UNIVERSITAT ROVIRA I VIRGILI

DESIGN, FABRICATION AND CHARACTERIZATION OF A GAS PRECONCENTRATOR BASED ON THERMAL PROGRAMMED ADSORPTION/DESORPTION FOR GAS PHASE MICRODETECTION SYSTEMS

Houda Lahlou

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DESIGN, FABRICATION AND CHARACTERIZATION OF A GAS PRECONCENTRATOR BASED ON THERMAL PROGRAMMED ADSORPTION/DESORPTION FOR GAS PHASE MICRODETECTION SYSTEMS

Doctoral Thesis

developed under the supervision of

Pr. Xavier Vilanova Salas
Pr. Xavier Correig Blanchar

Department of Electronic,
Electrical and Automatic Control Engineering

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ROVIRA I VIRGILI

ESCOLA TÈCNICA SUPERIOR D'ENGINYERIA
DEPARTAMENT D'ENGINYERIA ELECTRONICA, ELÈCTRICA I AUTOMÀTICA

Avinguda dels Països Catalans, 26
Campus sescelades
43007 Tarragona
Tel. (977) 55 96 10
Fax (977) 55 96 05
e-mail: secelec@etse.urv.es
http://www.etse.urv.es/DEEEA/

I hereby confirm that this thesis entitled "Design, fabrication and characterization of a gas preconcentrator based on thermal programmed adsorption/desorption for gas phase microdetection systems" presented by Houda Lahlou for being awarded the Doctorate Degree has been conducted under my supervision at the Department of Electronic, Electrical and Automation Engineering of this University and meets the requirements for opting to the European Mention.

Tarragona, the 15 th of April 2011.

Prof. Xavier Vilanova Salas

Prof. Xavier Correig Blanchar

Thesis Supervisors

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Dedicated, with all my love,
to my wonderful sister Loubna,
« Although she deserves much better !!! »

Abstract

Trace detection of volatile organic compounds (VOCs) is an important issue for any analytical system or MEMS based chemical sensor involved in applications such as environmental monitoring. A pre-concentrator placed in front of the detection system can improve its noise to signal ratio and lower its detection limit. Analyte pre-concentration is performed by collecting an analyte over a period of time and then, through a thermal heat pulse applied to the preconcentrator, the collected analytes are released as a concentrated wave into the detector placed at the output, resulting in an improvement of the system sensitivity towards that analyte.

Nowadays, micromachining technology has allowed to fabricate small size, low thermal mass, low dead volume and low power consumption gas detection devices. Miniaturized pre-concentrators are available in different structures from planar to 3D microconcentrators and their low size allows them to be incorporated on the same chip with a detection microsystem. More especially, the planar microhotplate structure could be a simpler fabrication option. However, the concentration factors obtained with this structure are generally lower than 3D based pre-concentrators, because of the lower amount of absorbing material which it could host. This problem could be overcome by choosing a high adsorption capacity adsorbent as well as optimizing the operating conditions of such devices.

In that sense, a high area planar microconcentrator was fabricated in the National Center of Micro-electronics in Bellaterra (CNM-IMB-CSIC). This microfabricated pre-concentrator was conceived for the detection of benzene, a cancerigenic compound at low ppb level which can be found in carbon dioxide used in gaseous beverage production or in air from petrochemical industry stations, automobile exhaust, etc. In this thesis, different carbonaceous adsorbents have been tested towards benzene preconcentration, however, activated carbon has been selected as the most suitable adsorbing material and its deposition was adapted to the microconcentrator design. A characterization technique based on mass spectrometry was set-up during this thesis in order to evaluate the concentration factor of the device and optimize its operating conditions before integrating it in a detection microsystem. The preconcentrator demonstrated a good performance towards benzene preconcentration unaffected by the presence of some current interfering species of benzene such as toluene and butadiene as well as moisture. Finally, the final developed microconcentrator was validated for an application with a micro-detection system including a silicon micro-chromatographic column in front of a metal oxide gas sensor. The operating conditions of the system were optimized step by step and finally the preconcentrator was proven to improve the electrical response and detection limit of the system, allowing a sensitive and selective detection of benzene in presence of butadiene.

Keywords

Activated carbon, Carbon nanotubes, Airbrushing, Benzene, Toluene, 1,3 butadiene, Gas preconcentration, Planar silicon microhotplate membrane, Mass spectrometry, Adsorption interference, Metal oxide gas sensor, Silicon chromatographic microcolumn, Selective detection, Gas detection microsystem.

Resumen

La detección de compuestos orgánicos volátiles (COVs) a nivel de trazas es un importante reto para cualquier sistema de análisis químico o sensor de gas micromecanizado involucrado en aplicaciones tan importantes como el control del medio ambiente. Un preconcentrador colocado delante de un sistema de detección puede mejorar su relación señal/ruido y así rebajar su límite de detección. La preconcentración de un analito se realiza mediante su acumulación en el adsorbente del mismo a temperatura ambiente durante un periodo de tiempo, y después bajo la aplicación de un pulso de temperatura, el analito acumulado se libera con una concentración superior y es arrastrado hacia el detector colocado a la salida del preconcentrador, lo que resulta en una mejora de su sensibilidad hacia ese analito.

Hoy en día, la tecnología de microfabricación ha permitido realizar dispositivos de detección de gas caracterizados por su pequeño tamaño, baja masa térmica, pequeño volumen muerto y bajo consumo de potencia. Los preconcentradores miniaturizados están disponibles tanto en estructuras tipo membranas como en estructuras en tres dimensiones, y su reducido tamaño les permite ser incorporados en el mismo chip con un microsistema de detección. Frente a esta diversidad de estructuras, la estructura "microhtoplate" plana, en particular, podría ser una opción de fabricación más simple, y además ofrece un mejor aislamiento térmico con el resto de unidades del microsistema. Sin embargo, los factores de concentración obtenidos con dicha estructura son generalmente más bajos comparado con la estructura 3D, debido a la menor cantidad de material absorbente que puede alojar. Este problema podría entonces ser superado por la elección de un absorbente con una alta capacidad de adsorción, así como la optimización de las condiciones de funcionamiento del dispositivo.

En ese sentido, un microconcentrador plano de gran superficie fue fabricado en el Centro Nacional de Microelectrónica en Bellaterra (IMB-CNM-CSIC). Este dispositivo fue diseñado para la detección de benceno, un compuesto cancerígeno para un nivel de exposición de ppb y que se puede encontrar como contaminante en el dióxido de carbón utilizado en la producción de las bebidas gaseosas o en el aire de las estaciones de industria petroquímica, el escape de los coches, etc. En la presente tesis, diferentes adsorbentes basados en carbón fueron probados para la preconcentración del benceno pero el carbón activado fue seleccionado como el material adsorbente más adecuado y su deposición fue adaptada al diseño del microconcentrator. Una técnica de caracterización por espectrometría de masas fue puesta a punto en esta tesis con el fin de evaluar el factor de concentración del dispositivo y optimizar sus condiciones de operación antes de su integración en un microsistema de detección. Así,

el preconcentrador demostró una capacidad de preconcentración de benceno bastante prometedora, inafectada por la presencia de interferentes usuales como el tolueno y la humedad. Por último, el microconcentrador final fue validado para una aplicación con un sistema de microdetección que incluye una microcolumna cromatografica acoplada a un sensor basado en oxidos metalicos. Optimizando las condiciones de funcionamiento del sistema, el preconcentrador logró mejorar la respuesta eléctrica y el límite de detección del sistema, lo que permitió una detección sensible y selectiva del benceno en presencia del butadieno.

Resum

Últimament, la detecció de compostos orgànics volàtils a nivell de traces ha sigut un dels majors desafiaments per qualsevol tipus de sistema d'anàlisi química o sensor de gasos micromeanitzat implicat en aplicacions tan importants com es el cas del control del medi ambient. Un preconcentrador col•locat davant un sistema de detecció pot millorar la seva relació senyal/soroll y així baixar el seu límit de detecció. La preconcentració d'un compost es fa mitjançant la seva acumulació a l'adsorbent a temperatura ambient durant un període de temps, y desprès, per aplicació d'un pols de temperatura, el compost concentrat pot alliberar-se del preconcentrador en forma d'una ona concentrada que s'arrossega cap al detector, col•locat a la sortida del preconcentrador. Això fa que es millori considerablement la seva sensibilitat cap al compost d'interès.

Avui en dia, la tecnologia de microfabricació de silici permet realitzar dispositius de detecció de gas miniaturitzats, de baixa massa tèrmica y petit volum mort així com un baix consum d'energia. Aquests preconcentradors microfabricats estan disponibles en diferents estructures que varien entre membranes planes fins a concentradors en tres dimensions (3D). A més a més, la seva petita mida els permet de ser introduïts en el mateix chip amb el microsistema de detecció. Davant aquesta diversitat d'estructures, l'estructura "microhotplate" plana, pot ser una opció de fabricació més simple d'una banda, i d'altre banda, ofereix un millor aïllament tèrmic amb el resta de les unitats del microsistema. No obstant, els factors de concentració obtinguts amb aquest tipus d'estructura queden generalment més baixos que els que s'aconsegueix amb l'estructura 3 D, per causa de la menor quantitat de material absorbent que pot acollir. Es pot superar aquest problema mitjançant la selecció d'un adsorbent d'alta capacitat d'adsorció, així com l'optimització de les condicions de funcionament del dispositiu.

En aquest sentit, un microconcentrador pla de gran superfície va ser fabricat pel Centro Nacional de Microelectrónica a Bellaterra (IMB-CNM-CSIC). Aquest dispositiu va ser dissenyat per la detecció del benzè, un compost cancerigen en exposicions a nivell de ppb, el qual es pot trobar generalment com a contaminant al diòxid de carbó utilitzat durant la producció de les begudes gasoses, a l'aire provinent de les estacions d'indústria petroquímica o bé de les fuites dels cotxes, etc. En la present tesi, diferents adsorbents de carbó van ser provats per la preconcentració del benzè però finalment, el carbó activat va ser seleccionat com a material absorbent més adequat pel benzè i la seva deposició va ser adaptada correctament al disseny del microconcentrador. A més a més, es va posar a punt una tècnica de caracterització pel espectrometria de masses que va permetre d'avaluar el factor de

concentració del dispositiu així com d'optimitzar les condiciones de la seva operació abans d'integrar-lo juntament amb un microsistema de detecció.

El preconcentrador va demostrar una excel•lent capacitat de preconcentració pel benzè, que sembla que no és afectada per la presencia d'uns dels seus interferents més comuns a l'aire, com es el cas del toluè i de la humectat. Per últim, el microconcentrador final va ser validat dins una aplicació amb un microsistema cromatogràphic basat en l'acoblament d'una microcolumna cromatogràfica amb un sensor d'òxid metal·lic. Ajustant les condicions de funcionament del sistema, el preconcentrador va aconseguir millorar la resposta elèctrica i el límit de detecció del sistema, permetent a al final una detecció sensible y selectiva del benzè en una barreja amb el butadiè.

Résumé

La détection des composés organiques volatiles (COVs) constitue un enjeu majeur pour n'importe quel type de système de détection de gaz impliqué dans des applications aussi importantes que le cas du contrôle de l'environnement. Un préconcentrateur placé en amont avec un système de détection peut améliorer le rapport signal/bruit de ce dernier et diminuer sa limite de détection vers le polluant cible. En effet, la préconcentration des polluants se réalise à travers l'accumulation de ceux-ci pendant une durée de temps déterminée pour ensuite les libérer, sous l'effet de l'application d'une impulsion de température au concentrateur, sous forme d'une onde concentrée vers un détecteur placé à la sortie, ce qui contribue à l'amélioration de la réponse du système envers ces polluants.

De nos jours, le développement des technologies de microfabrication a permis de réaliser des dispositifs de détection de gaz miniaturisés, bénéficiant de faible masse thermique, petit volume mort et faible consommation électrique. Ainsi, les microconcentrateurs de gaz existent sous forme plane ou 3D et leur taille réduite leur permet d'être intégrés dans le même chip avec un microsystème. Face à cette diversité de structures, la structure "microhotplate" plane, en particulier, reste une option de fabrication plus simple et offre l'avantage d'une meilleure isolation thermique par rapport au reste des unités du microsystème. Néanmoins, les facteurs de concentrations obtenus avec cette structure s'avèrent généralement plus faibles que ceux que peuvent atteindre les concentrateurs 3D, et ceci est dû à la faible quantité d'adsorbant que peut accueillir cette structure. Cet inconvénient peut être facilement franchi par le choix d'un adsorbant adéquat doté d'une forte capacité d'adsorption vis à vis du polluant cible, d'une part, et l'optimisation des conditions de fonctionnement du dispositif, d'autre part.

Dans ce contexte, un microconcentrateur plan de surface importante fut fabriqué par le Centre National de Microélectronique à Bellaterra (IBM-CNM-CSIC). Ce dispositif fut conçu plus spécialement pour la détection du benzène, un polluant cancérigène à de faibles concentrations en ppb. Celui-ci peut se trouver comme contaminant dans le dioxyde de carbone utilisé lors de la production des boissons gazeuses, mais également dans l'air provenant des raffineries ou des pots d'échappement des voitures, etc. Dans cette thèse, différents adsorbants furent testés envers la préconcentration du benzène, mais finalement le charbon actif fut sélectionné comme étant le matériau adsorbant le plus adéquat et son dépôt fut adapté à la conception du microconcentrateur. En outre, une technique de caractérisation basée sur la spectrométrie de masse fut mise en place en vue de pouvoir évaluer préalablement le facteur de concentration du dispositif, ainsi qu'optimiser les conditions de fonctionnement de celui-ci avant de l'intégrer dans un système de détection.

Le préconcentrateur a ainsi démontré une bonne capacité de préconcentration vis-à-vis du benzène, qui s'est avérée indépendante de la présence d'un de ses interférents les plus communs, comme le toluène et l'humidité. Finalement, l'intérêt du microconcentrateur fut enfin validé dans le cadre d'une application avec un microsystème chromatographique basé sur le couplage d'une microcolonne de silicium placée en amont avec un capteur d'oxyde métallique. En ajustant pas à pas les conditions de fonctionnement du système, le préconcentrateur fut capable d'améliorer considérablement la réponse électrique et la limite de détection du système, ce qui a permis enfin une détection sensible et sélective du benzène en présence du butadiene.

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Introduction

• Gas detection trends and needs for gas pre-concentration

Environmental monitoring has become, in the recent years, more stringent since the society has taken conscience about the importance of the presence of trace contaminants that affect human health and environmental safety. In the framework of environment and human health protection, the level of those contaminants in air must be as low as possible. So, efficient systems are recommended to control the presence of such contaminants in ambient air, especially in industrial spaces, where they may threat employers' health.

Benzene is one of the most studied volatile organic compounds (VOCs) in literature due to its carcinogenic effects at very low concentrations [1]. Occupational exposure to this vapor is likely to occur in air from petrochemical manufactures or stations, from automobile exhaust, etc [2]. Each country, through an environmental quality agency, sets tolerance limits for benzene. For example, in the United States, the threshold tolerance limit for this compound was fixed at 500 ppb in ambient air by the U.S. Environmental Protection Agency [3].

Benzene could also be found as contaminant in CO_2 used for gaseous beverage production such as sodas and beers. In this context, the International Society of Beverage Technologists (ISBT) has defined the quality standards for the CO_2 to be used in this application, defining a threshold limit for benzene in 20 ppb, while other hydrocarbons like methane can be present in concentration up to 30 ppm [2]. These limits are being continuously reviewed to lower levels.

Normally, the detection of benzene could be easily achieved at the ppb level using common analytical laboratory equipments, such as gas chromatographs (GC) coupled with Mass spectrometers (MS), Flame ionization detectors (FID) or Photoionization detectors (PID) [4]. However, their big size and high cost make them impractical for on-line monitoring.

Recently, the increasing needs for both inexpensive and small monitoring devices has suggested miniaturizing analysis systems. It is well known that miniaturization offers functional and economic benefits such as the reduction of sample size, reagent consumption and mass production cost [5]. The first effort work in this field was done by Terry el al. in 1979 [6]. Since then, many works have been carried out. The development of several kinds of microsensors has been reported [7, 8]. Metal oxide films are commonly used as gas sensors due to their high sensitivity to different gases, low production cost, and ease of use [7-10]. The use of multi gas sensor arrays enables the selective detection of different gases in a mixture. Another way to achieve the analysis of complex gas mixture is by using miniaturized analytical equipments such as gas chromatography (GC) microsystems.

Until now, miniaturized gas chromatographs have made the object of a lot of research. They rely on a separation column etched in silicon on which a suitable stationary phase is introduced [11]. These fluidic micro-devices allow separating a wide range of toxic gases and vapors in a mixture before the detection stage [12]. Coupling a microsensor or a micro-sensor array to an upstream separation column has been a good alternative to other classical chromatographic detectors such as Mass spectrometers (MS), Flame ionization (FID) or Photo-ionization detectors (PID) regarding its low cost and easy use.

In general, the term “trace analytes” refers to concentrations below 100 μg/g or 100 ppm and ultra-trace analytes at concentrations below 10 ng/g or 10 ppb [13]. A 1 ppm amount of hydrocarbon in air is equivalent to about 3 ng/mL [14]. Based on the sensitivity of current detectors one needs to introduce at least 10 mL of air to the detector to obtain a measurable signal. A preconcentration step is therefore necessary, in which the captured analytes are being desorbed into a much highly concentrated sample, which results in en enhancement of the detector sensitivity towards the analyte of interest.

