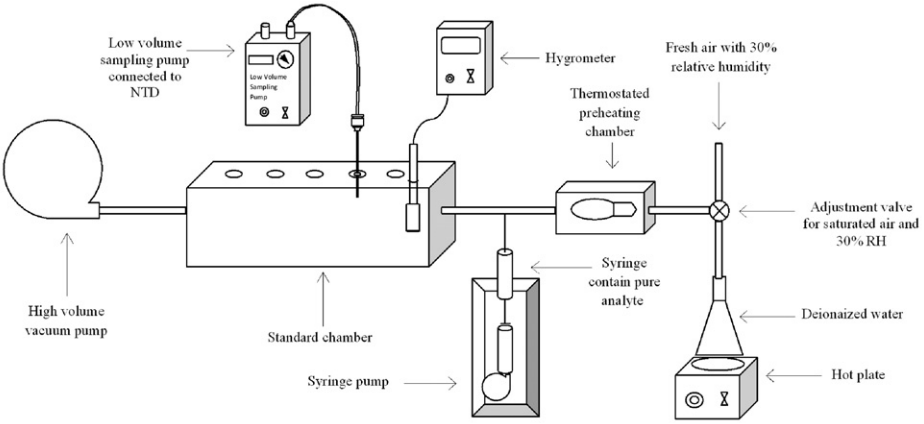

Fig. 2. Schematic of sampling set with standard chamber, syringe pump assisted of predetermined concentration of analyte injection, temperature and humidity adjustment inside standard chamber.

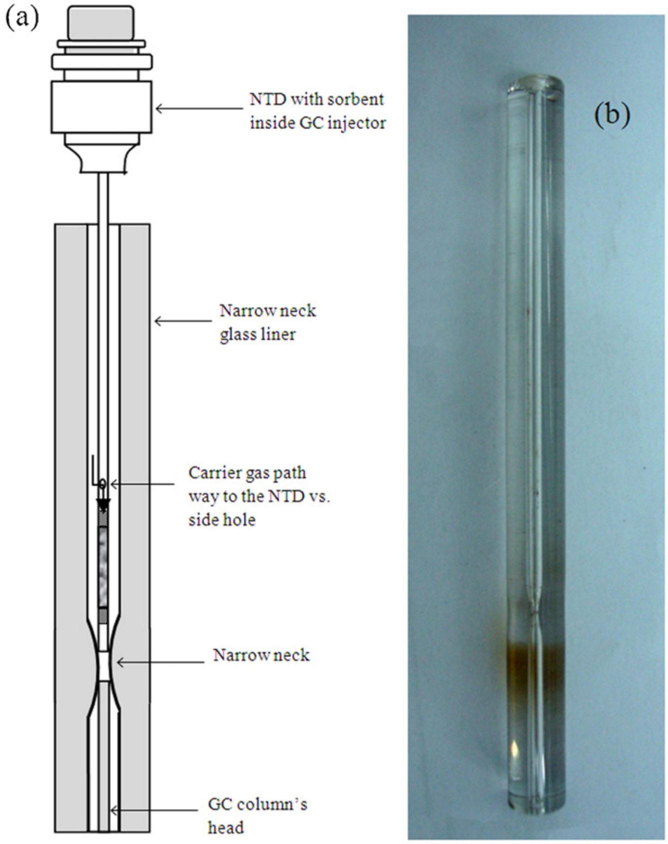

Fig. 3. (a) Schematic of desorption system with narrow neck glass liner and side hole system. (b) Picture of home-made narrow neck glass liner with neck diameter less than needle outside diameter.

cycles were performed. Eight sampling cycles also were carried out for assessment of sampling storage time on the NTD. Finally, for assessment of the GC parameters and desorption conditions (time and temperature) both on 6 levels, 12 sampling cycles were performed. For carrying out sampling and analysis with good precision, each sampling cycle was performed with three consecutive extractions of predetermined concentrations from the standard chamber. Also, validation of methods LOD and LOQ were directly determined by repeated analysis of predetermined concentrations from 0.001 to 1000 ng mL^{-1} of analytes of interest. Linearity and repeatability of the NTD method for sampling and analysis of analytes from air were performed by calibration curve slop and relative standard division calculation of analytes of interest from a concentration range of 0.01–250 ng mL^{-1}. For making a better judgment about performance of NTD packed with SWCNTs/silica composite a comparative study was carried out and results for the NTD compared with the NTD packed with commercial sorbent PDMS and the SPME technique with Carboxen/PDMS fiber.

3. Results and discussion

3.1. Breakthrough investigation

Sampling by NTD is a non-equilibrium method with an exhaustive extraction mode. This means analytes are completely extracted by the sorbent inside the needle, before breakthrough occurs. For a specific sorbent, breakthrough volume (BTV) depends on the length of the sorbent packed and the affinity of the analytes to the sorbent and also the concentration of analytes in the sample and the sampling flow rate that are inversely proportional to the BTV. For minimizing of the overall sampling time, the maximum sampling flow rate that did not cause breakthrough for any of the target compounds assessed and was considered as the optimum amount for further investigations. First, for breakthrough investigation, two needles were packed with the same length of SWCNTs/silica composite connected in a series. To examine the BTV, the head of the two-section NTD was connected to the sampling pump, and its end tip was exposed to the sample. A constant concentration (1 ng mL^{-1}) of the four analytes was drawn through the two-section NTD, and then desorption followed until analytes extracted by the back NTD could be detected by the GC/MS system. The breakthrough percentages were calculated using the Eq. (1).

$$\text{Break through percentage} = 100 \times \text{BT}/(\text{FT}+\text{BT}) \tag{1}$$

where FT and BT represent the extracted amounts in the front and back trap, respectively. Results for BTV investigation at three different temperatures revealed that the volume of more than 1500 mL at the concentration of 1 ng mL^{-1} for CTC, TCE, BCME and CMME was drawn until breakthrough was reached, and the mass of analytes extracted by the 1.5 cm sorbent inside the 21-gauge needle were more than 1.5 μg (Table 1). After determining BTV, breakthrough was assessed at different flow rates (1–10 mL min^{-1}) and results revealed that breakthrough did not occur until the flow rate was below 5 mL min^{-1}. Thus 3 mL min^{-1} was selected as the best flow rate for further investigation. Breakthrough investigation results illustrated that the NTD with SWCNTs/silica composite has a good capacity for adsorption of HVOCs compounds.

3.2. Effect of temperature on sampling efficiency

SWCNTs/silica composite is a solid sorbent, and retains analytes by the adsorption mechanism. One of the main strategies for validation of this technique was indoor air pollutant monitoring for occupational health exposure assessment. Hence, the effect of temperature was investigated on sampling efficiency of NTD packed with SWCNTs/silica composite. In this regard, three levels of temperatures were selected close to real ambient air amounts (10, 25 and 35 °C). For each, compounds and temperature sampling were performed below the breakthrough volume in predetermined concentrations of 1 mL min^{-1} for four HVOC analytes in a dynamic standard chamber. The results (Fig. 4a) show that the collection efficiency and extraction capacity of the NTD for the four HVOC compounds were decreased slightly by increasing the temperature from 10 to 35 °C. However, the slop of the decrease is not high, but when using an NTD as an air sampling device, the effect of ambient air temperature on loss of analytes should be considered. A decrease in the peak area for CTC and CMME was higher than two other compounds, and this may be as a result of higher volatility and vapor pressure of these compounds. This reality proves that in an adsorption mechanism, temperature has an adverse effect on the trapping efficiency, and increasing the ambient air temperature can decrease collection efficiency and breakthrough volume in an NTD during the sampling periods.

Table 1
Breakthrough volume (mL) of NTDs packed with SWCNTDs/silica composite for four analytes at three different temperatures.

Temperature (°C)	Breakthrough volume (mL)			
	CTC	TCE	BCME	CMME
10	2000	2200	2300	1800
25	1900	2100	2100	1600
35	1600	1800	2000	1500