The development of pre-concentrator devices was investigated by a lot of research teams [15-18]. In particular, the pre-concentration effect allows ppb level detection for a wide range of chemical compounds. It is envisioned that the sensitivity of a detector or any microdevice can be enhanced by providing on-line pre-concentration [19-20]. And this is the practical aspect behind the work realized during this thesis.

• From conventional to microfabricated pre-concentrators

The pre-concentrator is a support equipped with a heating element. An adsorbing material is deposited on the active area adjacent to the heating element [20]. Ideally, the sorptive material must absorb selectively one or more chemical species of interest over a time period necessary to concentrate the chemical compound in the absorptive material (Fig 1.a). Then, the sorptive layer must be heated with a pulse of temperature for providing narrow desorption peaks with relatively high concentration (Fig 1.b) to the connecting detectors (e.g. gas sensors, electronic nose or conventional analytical detectors such as gas chromatograph/mass spectrometers, etc). This process must allow the analytes present in a large air volume to be purified and concentrated, so increasing the efficiency of detection.

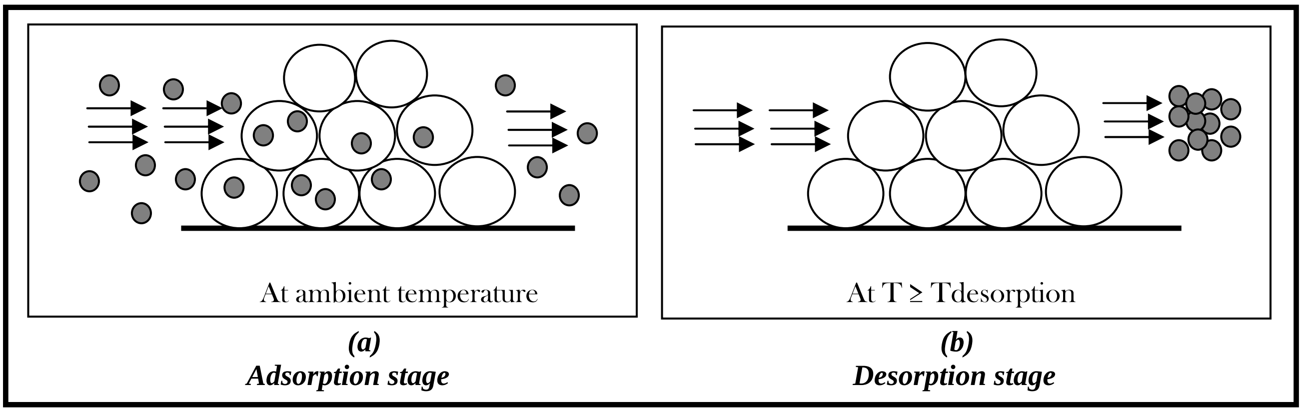

Figure 1: Operating principle of a gas pre-concentrator based on thermal programmed adsorption/desorption

One way to enhance the pre-concentration capacity is to fabricate a device able to host a high amount of adsorbent. Conventional pre-concentrators, so called microtraps, appeared in the 1970 s for air sampling applications [21-23]. They generally comprise a stainless steel or glass-capillary tube, are several centimeters long and have an inner diameter ranging from some few millimeters to 1 centimeter (Fig. 2).

Figure 2: Commercial thermal desorption preconcentration tube from CAMSCO inc., used with permission [31]

These devices are generally packed with one or more granular adsorbing material (such as Carboxen 1000, Carbopack X and carbosieve). A metal wire is enrolled on the tube to enable the heating of the adsorbents during the desorption stage. However, these devices present a high dead volume and limited heating efficiency due to their large thermal mass, which causes the release of a broad-time width pulse of vapor and their cost can reach up to 100 $ per tube [17, 24-31].

Microfabricated technology has allowed the fabrication of low cost and low power consumption miniaturized pre-concentrating devices which provide narrow-time-width pulses for subsequent analysis with miniaturized analytical detection systems [32], especially micro gas chromatographs and MEMS based gas sensors.

• Research motivation

The present thesis was granted by the Spanish research project registered under the reference TEC-2006-03671. The aim of this project is to fabricate a microsystem based on silicon microtechnology integrating a planar micro-concentrator and a gas detector on the same substrate; this design was chosen for its simpler fabrication technology. Concerning the pre-concentrator, a significant heated area was planned to be used for hosting the adsorbent. Thus, for reaching high concentration performances, suitable adsorbing materials have to be selected.

The specific objectives for this thesis, taking as main target analyte benzene, consisted of:

- Selection of a suitable adsorbing material.
- Development of a suitable coating method to cover the micro-concentrator structure with the selected adsorbent.
- Experimental set-up design for the device performance evaluation.
- Demonstration of the utility of the micro-preconcentrator in practical applications in a microsystem.

• Thesis structure

The present thesis is then organized in five chapters:

The first chapter consists of the state of art of the gas micro pre-concentrators based on thermal programmed adsorption/desorption, their role in current micro-detection systems, and the efforts devoted by the scientists for optimizing their efficiency by combining different pre-concentrator support structures with different adsorbing materials. Finally, we will focus on benzene micro-concentration and present some tools to select a suitable adsorbent for the application.

The second chapter will present the first experiments devoted to the selection of a suitable adsorbent for the preconcentration of benzene, including the experimental set-up used for the optimization of the deposition of the different adsorbents, the characterization of their optimal preconcentration conditions and their adsorption capacity towards benzene by means of a mass spectrometer based set-up. Once the best adsorbent is selected and deposited, chapter 3 will deal with the preconcentration tests of benzene in presence of other interferents, such as toluene, including their selective desorption tests and mutual adsorption interference in the selected preconcentrator. The effect of humidity on the preconcentration of benzene will be also addressed. Chapter 4 will deal with the results obtained with the preconcentrator directly coupled with a gas sensor, or used as injector/focuser in front a gas chromatographic column connected to a metal oxide (MOx) gas sensor, and the optimization of the system working parameters for a sensitive and selective analysis of benzene in presence of butadiene. All the experiments presented in previous chapters are performed using a testing self heated support of alumina. Finally, In the last chapter, the development of the final pre-concentrator based on a planar silicon microhotplate membrane will be presented, including the adjustment of the adsorbent deposition technique, the characterization of the preconcentration capacity of the device towards benzene and finally, the validation of its performance for a sensitive and selective detection of benzene in presence of butadiene using a GC microsystem, including a silicon microcolumn connected to a MOx gas sensor, using the optimal parameters already fixed in chapter 4.

By the following, we will review the efforts devoted by scientists in order to improve pre-concentration efficiency, through the fabrication of different pre-concentrating microstructures combined with different adsorbing materials for different applications such as the detection of chemical agents and especially for benzene.

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Chapter 1. Current trends in microfabricated pre-concentrators for gas phase detection

1.1. Gas micro-concentrators role in micro-detection devices

Recently, a micro pre-concentration stage is being introduced in front of gas micro-detection systems in order to decrease their detection limit. In particular, the pre-concentration effect allows ppb level detection for a wide range of chemical compounds [1]. More especially, the microfabrication has allowed the incorporation of the micro-concentrator with the detection analytical systems or MEMS based gas sensors on the same chip. The preconcentrator can perform sample extraction and injection into a single device for on-site analysis without human intervention in the transfer of sample from extraction media to the detector inlet.

Several authors have developed such systems and have implemented integrated prototypes based on the coupling of a concentrator-focuser in front of a micro-column and either a microsensor or a microsensor array [2-4]. These systems have been devoted to the selective analysis of gas phase mixtures at the ppb level. By the following, we will present some examples of such systems.

1.1.1. Micro-concentrators as sampler/injector

The first microsystem that includes a micromachined planar pre-concentrator was designed by the ChemLab at Sandia national laboratories in 1999 [5]. The µchemlab consisted of three microfabricated units: The pre-concentrator, a silicon micro-column and an array of surface acoustic wave sensors [6-11]. The pre-concentrator was based on a thin microporous polymer sol-gel layer spray coated onto a membrane.

In [12], a complete prototype was implemented by incorporating a multi-stage adsorbent pre-concentrator to two coupled separation columns and a microfabricated array of chemiresistive sensors. The response patterns from this array were used in conjunction with the chromatographic retention time to identify successfully elution mixture in just seven minutes.

Other works have been reported on the fabrication and characterization of complete GC miniaturized portable systems based on the coupling between a pre-concentrator, a micromachined column and a gas detector for the analysis of benzene, toluene and xylene, etc [2-4, 11]. However, very few works have been reported on the step by step optimization of the operating conditions of each working unit in the final system.

The primary roles of the preconcentrator in such systems remain improving sensitivity and sample injection; however, preconcentrators also offer opportunities for improved selectivity by providing a selective desorption of the adsorbed compounds.

1.1.2. Micro-concentrators as gas separator

In some cases, temporal separation of vapor mixtures can be obtained by the preconcentrator as different compounds desorb at different rates. In such cases, the preconcentrator is coupled directly with the gas sensor with no need of the chromatographic column.

Park and Zellers demonstrated quantitatively [13], using a porous styrenedivinylbenzene copolymer adsorbent in combination with a SAW sensor array, that the tested vapors desorbed after the initial humidity spike and were independent of the sampled humidity. Grate et al. [14] and Shaffer et al. [15], proposed a mechanism for discriminating DMMP in presence of some volatile organic vapors. While Nakamoto explored preconcentrator approaches that take advantage of different desorption characteristics of vapors and included methods to adjust temperature programming or collection time for autonomous improvements in performance [16-18]. Recently, Morris et al., described a programmed thermal desorption of vapors from a tenax-loaded preconcentrator to a set of semiconductor sensors at a rate of 10ºC/min [19]. It was shown that different vapors desorbed with peak maximums appearing at different times following the onset of heating, and multivariate curve resolution techniques were demonstrated to recover individual vapor response patterns and desorption traces from vapor mixtures.

Thus, there is a considerable interest in using a vapor preconcentrator to impart some chemical selectivity to gas detection devices. Interest in the use of advanced chemometrics with preconcentrator/sensor-array systems, in which the preconcentrator provides partial temporal separation, is evident in the reports by Shaffer et al. and Morris et al. [15, 19]. In each of these studies, the temporal resolution reported was described at only a single thermal ramp rate, which was very fast in the case of Shaffer et al. and very slow in the case of Morris et al.

Then, the sensor array alone is a first order measurement that provides only one vector of data per sample. The additional information content from a second-order system, the preconcentrator, can provide improved selectivity and the potential to quantify analytes in the presence of unknown interferences [20].

The desired operation of a preconcentrator for partial separations is fundamentally different from a preconcentrator used primarily as a preconcentration and injection method. In the latter case, the preconcentrator desorption should be as fast and sharp as possible in order to obtain the tallest detection peaks, and to minimize band broadening due to injection if coupled with a chromatographic step. If pre-separations are desired, however, then the vapors must be desorbed in a way that spreads them out over time [21]. Accordingly, the influence of the thermal ramp rate on the partial separation of vapor mixtures is a factor in the design of a preconcentrator/multivariate detector/advanced-chemometrics instrument.

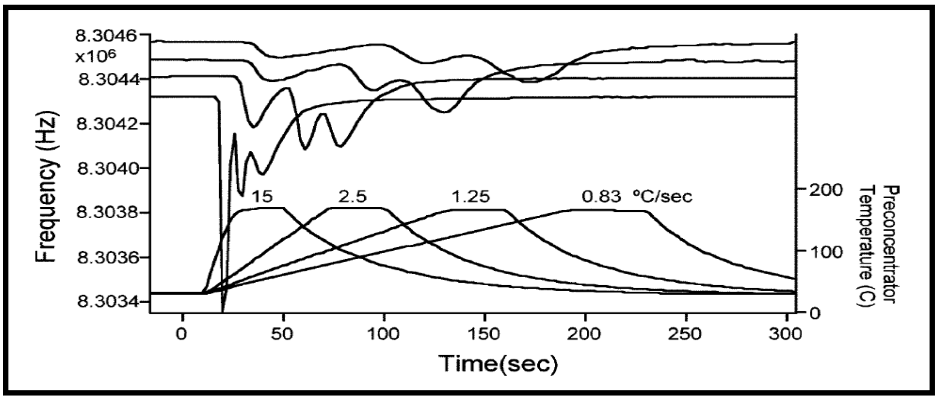

Figure 1: Response profiles for a three-vapor mixture as a function of preconcentrator heating ramp rate, at 10, 60, 120 and 180 s. The vapors are released in the order of MEK, TOL, and DMMP. The traces are offset for clarity [21]

Grate et al., designed a vapor preconcentrator with a porous polymer (Tenax) packed into a highly porous metal foam to facilitate thermal conductivity and temperature uniformity throughout the bed of the preconcentrator during heating [21-22]. Vapors were desorbed using linear temperature programming from room temperature to a maximum temperature of 170 or 200 °C; the programmed duration of the thermal ramp was varied from 10 to 180 s. The partial separation of vapor mixtures that are thermally desorbed from the preconcentrator, has been examined in terms of a metric for resolution, using methyl ethyl ketone (MEK), toluene, and dimethyl methylphosphonate (DMMP) as a test mixture (Fig. 1). Vapors desorbed as a sequence of partially separated overlapping peaks, as observed with a polymer-coated flexural plate wave sensor. It was shown that vapor mixture resolution improved as the total time of the thermal ramp was extended from 30 to 120 s.

In [23], the authors used a multiple-step desorption cycle up to 200ºC in order to separate a mixture of explosives during some few seconds from a porous metallic mesh to a chemical gas sensor. The aim being to build devices with improved performances towards the target application.

1.2. Current advances in pre-concentrator microfabrication technology

Until now, there are few preconcentrators with the advantage of small size, good reliability and low cost which are available in the markets. Researchers are working hard toward the development of devices that can detect analytes with a concentration within the ppb ranges, demonstrated by the huge number of patents present in literature.

In this section, we will review the efforts devoted by the scientists to develop high performance micro-concentrators including the different designed structures. However, it will be difficult to compare the performance of such structures because the authors use different criteria to define it. One of the most common criteria is the "concentration factor" (CF). This parameter has been commonly used as a metric to estimate the performance of preconcentrators, and is defined as the ratio of the concentration of the analyte in the sample delivered to the detector to the concentration originally present in the inlet airflow. However, there is no standard definition for the concentration factor. The most common definition is the concentration of the preconcentrated sample relative to the original concentration [24-31]. Other definitions include sample container volume to desorption volume [32] and breakthrough time difference [33]. It should be noted that CF on its own is ambiguous. This is because the CF depends on the analyte concentration, how long one collects them, and at what flow rate and, thus, is not strictly an intrinsic property of the preconcentrator itself [21].

Due to their low size, the amount of adsorbent to be confined in the microfabricated device is limited. For that, the concentration factors obtained with those devices are generally lower than the ones obtained with the conventional pre-concentrators based on trapping tubes. But there have been other ways to achieve higher collection efficiency with those miniaturized devices [34], by:

- Designing a pre-concentrator with high heated area in order to host a sufficient amount of adsorbent, including big area planar micro-pre-concentrators or 3 D structures with porous silicon, channels or spiral based structures.
- Using multiple pre-concentration stages.
- Choosing an adsorbent with high adsorption capacity and high surface area.
- Or increasing the gas adsorbed volume by optimizing the adsorption pressure or using high adsorption durations. During the desorption process, the dead volumes must be as low as possible for not to dilute the concentrated analyte.

Apart from the high adsorbent capacity, desirable pre-concentrator features include operation at high flow rates, low driving electrical power, uniform thermal heating with short time constants for minimum pulse width during the desorption process and selective sampling towards the analyte of interest [34]. The sorbent layer should, in fact, collect only the analyte and must allow passing its intereferents.

1.2.1. Available gas pre-concentration micro-structures

The main microfabricated structures which were reported include planar hotplate and complex 3 D structures depending on the type of vapors to be detected. Exhaustive overviews about those devices are available in [35-39]. We will present first the preconcentrators based on the planar hotplate structure and then we will move to the 3 D structures.

a. Planar hotplate pre-concentrators

These systems are based on a planar hotplate covered with an adsorbent coating. The reported designs include either hollow structures or hotplate membranes which can be made either from silicon or polyimide. The disadvantage of this type of preconcentrator is the limited area of the hotplate that restricts the collection capability of the device.

Planar micro-concentrators were generally used for the trapping of a single analyte. In this case, the hotplate is covered with a selective coating for to concentrate this specific analyte.

The μchemlab at Sandia National laboratories designed a planar preconcentrator in conjunction with a silicon micro-column and an array of surface acoustic wave sensors [5-11]. The pre-concentrator was based on a thin microporous polymer sol-gel layer spray-coated onto a planar membrane (Fig. 2).

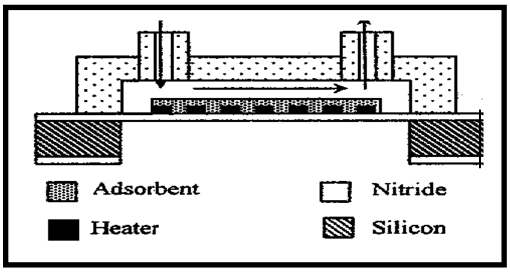

Figure 2: A sectional view of a planar preconcentrator designed by Sandia National Labs [5]

The same laboratory reported in [8-11, 40] the use of a concentrator suspended on a silicon nitride membrane of an area of 2.2. x 2.2 mm^2 and a thickness of 0.5 μm, coated with active carbon which acted as an absorbing material (Fig. 3). The pre-concentrator was coupled to an array of four chemiresistors based on conducting polymers. This system was aimed to measure xylene with a detection limit of 60 ppb [8] and chemical warfare agents (CWA) in a background of diesel fumes [11]. The same preconcentrator was tested with dimethyl methyl phosphonate (DMMP) using a flame ionization detector with low interference to xylene and methyl ethyl ketone. A concentration factor of 510 was achieved by collecting 5 ppm of the analyte over 1 min and desorbing it at 200ºC for 10 ms.

In [41-45], a pre-concentrator was fabricated in a perforated polyimide membrane with a thickness of 6 μm, suspended over a silicon substrate. The device consisted of perforated planar hotplate coated with a polymer (Carbosilane functionalized with hexafluoroisopropanol) based adsorbent using inkjet printing over an active area of 6.65 x 6.56 mm^2 [46-47]. The pre-concentrator was coupled with an ion mass spectrometer for the detection of explosives (DMMP, TNT, etc) [46]. The detector signal enhancement with the pre-concentrator was around 2 order of magnitude thanks to its high active area and to the flow-through hotplate design, which allows an efficient contact of the gas molecules with the adsorbing layer [44].

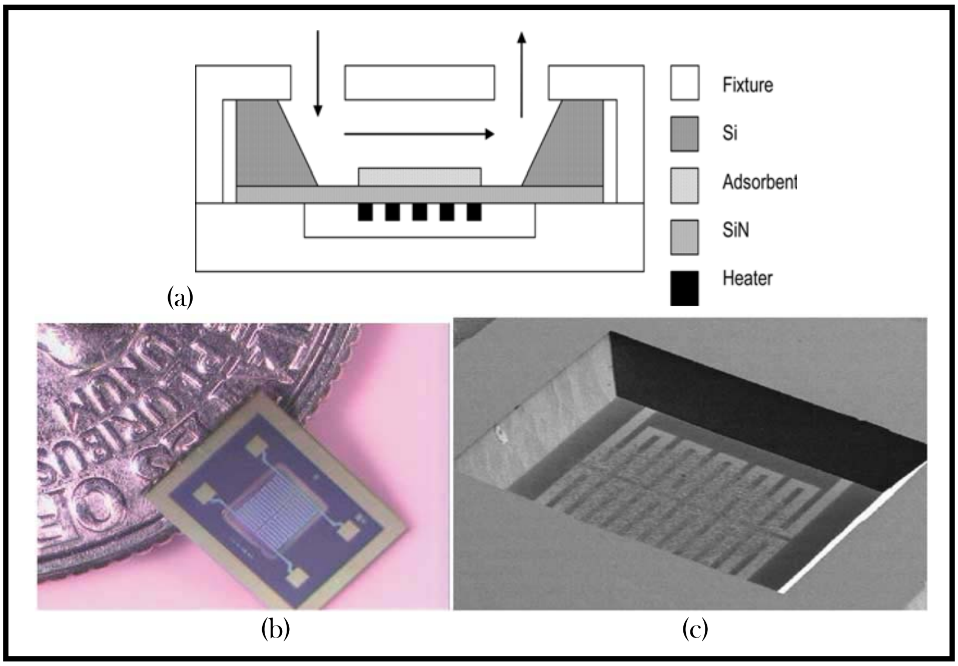

Figure 3: Microfabricated planar preconcentrator (a) Schematic side view (b) Image of the PC against the edge of a U.S. quarter dollar for scale. (b) SEM image of the backside cavity of the PC with a thin circular patch of adsorbing material centered on the membrane [8]

In a recent work [48], the same research team reported the use of a system utilizing a stack of microfabricated preconcentrator plates [42-45] capable of collecting samples in a sorbent polymer at flow rates up to 30 L/min (Fig. 4). A real-time controller and custom electronics were used to manage independent heating of up to 4 of these devices in either constant voltage or temperature modes. The preconcentrators were tested with a commercial Vapor Tracer II ion mobility spectrometer (IMS) against Trinitrotoluene (TNT) and Cyclotrimethylenetrinitramine (RDX) vapors, ranging in concentration from 2.6 ppt to 620 ppt under a variety of conditions. The study concerned the performance of single preconcentrators to RDX, multiple cascaded devices versus TNT and RDX detection and to compare sorbent coated and bare devices. The best results achieved with this system in terms of preconcentration factors were 38 with 2.6 ppt of RDX and 30 with 13 ppt of TNT, using 4 or 3 uncoated stacked pre-concentrators respectively. The collection time was adjusted to 30 sec and the collection flow rates to 5 and 3 L per minute respectively. This demonstrated the preconcentration capability of the bare polyimide structure even in the absence of the adsorbing layer.

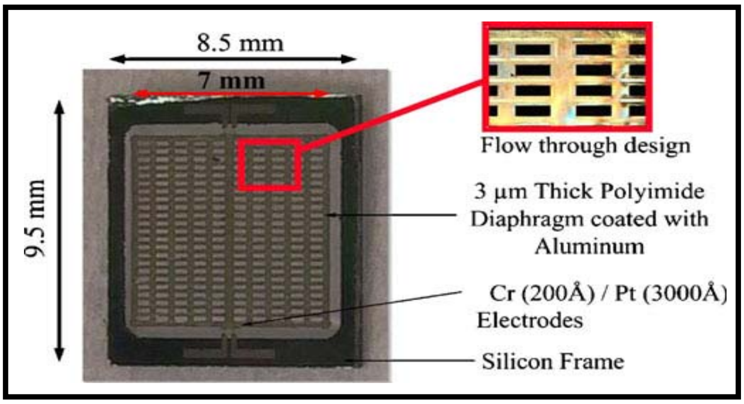

Figure 4: Design of a polyimide based stack of microfabricated preconcentrator plates [48]

A similar system was fabricated on backetched silicon structures using CMOS technology [49]. It consisted of an array of perforated individual micro-hotplate structures coated with the same polymer as before [46-47]. The chip dimensions were 4 x 4 mm^2, while the active area was 3.4 x 3.4 mm^2 [34, 49-50]. The device was tested with DMMP and TNT in front of an IMS detector [34]. The analytes were adsorbed during 1 min and 20 min respectively and released by applying a voltage pulse of 12 V, reaching a concentration factor of 6 and 3 respectively. Lower concentration factors were achieved in this case compared to the polyimide based structure reported before due to the limited dimensions of the CMOS device.

F. Blanco et al. reported a planar pre-concentrator based on activated carbon and commercial Carbopack characterized by a Gas chromatograph/Mass spectrometer (GC/MS) for the detection of benzene [51]. The adsorbing material was stuck on the pre-concentrator support using a layer of tempflex. High concentration factors of about 600 per mg of adsorbent were achieved, collecting the analyte during 5 min at a flow of 200 ml/min and desorbing it at a temperature pulse of 200ºC.

In general, the planar microconcentrators based on silicon and polyimide structures achieve quite acceptable concentration factors and low power consumption. In particular, the hollow-flow-through structure allows an efficient contact of the gas molecules with the adsorbing layer.

In order to further increase the active surface area with a good heating efficiency and low dead volume, a 3 D structure was proposed.

b. 3 D pre-concentrators

3 D structures consist of microcavities etched in silicon wafers using Deep reactive-ion etching (DRIE), which are either packed or coated with the adsorbing layer.

❖ Packed structure

In this case, the structure is based on thick hotplates (> 500 µm) etched in silicon with deep trenches that can hold a large quantity of material and large heating area. The microheaters are surrounded by air-gaps in order to promote the thermal insulation of the microstructure. The adsorbent packing is achieved by filling the µconcentrator manually with adsorbent slurry using a syringe or with the help of pumps at low to moderate pressure. However, the microstructures, fittings, and device packaging usually cannot tolerate the harsh conditions of granular adsorbent packing such as high pressures and the application of ultrasonication which is crucial to achieve good packing density [52].

The hotplate microcavities could be packed with one or multiple stage adsorbents depending on the number and type of targets to be pre-concentrated:

╋ Single stage pre-concentration

Single stage pre-concentrators are preferred for the adsorption of a specific target gas. In this case, the adsorbent is selected so as to have a selective adsorption behavior towards the analyte of interest.

[53-54] reported that the deposition of thin polar or double layers plasma films in microchannels favors adsorption. The use of microchannels modified by 2-propanol or double layer plasma films can be useful for the preconcentration of polar organic compounds in gaseous or liquid mixtures.

The previous technique was reviewed aiming to obtain preconcentrator microstructures. It was demonstrated that the presence of constrictions in the microchannels can be useful for the preconcentration of lower concentrations of non polar compounds such as n-Hexane (C_6H_{14}) [55].

In [28], the preconcentrator was designed to have 16 silicon microchannels (270 µm width, 3 mm long and 540 µm thick for each channel), a symmetrical manifold fluidic system at both inlet and outlet ports, a micro filter at the outlet port to keep the adsorption material inside the channels and a meander shaped platinum heater (Fig 5). The microstructure design was optimized and the pre-concentration conditions for ethylene were characterized. Finally, a concentration factor up to 1000 was achieved by 5.8 mg of Carboxen 1000 and increasing the desorption flow from 10 to 40 sccm.

The sample accumulation was performed during 10 min under an adsorption flow of 165 sccm. The detector used was a photo-ionization detector (PID) system. The whole analyte was desorbed in 1 min.

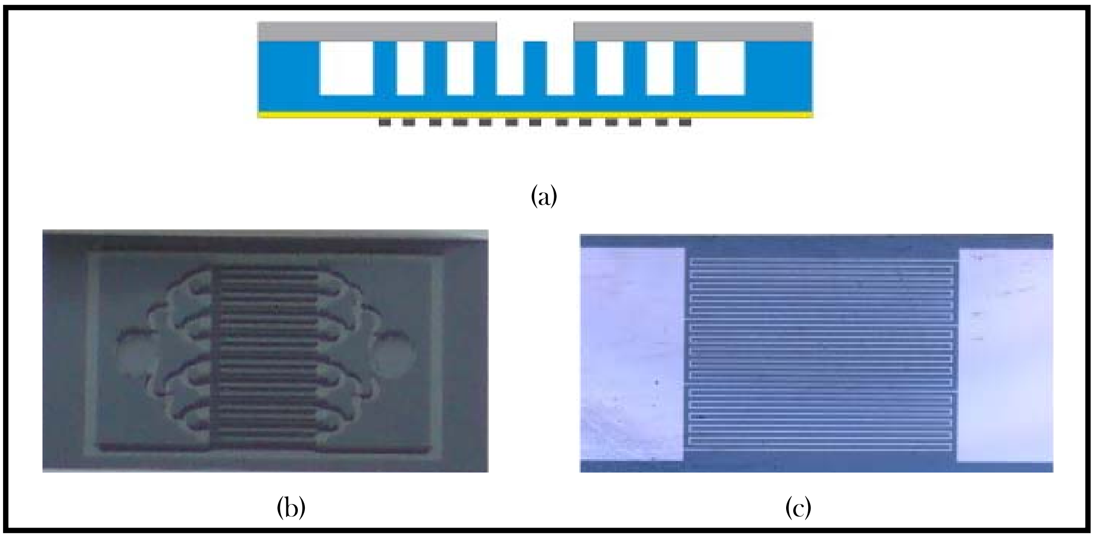

Figure 5: 3D microchannel packed structure (a) side view schematic design (b) Top view image of the device (c) Bottom view [28]

Pijolat et al. presented the development of a gas preconcentrator based on a micro-channel in porous silicon filled with carbon nanopowders by a micro-fluidic process [56-57]. The benefits of using porous silicon was to ease the fixing of the carbon absorbent in the micro-channels and to modify the gas desorption kinetics. Besides, the high specific area offered by porous silicon can be used as an interesting support to increase the quantity of adsorbent materials fixed in the micro-channels when made of this material. The device was tested with a gas sensor for benzene preconcentration. Porous silicon presented in itself a high adsorption capacity of molecules which has been already applied directly to the detection of gases. An adsorption time of 5 min provided a “practical” preconcentration factor of 55.

A pre-concentrator was fabricated by Tian et al. in a silicon microhotplate structure formed by an array of thermally isolated heating elements [58-59]. A wide 500 µm-air gap was created around the microheaters in order to improve the thermal insulation of the device. The microfabricated compartment was 3 x 3 mm^2 filled with 1.8 mg of Carbopack X, sandwiched between two pyrex plates with flow inlet and outlet. The device was characterized by a flame ionization detector (FID) in presence of benzene, m-xylene and α-pinene achieving a concentration factor in the range of 5200-1260 [58]. The device provided a thermal desorption pulse width of 6.5 sec at 3.3 ml/min. For further reducing the pulse width, they implemented a so-called “stop-flow” time into the pre-concentration operation. The idea was to stop the carrier gas flow at the start of the heating cycle to sharpen the desorption profile. A pulse width of 0.8 sec was achieved using a stop-flow time of 25 sec.

- Multiple stage pre-concentration

In order to increase the range of detected vapors, a multiple-stage pre-concentrator was proposed, by providing a larger adsorption capacity to a larger range of compounds with different volatilities. The pre-concentrator consisted of a micro-channel based structure. Each stage comprised a given adsorbent, being compatible with a specific surface area, pore morphology and pore-size distribution, which enables to trap compounds within a specific range of vapor pressures [11, 60-67]. Then, the first stage will trap lower volatility compounds, while the second will collect higher volatility vapors and so one. Higher surface area adsorbents are designed to trap higher volatility vapors, so they are placed in the last stage.

Tian et al. [59, 65] presented an extended volatility range three-stage micro-pre-concentrator (μ-PCF) for micro gas chromatography using three adsorbing materials based on granular carbon including Carbopack B, Carbopack X and Carboxen 1000 (Fig. 6). Significant improvements on heating efficiency and desorption performance were obtained by reducing the dead volume, thermal mass and pressure drop of the planar single-stage μ-PCF [11].

Compounds with vapors in the range of 0.01-29 torr were trapped by 1.6 mg of Carbopack B (with a surface area of 100 m^2/g) in the first stage, while 1 mg of Carbopack X (surface area of 250 m^2/g) was placed in the second stage and trapped vapors in the range of 29- 95 torr. Finally, 0.6 mg of Carboxen 1000 with a higher surface area (1200 m^2/g) was placed in the third stage and allowed to trap compounds with vapor pressures between 95 and 231 torr.

In [59], it was also demonstrated that the faster desorption flow rate and higher desorption temperature are two important factors to improve the performance of the device. This system showed his successful capture, desorption and high-resolution chromatographic separation of a mixture of 30 common organic vapors, whose concentration was in the range of ppb using a FID. The concentration factors were in a range of 5000 to 10000.

A new three-stage cavity microheater [65] was then designed with an integrated temperature and flow rate sensors. Quantitative capture of 29 ppb of the highly volatile vapors as acetone was achieved. This preconcentrator was also proved to be capable to act as an injector into a gas chromatograph by thermal desorption of 20 ppb-L of acetone, trichloroethylene and n-decane at 300ºC.

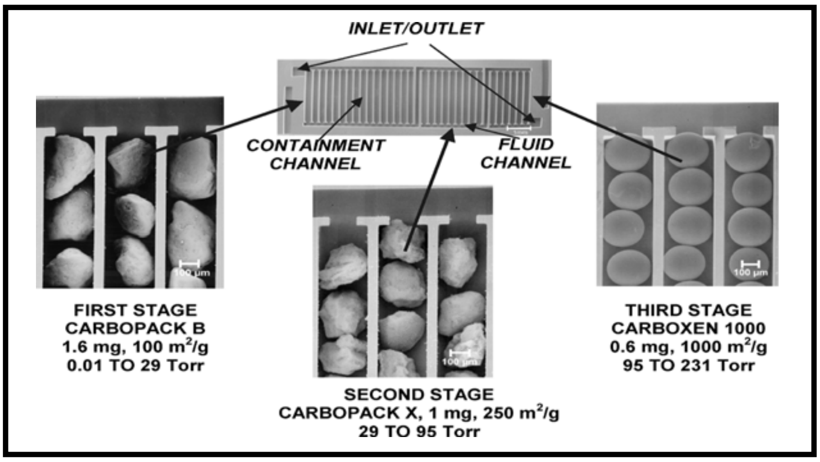

Figure 6: Three-stage microfabricated preconcentrator-focuser using thick microheater packed with three carbon adsorbents to cover a wide range of compound volatilities [63].

More recently, Sukaew et al. [68], reported the development of multi-stage preconcentrator/focuser module designed to enable trace level determination of trichloroethylene (TCE) in the sub-ppb level. This module consisted of three adsorbent-packed devices arranged in series: a pre-trap of conventional (tubular metal) design for capturing interferences with vapor pressures <3 torr; a high-volume sampler, also of conventional design, for capturing (and transferring) TCE and other compounds with vapor pressures within the range of 3 to 95 torr; and a microfocuser (µF) consisting of a micromachined Si chamber with an integrated microheater for focusing and injecting samples into the separation module, made of a conventional downstream capillary column and electron-capture detector. This assembled preconcentrating module was designed to be integrated with a microfabricated gas chromatograph (mGC) to detect selectively trichloroethylene in the presence of common indoor air co-contaminants in residences at risk of vapor intrusion (VI) from surrounding TCE-contaminated soil. A preconcentration factor of $8.\ 10^5$ was achieved from a 20 L air sample.