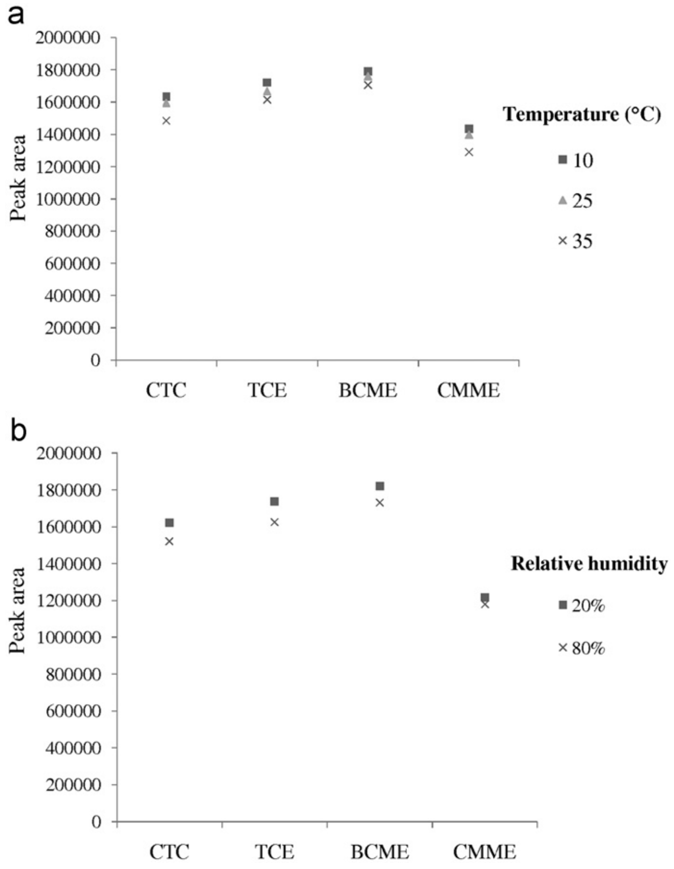

Fig. 4. Peak area response of NTD with SWCNTs/silica composite for effect of temperature (a) and relative humidity (b) on sampling efficiency.

3.3. *Effect of humidity on sampling efficiency*

The interference of air contained moisture on the fiber's adsorption properties, such as adsorption capacity and peak response, was investigated. When using NTD as air sampling instruments with an adsorption mechanism of sample collection by SWCNTs/silica composite as sorbent, the water molecules can deactivate the sorbent surface by blocking the active sites. For this issue, standard samples with relative humidity at two levels of 20% and 80% were prepared, and the efficiency of sample collection was monitored by GC. This study indicated that at higher relative humidity, molecules of water in the air can decrease the active sites of sorbent surface. Also, nanosorbent packed inside NTD in higher relative humidity may be clogged, and the size of sorbent particles may change from nanometer to micrometer. The consequence of a change in sorbent particle size and a decrease in sorbent active surfaces is a reduction in the amount of analytes extracted, and it can quite simply cause a reduction in collection efficiency, extraction capacity and breakthrough volume as well. Fig. 4b shows that humidity has been demonstrated to play a role in analyte adsorption.

3.4. *Desorption time and temperature*

Both temperature and time of desorption have significant effects on peak properties, so, both were investigated. Higher temperatures can cause better desorption with less carryover on the sorbent surface, but this is restricted by thermal stability of the sorbent and interested compounds. This may also reduces the life span of the sorbent. For these reasons, optimum desorption time and temperature should be selected carefully. Desorption temperature was investigated over the range of 270–320 °C. For the narrow neck glass liner and side hole desorption system, the maximum peak area was observed at 300 °C (Fig. 5a). In this desorption system, carrier gas in the injector heat zone was directly drawn into the NTD via the side hole, but this desorption system has some drawbacks, such as the plugging of the needle by septum pieces when the operator wants to insert the needle inside the GC injection port. Needle plugging by septum pieces may happens commonly, and it can cause tailed, broadened and disrupted peak response, which can make the analysis time consuming. Another problem with this desorption system is the carrier gas pressure drop inside the needle by packed sorbent.

For the syringe pump assisted desorption system, the maximum peak area corresponded to 310 °C. It seems that the temperature of the carrier gas, in this mode and at the same GC parameters, is less than the mentioned one, because the carrier gas was drawn into the NTD from outside the GC injector via syringe pump at room temperature and higher temperature at heat zone of GC injection port are needed to efficient desorption accurse. According to the optimum desorption time that was investigated for efficient desorption, the needle was inserted into the injector without drawing carrier gas for 2 min. This time was established as the heat equilibration time in syringe pump assisted desorption mode. After this time, carrier gas was drawn for 2 min to take the analytes into the GC column. Because there is no need for making the tip of needle squared, in the syringe pump assisted desorption system, the sharp tip of the needle can reduce the probability of needle plugging by septum pieces. Forced drawing of carrier gas can also travel easily through the needle, even when the needle is partially plugged by septum pieces. Despite the narrow neck liner and side hole needle system, with the syringe pump assisted injection system, the amount of carrier gas flow drawn into the NTD is under control by the operator throughout the analysis, to acquire good peak responses quality for further investigations.