Effectively, the multiple stage hotplate based structure, when combined with a high adsorption capacity adsorbent, allows increasing significantly the concentration factor and enables the detection of a wide range of complex vapors, compared to the single stage pre-concentrator. The disadvantage of this type of devices is their high power consumption and the complexity of their fabrication technique.

On the other hand, coated µPCs consist of microchannels covered with a thin film of adsorbing material. The coating is done either by spin coating [67], plasma deposition [69], inkjet printing [34], electroplating [70], or conventional methods used to coat chromatographic open tubular capillary columns [71]. However, thin films have limited adsorption capacity and may be susceptible to degradation related to low surface adhesion and/or thermal instability.

- Microcavity based structure

A 3D structure was fabricated using Bosch DRIE etching process [11]. The Si structure is suspended on the central part of the membrane. Nanoporous carbons, sol gels and commercial packing materials were used as adsorbents and tested towards DMMP [11]. Inlet Parallel flow (Fig 7. a) shows a better performance than perpendicular flow configuration (Fig. 7 b). However, the 3 D structure with perpendicular flow was able to achieve a temperature of 200ºC with only 150 mW, by comparison to the parallel flow 3 D which consumed 0.6 W in the same conditions. While the planar configuration consumed only 100 mW to achieve the same desorption temperature.

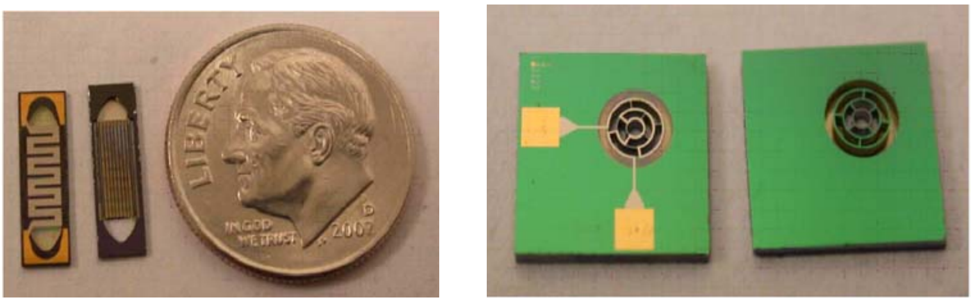
(a) (b)

Figure 7: 3 D preconcentrators fabricated by Sandia National laboratories with (a) Parallel flow and (b) Perpendicular flow [11]

In a recent work, the same authors reported the fabrication of a tortuous path chemical preconcentrator [72]. The tortuosity provided repeated twists, turns and bends to the flow, thereby increasing the interfacial contact between sample fluid steam and the adsorptive material. Also, the thermal efficiency of this structure was comparable or superior to the prior non planar chemical preconcentrator structure.

An interesting work was reported by Markowitz et al, presenting a cascade sorbent plate array preconcentrator consisting of a series of stacked thin membrane hotplate, each with a coating of a sorbent material [73]. Template directed molecular imprinting was used to functionalize the organosilica sorbent with surface active molecules of a structure similar to that of the targeted analyte, during the synthesis process, which acted as molecular recognition sites in its surface. The preconcentrator was tested towards 0.0010 mg/m^3 of DMMP, by adsorbing it during 5 min at a flow of 500 ml/min and desorbing it at 180ºC for 3 sec. The preconcentrator showed significant enhancement of the detector to DMMP when compared to the signal with no preconcentration step.

Other designs were reported by [74-76]. They embedded a "zig-zag" micro-structure in a microcavity. However, it was difficult to achieve uniform and full coverage coating on such structures due to the channeling of the coating solution in the cavity.

More recently, Camara et al. proposed a different design based on "Straight" micro-channels (Fig. 8) [77]. Four different adsorbing materials were compared including tenax TA, activated nanocarbon powder, single (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). SWCNTs were finally chosen as the adequate adsorbent for the preconcentration of benzene because of their high specific area and adsorption capacity and their low desorption temperature.

Figure 8: Schematic top view of the "Neutral", "Straight" and "Zigzag" designs [77].

Other 3 D structures consisted of embedded high-aspect ratio three-dimensional (3D) micro pillars coated with an adsorbent polymer. The silicon-glass die had outer dimensions of 7 mm × 7 mm, total inner surface area of 10 m^2/g, and a total inner volume of 6.5 µL. The micro-concentrator had on-chip thermal desorption capability and comprised more than 3500 micropillars with dimensions of 30 µm × 120 µm × 240 µm (Fig. 9) [37, 78]. Other 3D structures were proposed in [38] and [79].

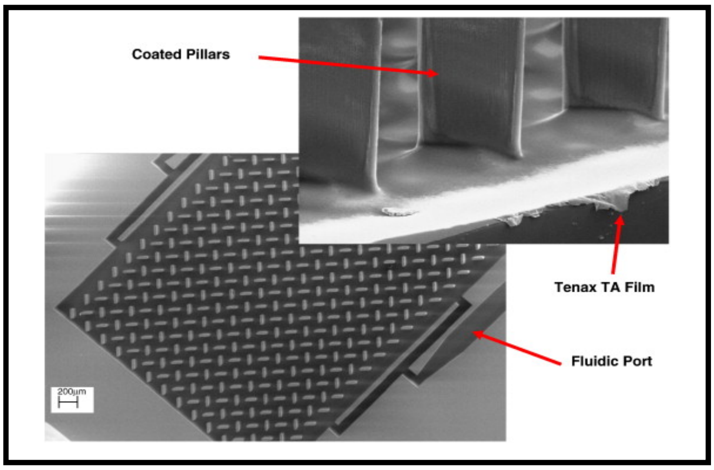

Figure 9: SEM micrograph showing the structure of the µPC. Inset shows the uniformity of the inkjet coating of Tenax TA [78]

In [79], a 3 D microchannel pre-concentrator with an array of microposts was developed. With an input power of 12 W, the micro-concentrator could reach 250°C within 100 ms, consuming only 1.2 J of energy. The device coated with high-surface-area metal organic framework (MOF) molecules was integrated into a microfluidic detector to enhance the overall detection limit of a trace concentration of a toxic vapor stimulant (e.g. isopropylsulfonylchloride). A sharp increase in the electrochemical potential from the micro-detector was observed upon heating of the micro-concentrator with a 3 s pulse.

Finally, an original work was reported on the use of a microchannel based structure coverage covered with electroplated gold layer which served at the same time as heating and adsorbing material [70, 80]. The high porosity of the gold layer maximized the adsorbent surface area and allowed to reach high concentration factors of about 6000 towards methanol over 1-propanol and acetone with an accumulation time of about 15 min using a FID detector.

Other designs are then proposed for the analysis of complex vapors which allow to further increase the collection area while minimizing power consumption, including spiral shaped channel based structures. These elements are designed for to be integrated with GC system.

- Spiral shaped channel structure

In this case, the structure is based on a serpentine microchannel DRIE etched in silicon with a thin heating layer deposited on the top.

In [67], a pre-concentrator with spiral structure was fabricated. The heating layer consisted of aluminum protected with a spin-on-glass layer. A polymer adsorbing material was deposited on the channels by spin coating and covered with a quartz plate. This device was tested with a FID towards a mixture of benzene, toluene and ethyl benzene (BTEX) at the ppm level, achieving a concentration factor of 14.

Figure 10: Schematic view of the fabricated spiral micro-concentrator [81]

Blanco et al. proposed a spiral-shaped configuration with a 10-cm length, and a width/depth of 300 μm. The Pt heater was defined in a pyrex substrate which was anodically sealed to the silicon substrate. Carbopack X was used as adsorbent (Fig. 10). Concentration factors using a GC/MS system were up to 300 and were achieved at an adsorption flow rate of 35 sccm during 25 min. The pre-concentrator allowed enhancing the response of tin oxide gas sensors by up to 5 times [81-82].

So, in general, the coated pre-concentrator structure provides high active area and achieves high concentration factors. However, the packed structure present much higher concentration factors due to the higher yield of adsorbing material which can be hosted by such structure.

b. Summary

In general, the 3D pre-concentrator allows holding higher amount of material compared to the planar structure which allows slowing the breakthrough of the pre-concentrator. This structure is useful for the trapping of low volatile compounds that are put in closer contact with the adsorbent, by contrary to the case of planar configuration. However, the fabrication technology of the planar structure is simpler, the thermal isolation is better and the power consumption is generally much lower.

In next section, we will summary the results reported in literature on the special case of benzene, as it is the main target analyte in the current thesis.

1.3. Micro-pre-concentration of benzene

1.3.1. Available structures

Table 2 below summarizes the micro-preconcentrating structures of benzene available in literature. As could be observed from the table, the majority of pre-concentrators used for benzene pre-concentration are based on the 3 D structure; only 2 planar structures have been reported towards the pre-concentration of this compound [9, 51]. This vapor was either analyzed alone, with commercial analytical equipments such GC/MS, GC/FID or PID, or in presence of toluene, xylene and ethylbenzene (BTEX), which are its main interferents in air, using silicon micro-columns connected to sensors or detectors to achieve the separation of the mixture. It was also analyzed in presence of explosive agents such as DMMP. Good concentration capability was achieved for benzene with either planar or 3 D structures. In general, the best results were achieved with carbonaceous adsorbents such as Carbopacks, activated carbon and SWCNTs compared to polymer based adsorbents such as tenax and OV17, etc. However, very few works have been reported on the optimization of the pre-concentration conditions of this vapor, especially before the pre-concentrator coupling with GC micro-columns [51, 77, 83]. Blanco et al. reported a work about the optimization of the flow distribution in a preconcentrator made up of a grid of suspended silicon bars [58]. The silicon grid allowed holding a large amount of adsorbent (Carbopack X) and provided efficient heat diffusion with less than 600 mW at a working temperature of 250°C. The authors showed that by optimizing the gas-flow through the device, the preconcentration factor can be increased by 85%, without increasing the complexity of the adsorption system.

Table 2: Summary of benzene microconcentration conditions reported in literature

µPC structure	**Front end unit**	**Adsorbing material**	**Analyte**	**Working conditions**	**CF**	**Power consumption**	**[Ref] (Year)**
Silicon Micro-cartridge ($25*12*1.3$ mm^3)	Silicon µ-column (50 cm*0.8 mm^2) +4 Mox sensor array	Quinoxaline-bridged Cavitand (QxCav)	0.1 ppb BTEX	Adsorption 55 min at 50 sccm Desorption 5 min at 100ºC for 5-30 sec	NS	NS	[2-4] (2003-2009)
Microfabricated planar hotplate	Spiral µcolumn (1 m-long, 40 µm thick and 300 µm deep walls) + 4-SAW detectors	Microporous oxide	BTX and CWA agents	Adsorption for 40 sec Desorption at 200ºC	>100	105 mW (200ºC)	[9] (1999)
Spiral structure with heated channel of (450 µm-wide 300 µm-deep, 16 cm-long)	GC/FID	Polymer OV17 Deposited by Spin coating	BTEX/N_2 at ppm level	Adsorption at 7 ml/min Desorption 120ºC for 1-3 sec	14	NS	[67] (2003)
3 x 3 mm^2 microfabricated compartment with wide 500 µm-air gap around the microheaters with packed adsorbent (Dead volume=8.16 µL)	GC/FID	1 stage: 1.8 mg of Carbopack X sandwiched between two pyrex plates	benzene, m-xylene and α-pinene	Desorption at 3.3 ml/min	5600	2.1 W (300ºC)	[59] (2003)
Fluid flow channels structure: 220 µm wide and 3000 µm long (Dead volume= 2.62 µL per stage)		3-stage: 1 mg of Carbopack X +1.6 mg Carbopack B +0.6 mg Carboxen 1000	100 ppb of 30 vapor mixture (Benzene, toluene, etc)	Adsorption at 25 cm^3/min during 10 min Desorption at 2 cm^3/min at 300ºC for 40 sec	> 5600	0.8 W per stage (250ºC)	[59, 65] (2003, 2005

3 mm × 3 mm silicon suspended microgrid with 40 µm-wide, 3000 µm-long bars 230 µm-spaced Packed with the adsorbent	GC/MS	390 µg of Carbopack X	150 ppb benzene/CO_2	Adsorption at 300 sccm For 10 min Desorption at 250ºC for 30 sec	20	< 600 mW (250ºC)	[82] (2007)
	MOx microsensors	270 µg of Carbopack X		Adsorption at 100 ml/min for 10 min and desorption at 100 ml/min and 250ºC for 30 sec	3		
3D straight microchannel on porous silicon with an area of 20 mm × 10 mm with 325 µm-deep inlets and outlets, with channels 120 µm-deep and 50 µm-wide walls	Micro-PID analyzer	0.30 mg of commercial activated charcoal deposited by fluidic deposition process	1.3 ppm of benzene/ dry air	Adsorption for 11 h until breakthrough at 2.4 min Desorption at 160ºC	NS	NS	[56] (2007)
1cm^2 Alumina substrate with screen printed Pt heater	GC/MS	2.4 mg of Carbopack X	150 ppb benzene/CO_2	Adsorption at 200 ml/min for 60 min Desorption at 100 ml/min at 250ºC for 5 min	150	NS	[51] (2008)
		Three different activated carbon: 0.3-1.3 mg Stuck by tempflex			240-800		
Spiral configuration (10-cm long, and 300 µm wide and deep)	GS/MS	400 µg of Carbopack X	150 ppb benzene/CO_2	35 sccm during 25 min Desorption: 30 sec at 200ºC	311	3 W (200ºC)	[81] (2008)
	Pure and doped WO_3 sensors				5		
	Pure and doped SnO_2 sensors				8 and 11		
1 mm x 3 mm of suspended silicon microgrid structure with 400 µm-wide, 3000 µm-long and 230 µm-spaced bars	GC/MS	270 µg of Carbopack X	150 ppb benzene /CO_2	Adsorption at 200 ml/min for 60 min Desorption at 250ºC during 30 sec	32	< 600 mW (250ºC)	[83] (2008)

Porous silicon zigzag microchannel (325 µm-deep with a total area of 10 mm*15 mm)	Micro-PID Analyzer .	Nanporous Carbon	250 ppb Benzene/Dry air	Adsorption flow of 10 L/h for 5 min Desorption for 5 min at 2L/h and heating at 160ºC/min	36	NS	[77] (2009)
		SWCNTs Deposited by fluidic process			16		
Porous silicon with zigzag microchannel (325 deep channels with a total area of 10 mm*15 mm)	TGS 2620 from figaro	0.83 mg of activated Carbon nanopowder	250 ppb benzene/air	Adsorption at 167 ml/min for 5 min Desorption at 200ºC at 5ºC/min	64	NS	[57] (2010)
Microcavity (array of parabolic reflectors within a 7 mm x 7 mm x 0.38 mm cavity with a middle spacing of 100 µm and a side spacing of 250 µm)	Commercial FID	Tenax TA deposited by Inkjet printing	$2.5\ 10^9$ µg/ml of benzene/N_2	Adsorption at 1 ml/min at 35ºC until breakthrough. Desorption: At 100ºC/sec to 250ºC	NS	NS	[78] (2010)
Porous silicon With zigzag microchannel (325-deep channels with a total area of 10 mm*15 mm)	PID analyzer	1 mg of adsorbent deposited by fluidic process Nanporous Carbon	250 ppb Benzene in Dry air and 50 % humid air	Adsorption at 167 ml/min for 5 min Desorption for 5 min At 200ºC	Around 36 (16 in humid air)	NS	[84] (2011)
		SWCNTS		At 240ºC	Around 16 (14 in Humid air)		

NS: Not stated;

BTEX: Benzene, Toluene, Ethylbenzene, Xylene.

Due to its simpler fabrication technology, the planar structure could be used for the fabrication of the pre-concentrator. Despite its lower concentration factors, this structure presents the advantage of low power consumption, a better thermal insulation of the pre-concentrator with the rest of the microsystem and a narrower desorption pulse.

The preconcentration capability of this type of structure could be optimized by selecting the right adsorbent with a high adsorption capacity, as well as optimizing the experimental adsorption and desorption conditions.

By the following, we will present some key tools to choose the right adsorbent for the preconcentration in general, and for the specific case of benzene in particular. The adsorption properties of those adsorbents will be compared with a special focus on carbonaceous materials which were demonstrated to be the best for benzene trapping.

1.3.2. Available adsorbents

The fundamental mechanism behind preconcentration in this research is physical adsorption, or physisorption. Physisorption is due to weak, intermolecular non specific and specific forces between the gaseous phase, called the adsorbate, and the solid surface, termed the adsorbent. During extraction at room temperature, the adsorbent takes up the adsorbate because physisorption is a spontaneous, exothermic process; during injection, the adsorbate flies off the adsorbent because the high thermal desorption temperature imparts kinetic energy to the adsorbates to escape the adsorbent [85]. However, this temperature must be adjusted so as not to cause a thermal decomposition of the target analyte.