Desorption times were used in the range of 1–6 min, and maximum peak area with no significant carryover was observed at 4 min after inserting the NTD in the GC injection port (Fig. 5b). Temperatures of 300 °C and 310 °C for the two different injection systems and an injection duration of 4 min were selected as the optimum desorption parameters for NTD.

3.5. *NTD sample storage time*

Investigation of storage capability of NTD after sampling is very important when NTDs are used as field samplers, because of necessity to storage and transport of samples. For this issue, the NTD was disconnected from the pump after sampling, the two ends and side hole of the needles were covered by a Teflon cap, and then the NTD was inserted into a glass container for storage in laboratory conditions (25 °C). The storage times were varied from 1–7 days, after which the samples were analyzed by inserting the NTD into the GC injection port, and then the response (peak area) of the analytes of interest was compared with the response obtained by injections done immediately after sampling. Fig. 5c shows that even after 7 days, the amount of analytes extracted from the NTD are very close to those analytes obtained immediately after sampling. It means that SWCNTs/silica composite has a strong affinity to HVOC compounds, and that NTD packed with this sorbent can be used as a field sampler with effective storage capabilities. Fig. 6 shows scanning electron micrograph of the SWCNTs/silica composite that prepared by sol–gel technique.

3.6. *Carryover of NTD packed with SWCNTs/silica composite*

The percentage of carryover depends on desorption time and temperature, and these GC parameters should be selected

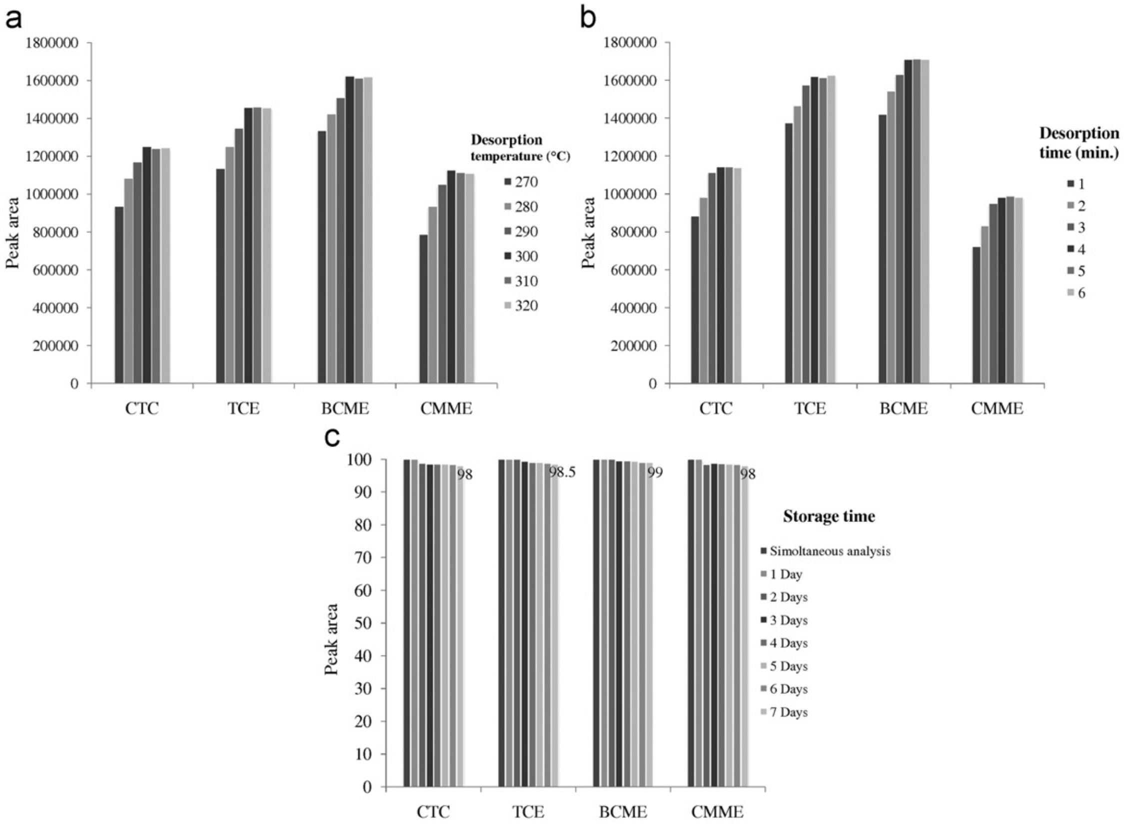

Fig. 5. Peak area response for analytical performance of NTD packed with SWCNTs/silica composite at different levels of desorption temperature (a), desorption time (b) and storage time (c).

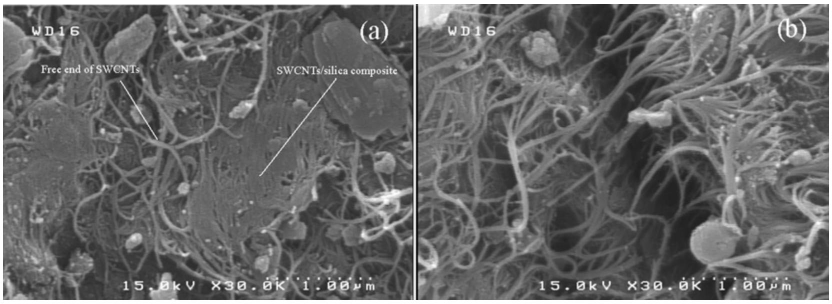

Fig. 6. Scanning electron micrograph of the SWCNTs/silica composite, prepared by sol–gel technique (a) and (b).

in a way that quantitative desorption occurs with the least amount of carryover. For selected desorption temperature (300 °C) and desorption time (4 min), carryover was investigated. The percentages of carryover for analytes are summarized in Table 2. The results reveal that carryover increased when volatility of organohalogen compounds decreased, and demonstrate that volatility of HVOCs plays a significant role in carryover process. 1 min after second desorption of analytes form NTD, inside the GC injection port (at optimum time and temperature), amounts of analytes were negligible and confirmed that the selected desorption time and temperature were corrected. For prevention of memory effect on further use of the NTD, carryover should not be detected, and the NTD should be well conditioned. Results demonstrated that after 4 min conditioning time, no carryover was observed. Thus the NTD could be used for further sampling and analysis with no memory effect.

Table 2
Carryover of HVOCs for different desorption time.

Desorption time (min)	Amount of analyte detected (%)			
	CTC	TCE	BCME	CMME
1	0.55	0.75	1.1	0.42
2	0.21	0.32	0.37	0.18
3	0.11	0.15	0.15	0.1
4	ND[a]	ND	ND	ND
5	ND	ND	ND	ND

[a] Not detected

3.7. Analytical performances

The limit of detection (LOD) was determined by exhaustive sampling of CTC, TCE, BCME and CMME using the NTD containing

SWCNTs/silica composite as a solid phase sorbent with a sampling flow rate of 3 mL min^{-1} and a total sampling volume of 30 mL. The NTD was exposed in the standard chamber in which predetermined concentrations of each analyte were prepared by dilution and injection flow rate adjustment of the syringe pump into the standard chamber. According to the results shown in Table 4, the method detection limits estimated, based on signal-to-noise ratios (S/N) of 3, for NTD packed with proposed sorbent, was 0.01 ng mL^{-1} for CTC and TCE and 0.001 ng mL^{-1} for BCME and CMME. The limit of quantitation (LOQ) determined by calculating concentration corresponds to a signal-to-noise ratio of 10. LOQs for CTC, TCE, BCME and CMME were 0.03, 0.04, 0.06 and 0.07 ng mL^{-1}, respectively. Comparing of LODs and LOQs for organohalogens sampling by NTD, relative to amounts reported by NIOSH, (NIOSH 1003, Table 4), shown that the proposed NTD method can detect lower concentrations of HVOCs. The NTD is an exhaustive method in which amounts of analytes can be adsorbed completely until breakthrough occurs. Also, the NTD is a solventless sampling method. These capabilities of NTD offer the advantages of sampling and measurement for very low concentrations of halogenated organic compounds.

3.8. Linearity and repeatability

Linearity was determined by calculating correlation coefficients of the regression equations of the calibration curves. For each analyte, a calibration curve was obtained with 10 points at high, medium, and low concentrations from 0.01–250 ng mL^{-1} (0.01, 0.05, 0.1, 0.5, 1, 5, 10, 50, 100 and 250 ng mL^{-1}). For each compound and concentration levels, triplicate measurements were made at different concentrations. As shown in Table 4, the calibration curves demonstrated good linearity with the suitable values of correlation coefficient (>0.99) for all of the analytes. The repeatability of the method was investigated for each analyte at five concentrations of 1, 10, 50, 100, and 250 ng mL^{-1} ($n=5$). Relative standard deviations (RSDs) of intra needle analysis were then used as a criteria for determination of the method's repeatability for SWCNTs/silica composite sorbent and CTC, TCE, BCME and CMME as analytes of interest. For each analyte and concentrations, sampling was repeated three times. The results demonstrate a reasonable repeatability for the proposed NTD method (Table 3).