When selecting the preferred adsorbent for a particular application, one must consider a wide range of physical and chemical properties of both the adsorbent as well as the analytes to be trapped and analyzed.

Breakthrough volume and the desorption efficiency are important characteristics of a concentrator. So, the ideal sorbent would have large breakthrough volume for the very volatile compounds, while providing rapid quantitative desorption of the larger molecules [86].

The breakthrough volume has also been referred to as retention volume and also the specific retention volume. This parameter is defined as the calculated volume of carrier gas per gram of adsorbent which causes the analyte molecules to migrate through the adsorbent at a specific temperature. The units of breakthrough volume are usually expressed as liters/ gram. For a quick and easy selection of an adsorbent for a specific analyte, manufacturer's tables of breakthrough volumes at different temperatures are referenced [87]. This data is necessary for the practical use of commercial adsorbents and the determination of the appropriate flow rates and temperature for the trapping of analytes in the adsorption process as well as their thermal extraction during the desorption process.

There are several parameters which may distort or alter the breakthrough volume [86]:

- ➢ The effect of water has been investigated by several authors. Indeed, if water condensates out of the gas phase, it can saturate the adsorbent and lend it useless for adsorption. So, a dry purge stage is usually added to reduce the relative humidity of the gas.
- ➢ The breakthrough volume can be also affected by the velocity of the gas during sampling. So, the result of excessive flow rate will be lower the breakthrough volume. This is because the analyte will be flying through the adsorbent at rates which do not permit it to react with the pores of the adsorbent.
- ➢ It was also demonstrated that the breakthrough volume can decrease as the temperature of the adsorbent is increased.

So, an ideal adsorbent, must have [88]:

- Large breakthrough volume towards the analyte of interest.
- Low affinity to water, for not to fasten its breakthrough.
- Low desorption temperature to avoid the thermal degradation of the analytes but also to ensure a low power consumption of the device.
- Complete desorption with fast kinetics for further rapid analysis.
- Good thermal and mechanical stability and multiple usability to avoid drift with time.
- Tuneable physico-chemical adsorption properties for adjusting its selectivity towards the analyte of interest. The selectivity of the adsorbent could be achieved, by:
  - ➢ Using microsieve based adsorbents, which act as mechanical filter allowing to pass only the analyte with a given molecular size, such as carbon molecular sieves or zeolites.
  - ➢ Playing with the affinity of the adsorbent towards a given adsorbate. For example, hydrophobic adsorbents will prefer non polar gas molecules, while the hydrophilic will attract the polar ones.
  - ➢ Combining different adsorbing materials with different affinities to different compounds.
  - ➢ Tuning the adsorption properties of the material either through the functionalization of its surface with some functional groups able to interact specifically with a given gas species

(e.g. O_2 functionalized carbon nanotubes for methane adsorption) or the activation of its porous structure for trapping a specific gas molecules (e.g. activated carbon towards VOCs)

The table 3 [89] bellow sheds some light on choosing the right adsorbent by demonstrating the relative differences [87] between those most commonly used in the literature. The main ones [90] are: the surface area and the porous structure of the adsorbent in one hand and the hydrophobicity and solubility of the analytes in another hand.

Table 3: Properties of some common adsorbing materials [89]

Material class	Type	Properties	Application
Graphitized Carbon	Carbopack Carbotrap	No porous, hydrophobic, Variable size of particles. High recuperation of the analytes. Good thermal Stability.	Organic substances, air contaminants
Carbon Molecular Sieves		Specific surface area: 5-100 m^2/g, porous, Hydrophobic	Specific adsorption depending on the pore form and size
	Carboxen	The specific surface area: 400-500 m^2/g	Small molecules at high humidity
	Carbosieve III	Specific surface area: 820 m^2/g, Defined pores:1.5-4 nm	High breakthrough volume
Active Carbon		Specific Surface area :1100m^2/g Thermally stable, Less hydrophobic, Polar groups	High ebullition points. High adsorption capacity
Porous polymers, Synthetic resin	Tenax TA	Polymeric oxide, stable until 350ºC, Specific surface of 35 m^2/g, Low polar affinity (H_2O). hydrophobic	Volatile and semi volatile substances, No polar HC,C_5-C_{12} in air
	Tenax GR	30% graphite	High breakthrough Volume, C_5-C_{12} in air
Polymers	PDMS	Polydimethylsiloxane (no polar), polyaminopropyl- Methyl-siloxane (polar), PCPMS (polar)	Polar and semi-volatile Substances, high molecular mass
Inorganic adsorbent: Silica gel	Porasil	Surface<750 m^2/g	Polar analytes

Different adsorbents have been reported in literature. The main adsorbents are inorganic oxide powders [2, 4, 91], polymeric materials (PDMS, etc) [69, 92] and carbon-based particles [40]. Yet the corresponding concentration factors for benzene are still lower than those obtained with commercial carbon particles [93]. In the latter case, the concentration factors can reach values near 1000 using about tens of milligrams of adsorbent [94]. Furthermore, activated carbon was found to be a very efficient adsorbent, especially for benzene: even with very small amounts of adsorbent (lower than 1 mg), high concentration factors between 10^2 and 10^3 are obtained [51].

Because their surfaces are nonpolar or weakly polar, carbonaceous adsorbents are the best in terms of preferential adsorption of nonpolar adsorbates [95-96], as it is the case for benzene.

1.3.3. Carbonaceous materials applied to benzene pre-concentration

Generally, carbonaceous adsorbents are as diverse in pore structure and adsorptive properties as their biomass and synthetic precursors: wood, peat, coal, coconut shells, polymers, etc. The major categories are [88, 97]:

Graphitized carbon black (GCB) (such as Carbopack and Carbotrap), carbon molecular sieves (CMS) (such as Carboxen and Carbosieve), activated carbon and carbon nanotubes. The former are macroporous (width > 50 nm) and for benzene, being a small molecule, narrower pores are more preferable for its retention. Carbon molecular sieves are microporous but are known for their incomplete recovery of some compounds such as 1,3-butadiene.

For that, next section will be limited to the review of the adsorption properties of activated carbon and carbon nanotubes for benzene.

a. Activated carbon (AC):

ACs are microporous, amorphous carbons which were treated to open a enormous number of their pores, so-called, activation. Activation is indeed the process by which the porosity of a carbonaceous material is both open and developed, leading to sometimes extremely high surface areas [98-99]. Usually, the higher is the surface area of the adsorbent, the higher is the adsorption capacity; however, for activated carbons, it was shown that the adsorption performances are more closely related to pore-size distribution than to surface area [51].

Such materials comprise very narrow pores that are the most suitable for the retention of small molecules in the gas phase such as benzene (Fig.11) [100]. The possibility of adjusting the pore structure of carbons through the adjustment of activation parameters can be a key in designing optimized adsorbents. Thus, the concentration factors obtained for benzene with lab-made activated carbons are expected to be higher than those obtained with commercial carbons having much wider pores and much lower surface areas.

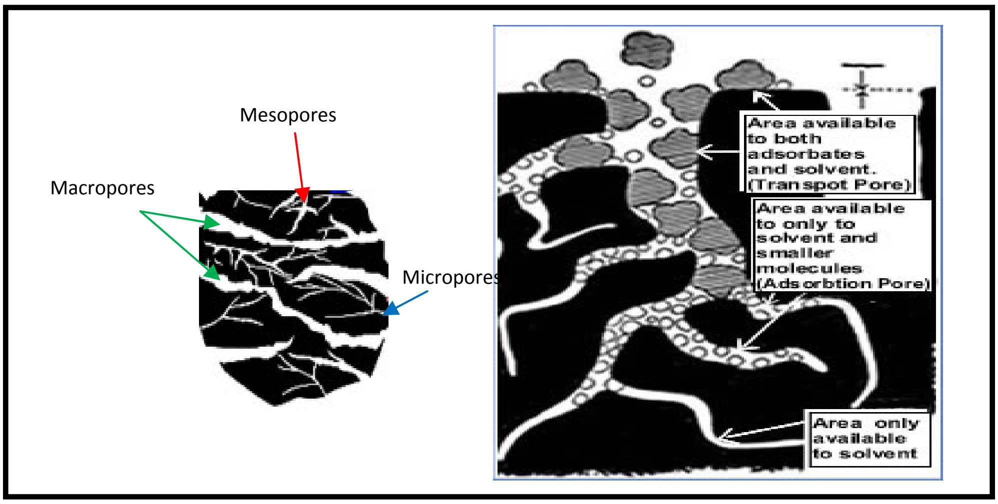

Figure 11: Activated carbon grain with different available porosities [100]

However, there are still gaps in our understanding of gas-to-particle partitioning in most carbon adsorbing materials because they are essentially structureless and have complex physicochemical properties. Moreover, their porous structure introduces mass transfer limitations, slowing both adsorption and desorption [97, 101].

In this context, due to its crystalline well-defined porous graphite-like structure, carbon nanotubes (CNTs), by contrast to activated carbon, can provide a better understanding of the relationships between sorption potential and carbon structures. Therefore the adsorption of organic vapors on CNTs is an important issue for both theoretical study and environmental applications [102-103].

b. Carbon nanotubes (CNTs):

CNTs consist of a graphene layer rolled coaxially into cylinders of nanometric diameter and can be classified into single-walled (0.4-3 nm) and multiwalled (1-100 nm) carbon nanotubes (Fig. 12). The latter presents additional concentric cylinders of carbon [104]. Double walled carbon nanotubes are the special case of multiwalled carbon nanotubes with two coaxial tubes.

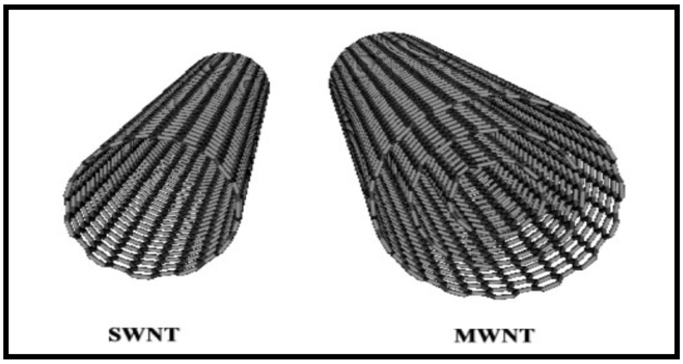

Figure 12: Molecular structures of carbon nanotubes: MWCNTs and SWCNTs [104]

Recently, CNTs have been studied as promising materials for the storage of hydrogen [105], the adsorption of methane [106] as well as the removal of volatile organic compounds from air streams [107] and polyaromatic compounds from aqueous solutions [108], etc. CNTs, moreover their excellent thermal, mechanical and electronic properties, present small diameter, narrow pore size distribution and high surface area, which can reach from 150 m^2/g to 3000 m^2/g [102]. The excellent features of CNTs, along with their nano-scale features, make them ideal candidates for micro-scale devices, such as microconcentrators. Different authors have reported the use of CNTs as adsorbing layers for gas pre-concentration [25, 106, 109-115]. An extensive review about the microconcentrating units based on CNTs is available in [116].

In the case of benzene, very few works have been reported on the use of CNTs for its pre-concentration [76-78]. However, very promising results indicating that CNTs can be used as adsorbents for benzene have been reported [102-103, 117]. For example, theoretical works have predicted the physical adsorption of this molecule on different sites within the CNTs by Van der Walls forces, through π-π interaction between the two rings of benzene and the nanotube. The adsorption of benzene can then occur in (Fig. 13): the grooves, the interstitial sites, the internal pores and the external wall of the CNTs (or CNT bundles) [118].

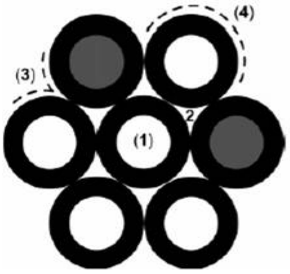

Figure 13: Different adsorption sites on a homogeneous bundle of partially open-ended SWNTs: (1) internal, (2) interstitial channel, (3) external groove site, and (4) external surface [118].

Different studies have been conducted to systematically compare adsorptive interactions between CNTs and benzene with significantly different physical chemical properties (e.g., polarity, functional groups, etc.) [102, 119-125]. In addition to the effect of surface chemical nature of the CNTs, other parameters can simultaneously affect their adsorption properties towards gases such as nanotube's shape [102], size [126], morphology, and also surface impurities (e.g., metal, amorphous carbon, etc) [120]. Therefore, research is still needed for a better understanding of the molecular interactions of CNTs and organic contaminants with different properties.

1.3.4. Summary

Different adsorbents have been proposed as adsorbing materials for gas pre-concentration. In the case of benzene, being a non polar molecular, carbonaceous materials seem to be good candidates for its preconcentration, especially CNTs and activated carbon which have tuneable adsorption properties for designing a benzene selective pre-concentrator.

1.4. Conclusion

- A look into the literature allowed us to evaluate the interest which has been devoted to the development of cycled pre-concentrating structures. A lot of advancements have been made to miniaturize those devices for incorporating them in detection micro-devices, where they played the role of either an injection or a separation unit.

- The majority of works have been focused on the monitoring of explosive agents such dimethylphosphonate (DMMP), using either 3 D or planar structures.

- For the special case of benzene, the planar structure seems to match between simple fabrication technology, low power consumption and better thermal insulation, which is a challenge for mass production. This structure suffers from size limitation compared to 3 D structures. However, this could be overcome by selecting the right adsorbent for benzene. Some selection tools and suggestions have been derived from literature.

- The planar structure will be then adopted for the fabrication of the final pre-concentrator developed for the current thesis. Activated carbon and carbon nanotubes will be tested as adsorbing material for the preconcentration of benzene. This choice is driven by the following considerations:

- Preferential adsorption of nonpolar adsorbates (e.g. benzene) over water (which exists in indoor air) → carbon
- Weak adsorption (for low desorption energy requirements) → physisorption
- Rapid adsorption/desorption kinetics → granular form
- Good thermal stability up to 400ºC with repeated regeneration
- Tuneable adsorption properties towards the selective adsorption of benzene:

Through activation in the case of activated carbon (or using different grain sizes, or different precursors) and through surface functionalization in the case of CNTs (or playing with CNTs structure, shape, etc)

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Chapter 2. Adsorbent deposition technique and adsorption capacity characterization

The selection of the adsorbent is the first important step for the development of the pre-concentrator. In this thesis, activated carbon and carbon nanotubes have been selected as possible adsorbents for benzene. Their pre-concentration capability towards this vapor will be checked and compared in this chapter.

In literature, the preconcentration performance is usually checked by coupling directly the preconcentrator with a gas sensor system. In our case, a characterization technique for the preconcentrator has been proposed and set-up. By this way, the pre-concentrator could be developed in optimal conditions and its characteristics could be known prior to couple it with any micro-detection device, which is on its self a quite complicated system, for example:

- ✓ The thermo-desorption response of benzene induced by application of a heat pulse could be monitored with time.
- ✓ The pre-concentration capability of the pre-concentrator could be optimized and quantified.
- ✓ The suitable adsorbent could be selected by comparing the pre-concentration capability of different adsorbents tested in the same conditions.

In our case, this technique used a standard analytical equipment which is the mass spectrometer. This equipment was selected for his many advantages over other kind of detectors which will be presented later.

2.1. Mass spectrometry characterization

2.1.1. Experimental Set-up

A characterization circuit has been designed including the analyte injection system, the pre-concentrator and the mass spectrometer "MS" (Fig. 1) [1]. A description of each unit is presented below:

a. <u>The GC/MS equipment</u>

A GC/MS Schimadzu instrument was used. It consists of coupling a gas chromatograph (GC-17A) and a mass spectrometer equipped with a quadrupole (QP5000). Helium with a purity of 99.9 % (Carburos Metalicos, SA) was used as sample carrier gas.

In the gas chromatograph "GC", the column is coated or packed with a stationary phase allowing to separate different compounds on the basis of the column temperature and inlet pressure. After chromatographic separation, sample molecules are ionized inside an ionization source. The quadrupole mass analyzer (QP5000) separates these molecular ions and their charged fragments according to their mass to charge ratio (m/z). Finally the ion current due to these mass-separated ions is detected by an electron multiplier detector, and displayed in the form of a mass spectrum. Each of these steps is carried out under high vacuum.

The equipment parameters are controlled through a software installed in a personal computer.