Linear dynamic range (LDR) of the proposed NTD method for the analytes of interest were also investigated and obtained 0.01–50 ng mL^{-1} for CTC and TCE, and 0.01–100 ng mL^{-1} for BCME and CMME, respectively.

A comparative study has also been carried out, and NTD performance packed with SWCNTs/silica composite was compared with different commercial SPME fibers. Carboxen/PDMS fiber has been considered to be the most appropriate in the analysis of volatile organic compounds [19,38,39]. Comparison of these two techniques was performed in optimized sampling and analysis conditions, which we determined as a result of this study (sampling temperature: 10 °C, relative humidity: 20%, desorption time: 4 min, desorption temperature: 300 °C). LOD, LOQ, LDR and repeatability for both methods show similar results (Table 4).

NTD and SPME were successfully applied in the analysis of the HVOC samples and SWCNTs/silica composite showed the same qualitative behavior when compared to the best SPME commercial fiber. However, NTD method has some advantages over the SPME technique. Despite the fact that, calculation of equilibrium time and diffusion coefficient is needed for SPME, calibration is no more needed for NTD and concentration can be calculated very easily. Much like SPME, NTD techniques are examples of solventless and one-step sample preparation and injection methods. But SPME has some drawbacks, such as very high price of fibers due to monopoly in production, fiber fragility and an unprotected stationary phase on the outer surface of the fiber. The frangibility of the exposed fused-silica rod requires extremely careful handling during the multiple extraction/desorption cycles. The NTD is a more robust sampling device than SPME fiber, because the sorbent particles are protected inside a steel needle.

Table 3
The values of relative standard deviations (RSD) of analytes response at five concentration levels.

Compound	RSD (%)				
	1 ng mL^{-1}	10 ng mL^{-1}	50 ng mL^{-1}	100 ng mL^{-1}	250 ng mL^{-1}
CTC	3.4	5.3	4.6	5.5	5.7
TCE	4.1	6.2	5.1	6.7	6.3
BCME	3.6	4.4	4.1	5.2	5.1
CMME	2.5	3.7	3.5	4.4	4.6

Table 4
Comparison of LOD, LOQ and LDR of NTD-SWCNTs/Silica composite, NTD-PDMS and SPME-Carboxen/PDMS for four organohalogen compounds, and the coefficients of determination (r^2), calculated (F_{cal}) and critical (F_{crit}) value of Mandel's fitting test.

Compound	Sampling technique	Range (ng mL^{-1})	LDR	r^2	F_{Cal}	F_{Crit}	RSD (%)	LOD (ng mL^{-1})	LOQ (ng mL^{-1})
CTC	NTD-SWCNTs/silica composite	0.01–100	0.01–50	0.9974	4.28	6.59	2.5	0.01	0.03
	NTD-PDMS	0.01–100	0.1–30	0.9654	5.87	6.59	7.3	0.25	0.75
	SPME-CAR/PDMS	0.01–100	0.01–80	0.9954	4.11	6.59	5.5	0.027	0.081
TCE	NTD-SWCNTs/silica composite	0.01–100	0.01–50	0.9965	5.77	6.59	4.8	0.01	0.04
	NTD-PDMS	0.01–100	1–40	0.9751	5.01	6.59	9.5	0.42	0.97
	SPME-CAR/PDMS	0.01–100	0.01–80	0.9951	5.01	6.59	3.4	0.033	0.087
BCME	NTD-SWCNTs/silica composite	0.01–100	0.01–100	0.9912	4.63	6.59	7.4	0.001	0.005
	NTD-PDMS	0.01–100	1–60	0.9644	5.23	6.59	13.8	0.31	0.91
	SPME-CAR/PDMS	0.01–100	0.1–80	0.9944	4.47	6.59	4.3	0.012	0.045
CMME	NTD-SWCNTs/silica composite	0.01–100	0.01–100	0.9845	5.23	6.59	9.2	0.001	0.007
	NTD-PDMS	0.01–100	1–60	0.9527	6.11	6.59	17.2	0.46	1.42
	SPME-CAR/PDMS	0.01–100	0.1–90	0.9927	5.81	6.59	6.5	0.009	0.031

Table 5
Comparison of analytical characteristics for proposed sorbent with other sorbent applied by NTD technique in different studies.