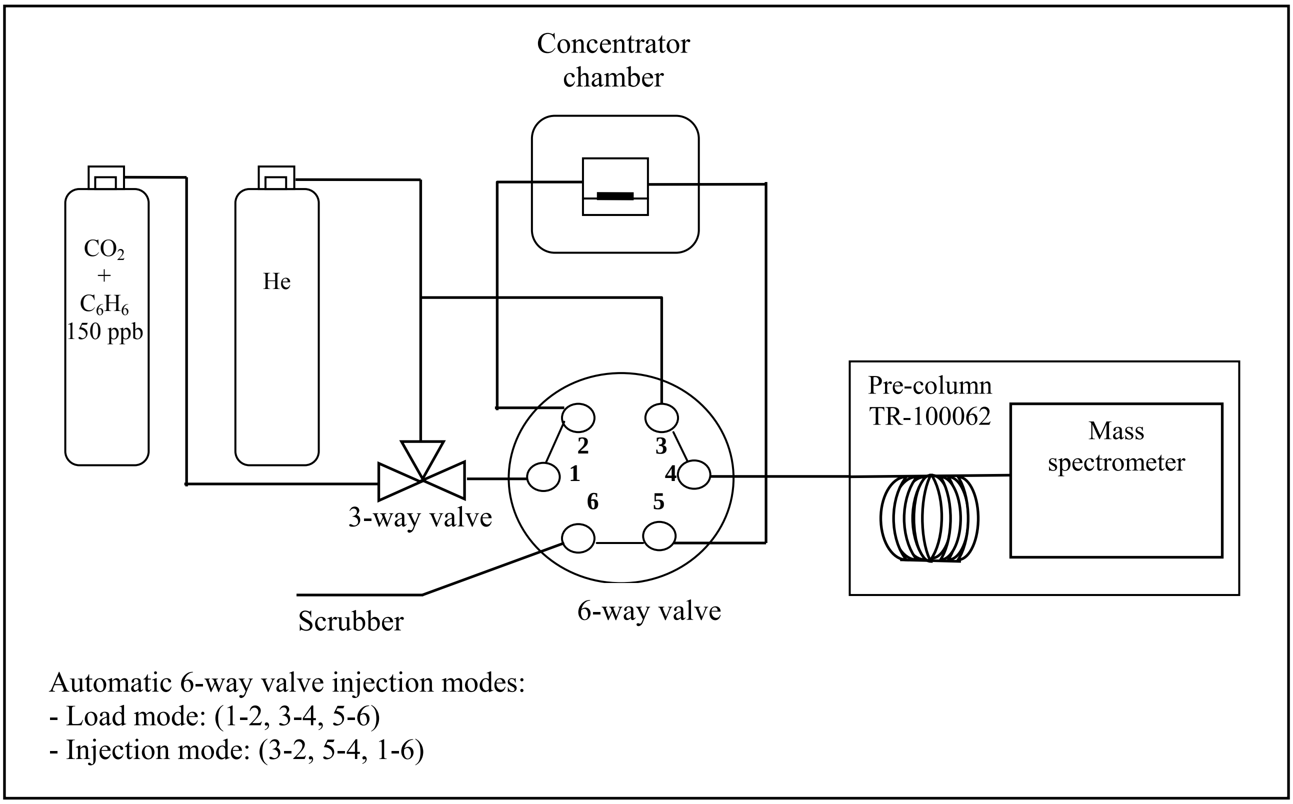


Figure 1: Description scheme of the mass spectrometry characterization circuit of the pre-concentrator

We have at first opted for the Gas chromatography/Mass spectrometry technique for analyzing the pre-concentrator response, because this technique is of high resolution and has the advantage of quantifying the volume desorbed from the concentrator, as was previously reported [2]. However, we will not be able for example to study the selective desorption of a mixture from the pre-concentrator because in this case, it's not possible to know whether the compounds are separated by the pre-concentrator or by the GC column. For that, the GC column of the equipment was replaced by a deactivated pre-column. This pre-column is free of filler material and only works as a transfer line between the injection port and the mass spectrometer.

The main advantage of mass spectrometry over other kind of detectors, such as flame ionization or photoionization detectors is its ability to identify selectively the gaseous species in a mixture without need for the GC column.

The equipment is coupled to a six-way valve (Valco Instruments Co. Inc.) that allows gas injection, the injection mode and time being automatically controlled by software. This can work either in load mode or in injection mode (Fig. 2).

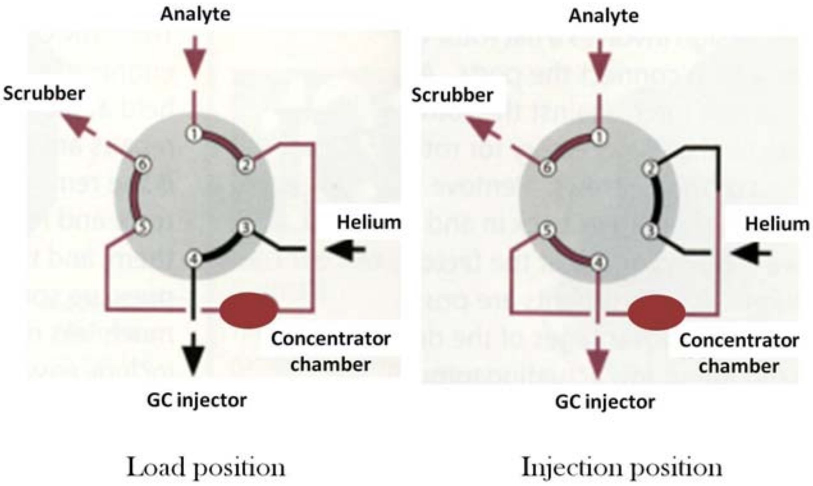


Figure 2: Six-way valve injection modes

<u>b. The gas pre-concentrator</u>: To perform the first trials of adsorbent deposition and selection, and optimize the pre-concentration parameters, a testing support based on a self heated 1 cm^2 planar alumina substrate is used [2]. More details about the fabrication of the substrate and the thermo-electrical characterization of the heater can be found in "Annex 1".

The pre-concentrator is housed in a teflon hermetic chamber containing electrical contacts for heating the concentrator and hence inducing thermal desorption (cf. Annex I). The teflon chamber is available in two configurations: the initial design where the gas flow is laminar, and a second design where a teflon thin wall was placed inside the internal volume of the chamber, perpendicularly to the gas inlet, forcing the gas to get closer contact with the adsorbing layer. A schematic descriptive view of the gas chamber with both designs is available in Annex I.

c. <u>Analyte injection system:</u> One of the important applications of our pre-concentrator is the detection of benzene present as traces (a few tens of ppb) in carbon dioxide used in carbonated beverages. The first characterization tests are made using calibrated cylinders of benzene balanced in carbon dioxide (Carburos Metalicos S.A.) connected to the characterization circuit through the six-way valve. The flow of the analyte is then controlled by a flow controller system connected at the cylinder outlet.

2.1.2. Characterization steps

The characterization of the pre-concentrator includes three main steps: the system purge, the adsorption and desorption cycles:

- The system purge: A purge is performed by commutating the six-way valve to the "injection" position and passing helium at 100 ml/min through the system. The pre-concentrator is heated in parallel at 250ºC during 10 min in order to desorb any contaminants which it would have adsorbed before.
- The absorption cycle: After the purge of the system, the adsorption procedure started. The six-way valve is commutated from the "injection" to the "load" position. Thus, the analyte from the calibrated cylinder is injected at a given flow rate and duration to the pre-concentrator kept at room temperature and then goes away through the scrubber.
- The desorption cycle: At the end of the adsorption stage, a desorption step is initiated by commutating the valve to the injection position. The analyte flow is stopped after the valve commutation to ensure that the whole proportion of the analyte is passed to the pre-concentrator and not to the scrubber.

During this cycle, the analyte coming from the concentrator chamber is carried out by helium at a fixed flow, then dispatched towards the MS inlet and analyzed. The concentrator heating starts 0.5 min after the injection starts. By this way, the residual analyte remaining in the concentrator chamber is injected first. Then the concentrator is heated for a sufficient time until all the analyte is released by the adsorbent. After the desorption cycle, the pre-concentrator is left to cool at ambient temperature during 10 min to initiate a new adsorption cycle.

2.1.3. Evaluation and quantification of pre-concentrator response

The MS response to benzene appeared as the peak corresponding to the characteristic mass of benzene: $m/z = 78$. This peak represents the variation of the spectrum intensity expressed in "counts" versus acquisition time. The number of counts is related to the number of the fragments with $m/z = 78$ and it gives us then information about the amount of benzene detected by the mass spectrometer with time.

- Concentration factor “CF”

The pre-concentration capacity of the pre-concentrator is estimated in our case on the basis of a “concentration factor”. But it’s not so easy to define this parameter since, for a given preconcentrator, the “amplification” of the concentration is closely related to the duration of the gas adsorption phase, the flow rates during adsorption and desorption phases, and the heating rate, etc. However, we will measure a “practical” concentration factor, which we defined as the ratio between the concentration of the desorbed analyte from the pre-concentrator and the initial concentration of the cylinder. If a perfect linear relationship between peak area and analyte concentration is obtained by the MS in the range of the concentrations studied, the pre-concentration factor will be then defined as the ratio of integrated areas of the desorbed analyte from the concentrator divided by the reference peak area from the gas cylinder concentration.

- Reference peak “Blank”

The reference peak, so-called “Blank” is calculated by averaging the bottle blank measured before and after the desorption. Each blank corresponds to the benzene concentration inside the cylinder, and is quantified by replacing the concentrator by an alumina substrate free of adsorbent. The preconcentrator chamber is then filled with the content of benzene coming from the bottle by flowing benzene at 100 mL min^{-1} during 4 min. This volume is then injected to the mass spectrometer, resulting in a peak equivalent to the initial concentration of the bottle.

Such quantification procedure using the “concentration factor” is correct whatever is the benzene concentration within the range of concentrations in which the MS response is linear.

- System Calibration procedure

In order to estimate this range of concentrations, a calibration of the MS response is performed. The reference peaks at different concentrations of benzene are made by injecting the content of different calibrated cylinders of 20, 70, 150, 1000 and 10000 ppb balanced with CO_2. The calibration curve of the MS towards benzene is then plotted as the integrated areas of the reference peaks versus the concentration of benzene (Fig. 3).

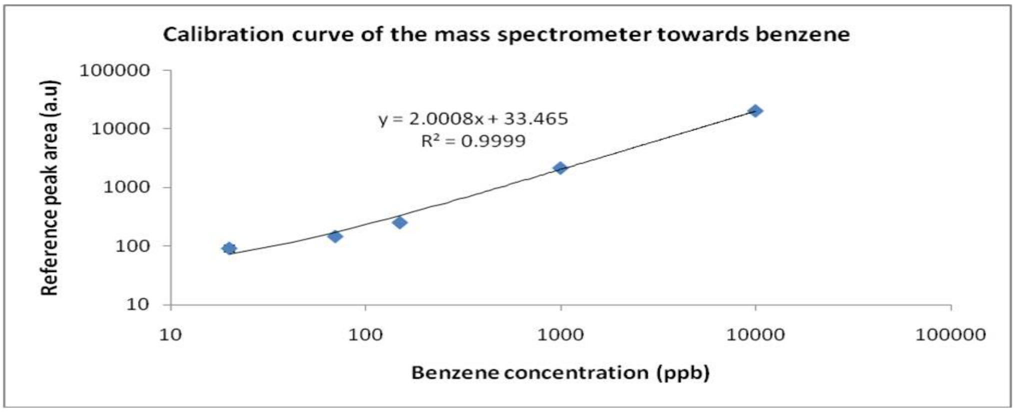


Figure 3: Calibration curve of the mass spectrometer towards benzene

As can be seen, the system is perfectly linear in this concentration range.

- Breakthrough measurements

In order to estimate the maximum adsorption capacity of the adsorbents, breakthrough measurements of benzene (of known concentrations in CO_2) and flowing throughout the pre-concentrators can be carried out. These measurements consisted in keeping the adsorption flow at a fixed value and increasing adsorption time until adsorbent saturation occurred. These measurements are made using three cylinders of benzene balanced with CO_2: 150, 1000 and 10000 ppb. They required long time and high amounts of sample; this is the reason why the study will not be performed for all the adsorbents but will only focus on the final selected material, which is the one exhibiting the highest adsorption capacity toward benzene.

2.1.4. Optimization of pre-concentration conditions

a. Selection of MS working conditions

Different experiments were performed to adjust the working parameters of the MS without affecting its response stability. In order not to saturate the MS, split injection mode is adopted. In this case, only a fraction of the analyte coming from the pre-concentrator is being injected to the column, the remaining portion is evacuated by a purge fan. This portion is called the “Split ratio” and is estimated as the ratio of the pre-column flow by the total flow of the pre-concentrated sample.

This is not a limitation for the determination of the pre-concentration factor, because the desorbed analyte as well as the reference analyte are analyzed in the same conditions. So, the pre-concentration factor, being a ratio of integrated area of both peaks, will be independent from the split ratio.

A 30-m long pre-column (TR-100062) operating at 1 ml/min was selected so as to avoid an overpressure (> 1 Pa) inside the vacuum chamber of the MS, which caused a drift of its sensitivity with time. The temperature of the column was then set at 80ºC. The detection temperature was set to 250ºC and data acquisition was performed each 0.5 sec.

b. Optimization of adsorption/desorption conditions

As mentioned before, the pre-concentration capability of the pre-concentrator will depend mainly on the adsorption and desorption conditions: including adsorption flow and time, desorption flow and temperature. We will study the effect of each one of these parameters on the concentration factor of benzene. For these experiments, the MS parameters were fixed as before, a pre-concentrator based on activated carbon deposited on an alumina substrate is used and a cylinder of 150 ppb of benzene balanced with CO_2 as testing analyte. These experiments are made using the two configurations of the pre-concentrator chamber, presented in Annex I.

- Selection of optimal pre-concentrator chamber design
    - ❖ Effect of adsorption conditions

As we know, in order to have high concentration factors, a high volume of gas must be adsorbed by the concentrator. For that, we can use high adsorption time or high adsorption flow. To study the effect of the adsorption flow on the concentration factor of our pre-concentrator, we fixed the adsorbed volume to 200 ml and then we tested different adsorption flows: 20, 100 and 150 ml/min corresponding to adsorption durations of: 10, 2 and 1.33 min, respectively. The desorption flow was kept constant at 20 ml/min during this experiment and the column flow at 1 ml/min. These experiments were repeated with the two configurations of the chamber: with and without wall, and were compared.

Figure 4 presents an example of the desorption peaks obtained at different adsorption flow rates for the initial configuration of the chamber, without wall, while Figure 5 shows the variation of the concentration factor of benzene normalized per milligram of adsorbent versus the adsorption flow, for both configurations.

From these figures, we could see that in both chamber configurations, a lower adsorption flow results in a higher concentration factor and this is due to the configuration of the gas entrance. In fact, in the initial design of the concentrator chamber, the flow entrance is laminar, thus it seems difficult for the gas to get in contact with the adsorbent. The lower is the flow, the lower is the gas velocity. So, the vapor has more time to diffuse in the adsorbent pores, which results in a higher adsorption capacity for benzene. The same explanation is valid for the second chamber design, however it could be observed that the concentration factors obtained with the second design are higher. In this case, the presence of the wall inside the concentrator chamber, forces the vapor to get in closer contact with the adsorbing layer, which results in a higher adsorption capacity towards benzene.

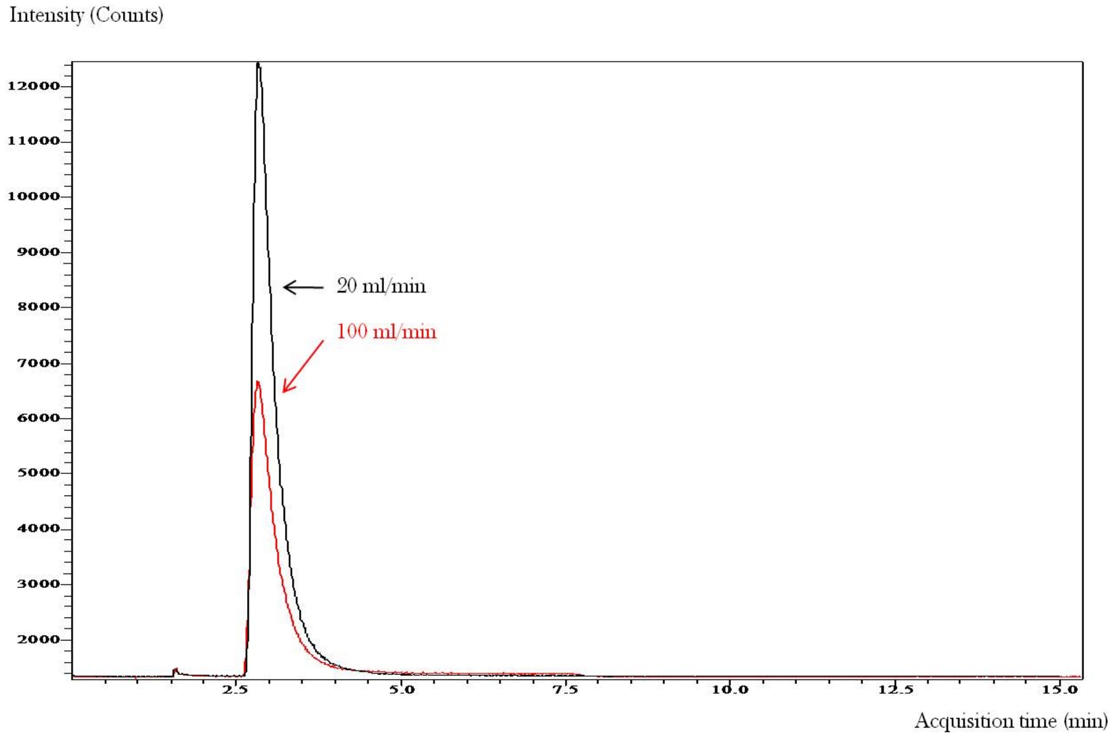


Figure 4: Desorption peaks of benzene at different adsorption flow rates

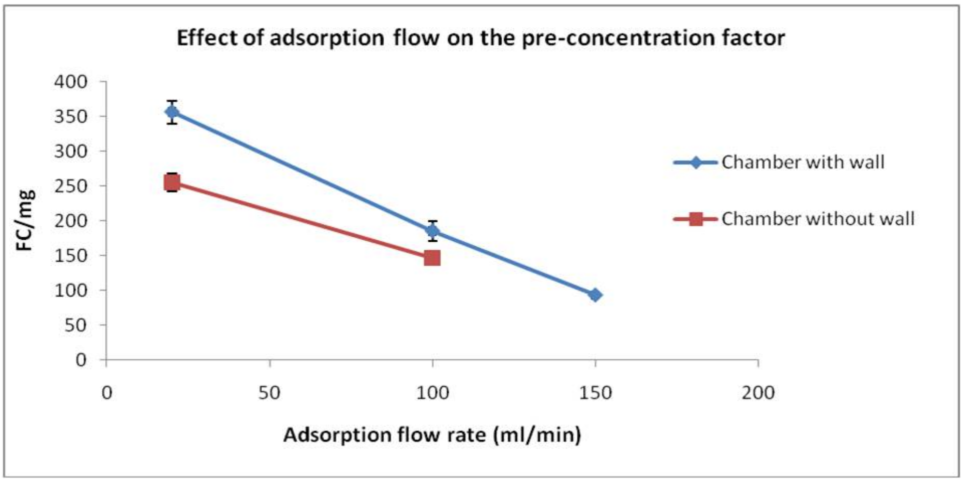


Figure 5: Effect of adsorption flow on the concentration factor of benzene

- Effect of desorption flow

To study the effect of desorption flow, the adsorption flow and time were fixed to 20 ml/min and 10 min respectively. Desorption flows of 100 ml/min and 50 ml/min were tested. However, in order to keep the split ratio the same, the pre-column flow was adjusted at 1 ml/min and 0.5 ml/min respectively.

Figure 6 shows the variation of the concentration factor of benzene normalized per milligram of adsorbent versus the desorption flow, for both chamber configurations.

From this figure, we could see that for both configurations of the chamber, the change of the desorption flow rate doesn't seem to affect significantly the pre-concentrator desorption efficiency. Another time, the concentration factors obtained with the second design are higher due to the more efficient adsorption and desorption provided by the presence of the wall inside the chamber.

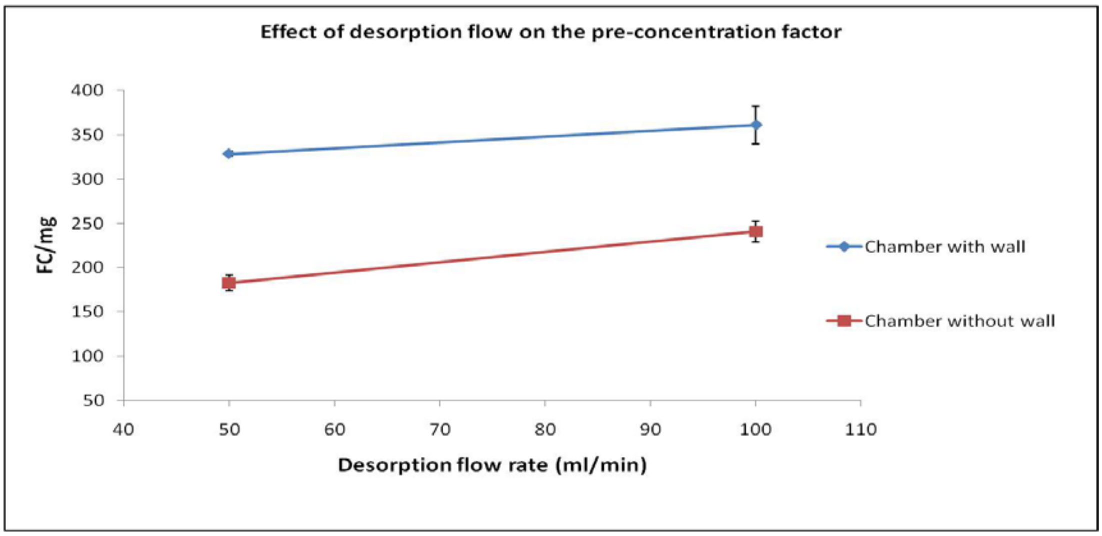


Figure 6: Effect of desorption flow on the concentration factor of benzene

- Selection of optimal fluidic conditions

In real application, it will be more practical to use short operation cycles of no more than 15 min. Also, to simplify the operation of the system, it will be more convenient to use a same flow rate for adsorption as well as for desorption. In our case, taking in account the previous approach, we will try to optimize the pre-concentrator operation for an adsorption time fixed at 10 min. For that we will compare the concentration factors obtained with flow rates of 50 and 100 ml/min.

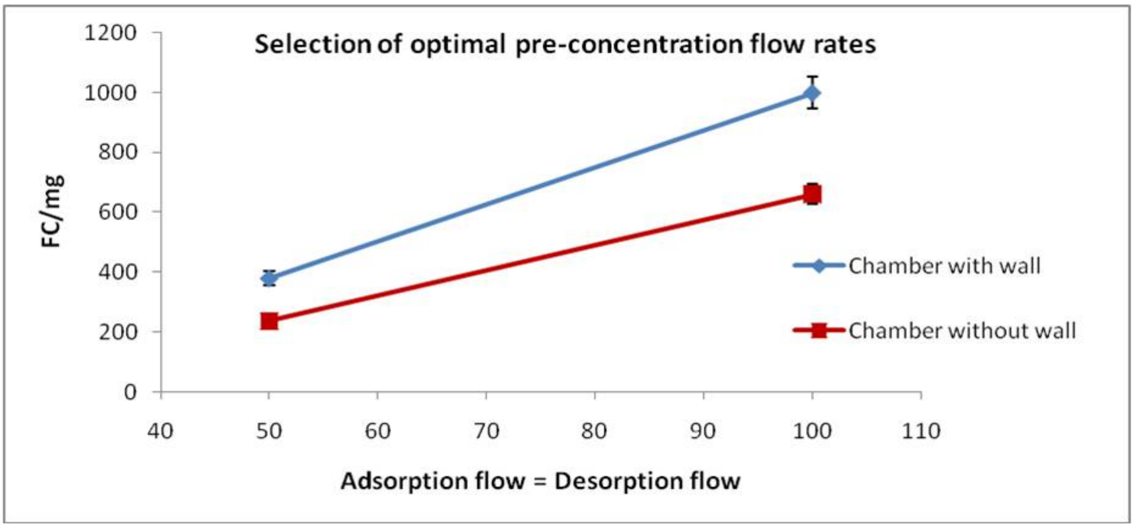


Figure 7: Effect of pre-concentration flow rate on the concentration factor of benzene

From figure 7, we could see that higher is the flow rate, higher is the concentration factor. The best results are then obtained with the second configuration of the pre-concentrator chamber (with wall) [3]. Experimentally, the pre-concentration factor to benzene is improved by a factor of about 1.5 compared to the initial design without wall.

- Selection of desorption temperature

Once the optimal chamber design was fixed (Second design), the optimal adsorption, desorption flow rates and adsorption duration were determined, these conditions will be maintained for studying the effect of the desorption temperature on the desorption profile and for determining the optimal temperature for the efficient desorption of benzene. The desorption temperature will depend on the type of adsorbent to be used. Each adsorbent has special desorption characteristics towards benzene.
In order to evaluate the time needed for a complete desorption of thus vapor at each desorption temperature, we subject the pre-concentrator to the heating during a maximum duration of 15 min at a given desorption profile, we perform a cooling of the pre-concentrator during 5 min and then we perform another heating cycle during 5 min at high pulse temperature, to check if it remains any residual benzene inside the pre-concentrator after the first desorption cycle.

2.2. Adsorbent deposition and adsorption capacity

Activated carbon and carbon nanotubes with different characteristics are tested in this chapter towards the pre-concentration of benzene [1]. For achieving a good adsorption capacity, it's important to select a suitable technique for depositing those materials over the pre-concentrator support. Some first deposition trials have been conducted to deposit a powder of activated carbon over the alumina substrate using conventional techniques such as screen printing, drop-coating or sticking the materials over the support using a commercial glue [2]. However, in all these cases, either a poor adherence of the material onto the support or a bad homogeneity was obtained. As alternative, air-brushing was found to overcome the limitations of the above techniques.

- General description of the air-brushing technique

This method consists in preparing a suspension of the adsorbent powder in a suitable dispersing solvent with an adequate weight ratio. The suspension is then subjected to sonication (Ultrasonic MEDI-II, 40 kHz, SELECTA) at room temperature during 15 min. Then poured in a spraying nozzle container (Fig. 8). The spraying nozzle has a gas inlet connected to N_2. When the spraying trigger is activated, the suspension is pushed by the N_2 flow at a given pressure and pulverized, while the pre-concentrator substrate is heated in parallel by means of a hotplate (Agimatic-E, SELECTA) equipped with a temperature controller (EKT HEICON, Heidolph). The temperature is adjusted so as to evaporate completely the dispersing solvent. In our case, the extent of the deposited area is limited to 16 mm^2 using a shadow mask.

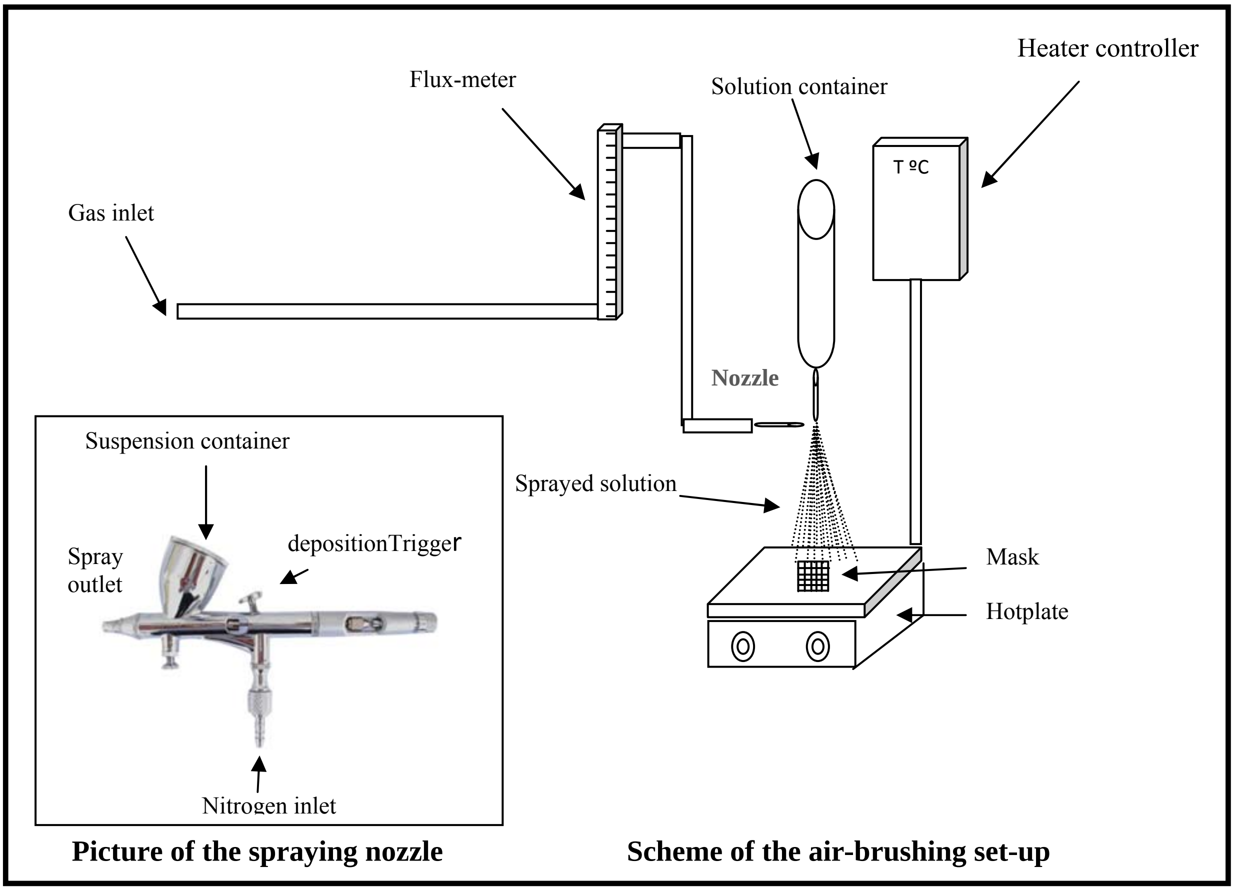


Figure 8: Scheme of the airbrushing system

Both the nitrogen flow and the distance between the nozzle and the substrate are adjusted for each material in order to reach the highest layer homogeneity. The thickness and amount of the adsorbing material deposited is controlled by varying the volume of the sprayed suspension prepared with the optimal concentration.

- Characterization procedure of the air-brushed layers

The reproducibility of the method is tested by preparing three substrates in the same conditions. Additionally, for checking a possible effect of the solvent on the adsorbent performances, some tests are performed. In the case of porous materials such as activated carbon, the BET surface area of the powder is checked before and after the use of the solvent. Then, any drop of the surface area indicates a destruction of the adsorbent pores.

After the deposition, especially in the case of use of high boiling point solvents, a thermal drying process could be performed to eliminate completely the solvent residues. It's preferable to perform it in an inert ambient so as not to affect the material surface properties.

The airbrushed layers are then characterized by environmental scanning electron microscopy (ESEM) FEI Quanta 600) for estimating layer homogeneity and thickness.

The adhesion of the deposited carbon layers to the substrate is evaluated as follows: a pre-concentrator is introduced inside a hermetic chamber and submitted during two months to synthetic air continuously flowing at 100 mL min^{-1}. The pre-concentrator is then weighted every day with a highly accurate balance (A&D Instruments LTD, GR-120-EC) in order to assess if some amount of adsorbent had left.

Herein, the air-brushing technique is applied for the deposition of activated carbon and carbon nanotubes above the alumina testing support. Then the adsorption capacity of those materials is checked by mass spectrometry following the optimized characterization procedure presented in section 2.1.

2.2.1. Activated carbon

Various microporous activated carbons of different origins, granularities and preparation conditions were studied. These materials were prepared from two different commercial precursors: Kraft lignin on one hand, and Norit active carbon on the other hand; with four different grain sizes for the former and two for the latter. The chemical activation of the precursors leads to adsorbents having different surface areas and pore size distributions. The preparation and characterization of those materials was carried out by Fierro et al. in Nancy (France). A detailed description of their characteristics is available in Table I, Annex I.

In total, eleven materials were tested:

✓ Three different materials were then prepared from Kraft Lignin using different activation conditions and were then referred to as L1, L2 and L3. More especially, the material L1 was available in four different grain sizes from 10 til up to 100 µm, called: L1-d1, L1-d2, L1-d3 and L1-d4.

✓ Five other adsorbents were derived from Norit with two different grain sizes [2-3]. These materials were then referred to as N5 and N20, 5 and 20 corresponding to the mean grain size expressed in µm. The as received materials were referred to as N5C and N20C respectively, When these materials were activated, they were then called: N5A and N20 A respectively. The material N5A was prepared using two different activations conditions and the resulting materials were named N5A1 and N5A2.