Reference	Sorbent used with NTD	Parameters for comparison					
		Analytes	LDR (ng mL^{-1})	R^2	LODs (ng mL^{-1})	LOQs (ng mL^{-1})	RSDs (%)
[26]	PDMS, DVB and Carboxen	BTEX	NR[a]	0.992–0.998	0.00023–0.0021	NR	2–9
[28]	Carbopack X	BTEX	NR	0.9996–0.9999	0.05–0.07	0.08–0.10	0.5–11.6
[29]	Carboxen 1000, Carbopack X and Tenax	VOCs	NR	0.98–0.99	0.0019–0.033	NR	2.2–19.7
[30]	Carbopack X	BTEX	50–300	NR	10–25	NR	NR
[31]	Porapak Q	BTEX	0.2–100	0.998–0.999	0.019–0.125	0.052–0.341	NR
[40]	DVB/Carbopack X/Carboxen	VOCs	0.31–961.57	0.89–0.99	0.00033–0.194	0.0011–0.647	9.59–21.08
	DVB/Carboxen	VOCs	0.27–829.63	0.90–0.99	0.00044–0.411	0.00145–1.372	4.50–40.14
	PDMS/Carbopack X/Carboxen	VOCs	0.27–829.63	0.94–0.99	0.00032–0.146	0.00107–0.489	6.45–31.07
	PDMS/Carboxen	VOCs	0.27–704.41	0.94–0.99	0.00455–0.168	0.01528–0.94615	17.17–67.66
This Work	SWCNTs/silica composite	HVOCs	0.01–100	0.9845–0.9974	0.001–0.01	0.007–0.04	2.5–9.2

[a] Not reported.

In the intra needle comparative study, NTDs packed with two different sorbent materials were compared. Results have shown that newly synthesized SWCNTs/silica composite had a better analytical performance when compared to commercial PDMS sorbent (Table 4). The analytical performance characteristics of the proposed method were compared with some of other reported NTD–GC methods in literature (Table 5). Despite of fact that almost all of studies related to NTD was carried out for VOCs, specially for BTEX analytes and most of them performed for aquatic matrices but as can be seen, the proposed method using sol–gel SWCNTs/silica composite for the determination of HVOCs in this work, showed a low or similar LOD, LOQ and RSD in most cases, or even superior in some cases, to the previously reported methods. The proposed sol–gel sorbent has a good analytical performance toward HVOCs in comparison to the reported sorbents and this behavior is very remarkable.

4. Conclusion

In this study, NTDs packed with newly synthesized sorbent of SWCNTs/silica composite with sol–gel technique were used for sampling of some volatile organohalogen compounds in air samples. Some laboratory and experimental parameters, such as sampling temperature and humidity, breakthrough volume, sampling flow rate, storage time and GC operation parameters, were investigated, and both device and sorbent performance were evaluated. The results have shown that NTD–GC system offer an inexpensive, robust, and reusable technique, and these advantages make this technique suitable for air monitoring and exhaustive sampling and analysis of occupational and environmental exposure to volatile organic and organohalogen compounds. The NTD also integrates sample preparation and separation into a single step and reduces analysis time. One of the challenges of this study is pressure drop during NTD injection into GC. With syringe pump assisted drawing, we overcame this problem. Overcoming of NTD pressure drop without syringe pump assisted drawing is suggested for future research in this case.

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References

[1] J. Dewulf, H.V. Langenhove, G Wittmann, Trends Anal. Chem. 21 (2002) 637.
[2] P. Fabian, O.N. Singh (Eds.), Part E: Reactive Halogen Compounds in the Atmosphere, vol. 4, Springer, Berlin, Heidelberg, New York, 1999, p. 155.
[3] P. Fabian, O.N. Singh (Eds.), Part E: Reactive Halogen Compounds in the Atmosphere, vol. 4, Springer, Berlin, Heidelberg, New York, 1999, p. 45.
[4] A. McCulloch, P.M. Midgley, Atmos. Environ. 30 (1996) 601–608.
[5] A. McCulloch, M.L. Aucott, T.E. Graedel, G. Kleiman, P.M. Midgley, Y.-F. Li J. Geophys. Res. 104 (1999) 8417–8428.
[6] S. Hellweg, E. Demou, M. Scheringer, T.E. McKone, K. Hungerbuhler, Environ. Sci. Technol. 39 (2005) 7741–7748.
[7] L. Zoccolillo, L. Amendola, G.A. Tarallo, Int. J. Environ. Anal. Chem. 63 (1996) 91–98.
[8] B. Buszewski, T. Ligor, Water Air Soil Pollut. 129 (2001) 155–165.
[9] N. Jakubowska, B. Zygmunt, Z. Polkowska, B. Zabiegała, J. Namiesnik J. Chromatogr. A 1216 (2009) 422–441.
[10] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145–2148.
[11] M. Biziuk, A. Przyjazny, J. Chromatogr. A 733 (1996) 417–448.
[12] Z. Polkowska, K. Kozłowska, J. Namiesnik, A. Przyjazny, Anal. Chem. 34 (2004) 105–119.
[13] H. Kataoka, TrAC-Trends Anal. Chem. 22 (2003) 232–244.
[14] P. Kuran, L. Sojak, J. Chromatogr. A 733 (1996) 119–141.
[15] M. Marczak, L. Wolska, W. Chrzanowski, J. Namiesnik, Microchim. Acta. 155 (2006) 331–348.
[16] A. Kloskowski, W. Chrzanowski, M. Pilarczy, J. Namiesnik, Anal. Chem. 37 (2007) 15–38.
[17] K. Demeestere, J. Dewulf, B.D. Witte, H.V. Langenhove, J. Chromatogr. A 1153 (2007) 130–144.
[18] J.A. Koziel, I. Novak, TrAC-Trends Anal. Chem. 21 (2002) 840–850.
[19] P.M.S. Juan, J.D. Carrillo, M.T. Tena, J. Chromatogr. A 1139 (2007) 27–35.
[20] A.D. Jackowska, A. Wasik, A. Przyjazny, J. Namiesnik, Pol. J. Environ. Stud. 16 (2007) 159–176.
[21] M. Banar, A. Ozkan, M. Kurkcuoglu, Environ. Monit. Assess. 121 (2006) 439–459.
[22] P.A. Ellis, M.O. Rivett, J. Contam. Hydrol. 91 (2007) 107–127.
[23] J.S. Alvardo, C. Rose, Talanta 62 (2004) 17–23.
[24] J.A. Koziel, M. Odziemkowski, J. Pawliszyn, Anal. Chem. 73 (2001) 47–54.
[25] S. Bigham, J. Medlar, A. Kabir, C. Shende, A. Alli, A. Malik, Anal. Chem. 74 (2002) 752–761.
[26] A. Wang, F. Fang, J. Pawliszyn, J. Chromatogr. A 1072 (2005) 127–135.
[27] I.Y. Eom, A.M. Tugulea, J. Pawliszyn, J. Chromatogr. A 1196–1197 (2008) 3–9.
[28] H. Jurdakova, R. Kubinec, M. Jurcisinova, Z. Krkosova, J. Blasko, I. Ostrovsky, L. Sojak, V.G. Berezkin, J. Chromatogr. A 1194 (2008) 161–164.
[29] M. Mieth, S. Kischkel, J.K. Schubert, D. Hein, W. Miekisch, Anal. Chem. 81 (2009) 5851–5857.
[30] J.D. Crom, S. Claeys, A. Godayol, M. Alonso, E. Antico, J.M. Sanchez, J. Sep. Sci. 33 (2010) 2833–2840.
[31] P. Prikryl, R. Kubinec, H. Jurdakova, J. Sevcık, I. Ostrovsky, L. Sojak, V. Berezkin, J. Chromatogr. 64 (2006) 65–70.
[32] S. Iijima, Nature 354 (1991) 56–58.
[33] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chem. 75 (2003) 2517–2521.
[34] Q. Zhou, J. Xiao, W. Wang, J. Chromatogr. A 1125 (2006) 152–158.
[35] Q. Zhou, Y. Ding, J. Xiao, J. Chromatogr. 65 (2007) 25–30.
[36] A. Kumar, Gaurav, A.K. Malik, D.K. Tewary, B. Singh, Anal. Chim. Acta. 610 (2008) 1–14.
[37] H. Bagheri, Z. Ayazi, A. Aghakhani, Anal. Chim. Acta. 683 (2010) 212–220.
[38] A. Alonso, M.A.F. Torroba, M.T. Tena, B. Pons, J. Chromatogr. 57 (2003) 369–378.
[39] C.M.M. Almeida, L. Vilas Boas, J. Environ. Monit. 6 (2004) 80–88.
[40] P. Trefz, S. Kischkel, D. Hein, E.S. James, J.K. Schubert, W. Miekisch, J. Chromatogr. A 1219 (2012) 29–38.