- Deposition parameters

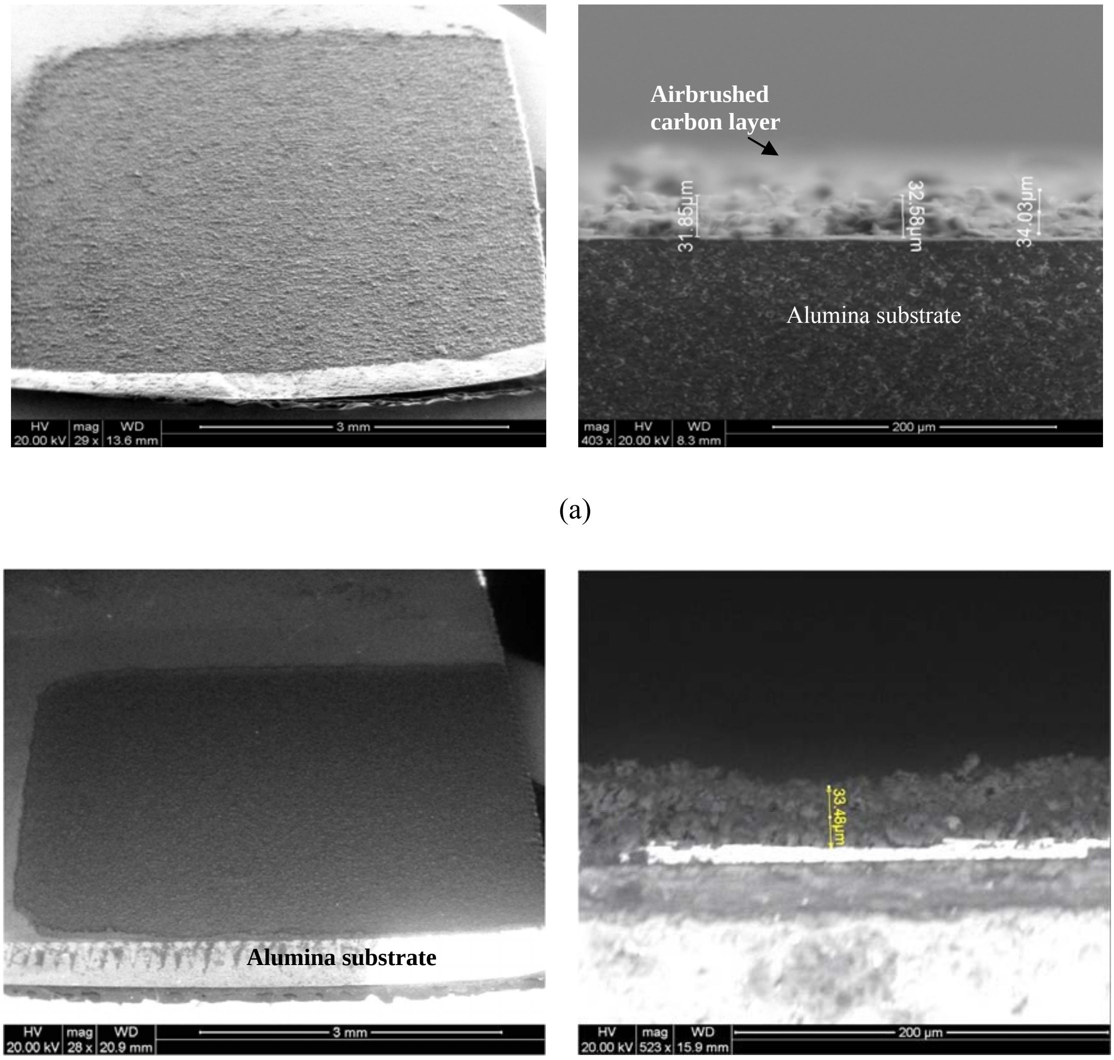
Different dispersing solvents have been tested for the dispersion of activated carbon grains, including: methanol, acetone and pentane. The most homogeneous suspension was obtained with n-pentane (HPLC Grade, 99% min, Alfa Aesar). This solvent being non polar, it dispersed better activated carbon. Table 1 presents the optimal air-brushing parameters adjusted for the different activated carbon adsorbents. In all cases, the optimal evaporation temperature of pentane was adjusted at around 70 – 80ºC. And for each material, the deposition was performed by adjusting the volume of prepared suspension, typically from 10 to 50 mL.

Table 1: Airbrushing parameters of activated carbon

Materials Parameters	L1	L2	L3	N5C	N5A1	N5A2	N20C	N20A
Suspension concentration (mg L^{-1})	100	200	100	150	150	100	150	150
Nitrogen flow (L min^{-1})	5	5	6	5	6	5	6	5
Substrate temperature (°C)	75	75	80	75	80	75	80	75
Nozzle – substrate distance (cm)	4.5	4.5	4.5	4.5	3.5	4.5	4.5	4.5

- Characterization of the air-brushed layers

Whatever is the material, the adsorbing layers deposited by airbrushing show good homogeneity. Figure 9 presents top and side views of L1 and N5A1 grains over the alumina substrate; the deposited amounts of activated carbon correspond to 40 and 50 mL, respectively, of airbrushed solution processed according to the parameters given in Table 1.



(a)

(b)

Figure 9: ESEM images of activated carbon airbrushed over alumina substrate (a) L1 (b) N5A1

The mean layer thickness was evaluated for each material from ESEM images. For that purpose, measurements were carried out on the basis of three layers of the same material deposited over alumina, always using the same volume of airbrushed solution.

The average thickness of the layers was studied versus the volume of airbrushed suspension, focusing only on N5A1, N20A and L1 materials. Doing so, adsorbents having different precursors and different grain sizes could be simultaneously compared. The average thicknesses of the layers are plotted in Figure 10. Despite the low number of data points, the expected linear dependence is observed (coefficient of linear regression R^2 between 0.97-0.99) until maximum deposited volumes of 40 and 50 mL are reached for the materials N20A and L1, and for N5A1, respectively. When these volumes are exceeded, the layer thicknesses start to drop, due to a lower adhesion of the activated carbon to the alumina support.

Using the airbrushing technique in the limit of the maximum, using aforementioned, suspension volumes, a very good adhesion of carbon layers to the substrate is achieved. The tested layers indeed perfectly survived 2 months of continuous gas cycling, since no change of adsorbent weight could be detected.

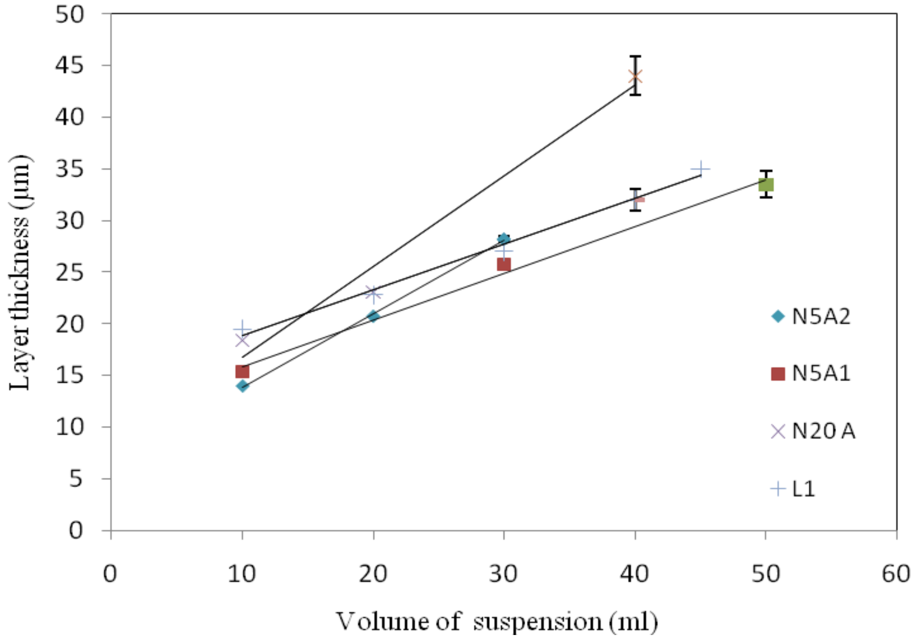


Figure 10: Study of the airbrushed layer thickness of different ACs samples versus the volume of airbrushed suspension

- Adsorption capacity towards benzene:

Adsorption of CO_2 could occur inside the same micropores of activated carbon, as benzene, but it's very low because benzene is a condensable vapor, so its affinity towards carbon is much higher than that of CO_2, this latter is then displaced by benzene as long as new C_6H_6 molecules arrive in the pre-concentrator.

At first, the desorption temperature of benzene from activated carbon was studied from room temperature to 200ºC using a pre-concentrator coated with 0.4 mg of adsorbent “L1-d2”. Figure 11 shows the desorption peaks obtained in each case. Benzene started then to desorb from the activated carbon at 60ºC. However, to get a narrower desorption peak in shorter desorption time, the pre-concentrator can be heated at [190ºC-250ºC] during 5 min. The complete desorption of the analyte is then achieved, as no residual peak of benzene was observed after performing the second heating cycle. Then this thermal desorption profile was fixed to study the other materials.

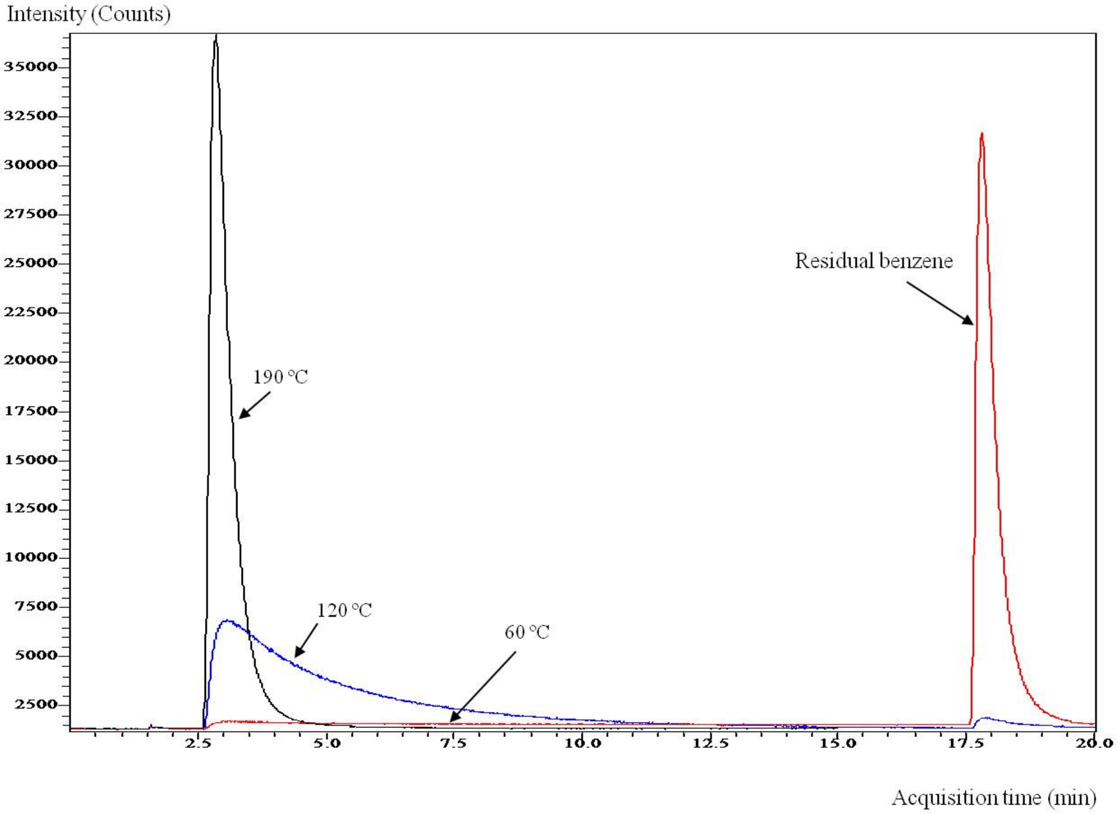


Figure 11: Selection of benzene desorption temperature

a. Effect of adsorbing layer thickness

In order to observe the effect of the thickness of the adsorbent layer on the concentration ability of the system, four pre-concentrators have been prepared on the basis of four deposited amounts of L1 activated carbon. The corresponding concentration factors are plotted in Figure 12 as a function of the layer thickness. As expected, the concentration factor increases with the amount of deposited adsorbent.

Thus, in the following, the discussion of the effect of experimental preparation conditions on the pre-concentrator performances is based on the adsorbent samples presenting the highest layer thickness. The corresponding concentration factors are listed in Table 2.

In order to compare the different adsorbents, normalized concentration factors have been calculated as the ratio of CF to the corresponding weight of activated carbon.

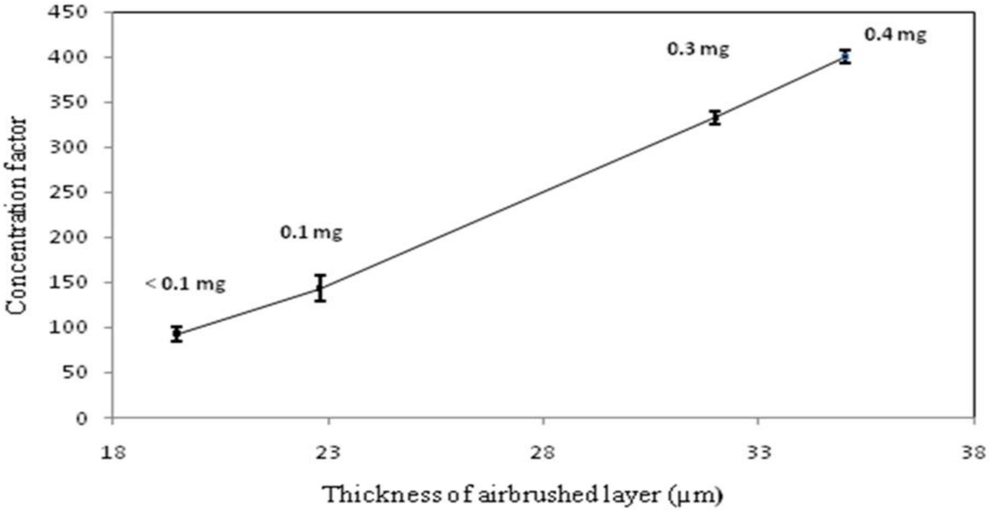


Figure 12: Study of concentration factor of benzene versus the airbrushed layer thickness

Table 2: Summary of the adsorption capacity obtained with the different AC materials

Adsorbent	Volume of airbrushed suspension (mL)	Average AC weight (mg)	Average layer thickness (µm)	Average CF	Normalised CF (mg^{-1})
L1-d1	40	0.25	-	237.4 (± 11.7 %)	949.5
L1-d2	40	0.3	32	332.7 (± 15%)	1109
L1-d3	40	0.3	-	207.4 (± 4.9)	691.3
L1-d4	40	0.3	-	183.1 (± 14.38)	610.4
L2	40	0.3	38	228.4 (± 9.1%)	761
L3	40	0.3	36	0.5 (± 15.1%)	1.6
N5C	40	0.36	-	83.7 (± 9.3%)	232
N5A1	50	0.26	33.5	250.5 (± 12.2%)	963
N5A2	30	0.36	28.2	254 (± 10.3%)	705
N20C	40	0.4	-	68.4 (± 6.5%)	171
N20A	40	0.33	44	75.8 (± 7.6%)	230

b. Influence of the nature of the carbonaceous adsorbent on the pre-concentrator performances

Several important conclusions may be drawn from the analysis of the results given in Table 2:

- Effect of grain size.

N5A2 and N20A are very comparable ACs (cf. Table 1, Annex I) prepared from similar precursors in the same experimental conditions; only initial and thus final grain sizes are different. Lower grain sizes clearly lead to higher concentration ability; the same behavior can be observed for N5C and N20C.

The same conclusion could be drawn for L1 from lignin. The best results are achieved with the smaller size materials: L1-d1 and L2-d2.

The effect of grain size is related to internal diffusion limitation. Even if their adsorption properties are expected to be identical at equilibrium, adsorbents having different grain sizes behave differently in dynamic conditions. At short adsorption time, big adsorbent particles are less effective for trapping molecules from a continuous stream. If adsorption is assumed to behave like a catalytic reaction, i.e., part of the benzene disappears on the carbon surface, thus Thiele modulus qualitatively accounts for the observed effect; it reads:

$$\Phi = \frac{V_p}{S_p}\sqrt{\frac{k\,RT}{D_e}} \qquad (1)$$

where k is the kinetic constant of the "reaction" (adsorption), Vp and Sp are the outer volume and outer surface area of a typical (spherical) particle, and De is the effective diffusivity of benzene.

The higher is the modulus, the higher is the limitation by internal diffusion. Since Φ is proportional to the grain diameter, all else being equal, then decreasing the particle size decreases diffusion limitation.

- Effect of chemical activation

The most obvious observation that can be made from Table 2 is that activation dramatically enhances the concentration factors, whatever is the considered adsorbent. This is the case for N5A1 and N5A2 when compared to N5C, and for N20A when compared to N20C; this should be also the case for lignin-based materials [4-5]. Opening and development of adsorbent porosity is thus definitely the best way of improving the pre-concentrator performances, in full agreement with [2]. Activation is indeed required for getting enough narrow pores, but excessive activation may also lead to pores that are wider than the optimal size for retaining the target molecule (here, benzene). Therefore, optimal activation conditions exist.

Comparison of (Table 1, Annex I) and Table 2 thus shows that, despite its higher surface area and micropore volume, N5A2 is less effective than N5A1 for concentrating benzene. Likewise, adsorbents derived from lignin are increasingly worse for this application when the amount of activating agent increases, whereas their microporosity is increasingly developed. These facts are readily explained by their micropore size distribution that broadens with the extent of the chemical activation (Fig. 2a, Annex I). It can be seen that, as already deduced from the shape of the nitrogen isotherms, these materials are indeed mainly microporous (most of pore widths being lower than 2 nm), and are thus suitable for benzene adsorption, except L3 (cf. the hysteresis loop of its nitrogen isotherms). Carbons derived from Norit precursors (cf. Fig. 2b, Annex I) are more mesoporous than the materials derived from lignin and present non negligible macroporosity as well. Again, N5A1 leads to the highest concentration factors among the Norit series due to its narrow micropore size distribution that is centered below 1 nm. Such a very favorable feature makes it almost as efficient as L1-d2 for the considered application.

- Effect of precursor

As it can be seen in Table 1 in Annex I, L1-d2 and N5A1 are rather similar adsorbents, having close surface areas and micropore volumes. Due to the presence of macroporosity in N5A1, the total pore volume is higher and so is the mean pore width; however, the relevant pore texture parameters for benzene adsorption are nearly the same. Here, the effect of precursor is only significant from the point of view of the porosity of the resultant activated carbons.

The final performances of a planar pre-concentrator based on layers of activated carbons thus depend on both adsorption capacity (related to pore-size distribution, itself related to preparation conditions and precursor) and adsorption kinetics (related to grain size). The combination of all these effects leads to Figure 13, in which it can be seen that the best materials are those characterized by a narrow microporosity and small particles. The two conditions need to be gathered; otherwise rather similar materials may lead to much lower normalized concentration factors.

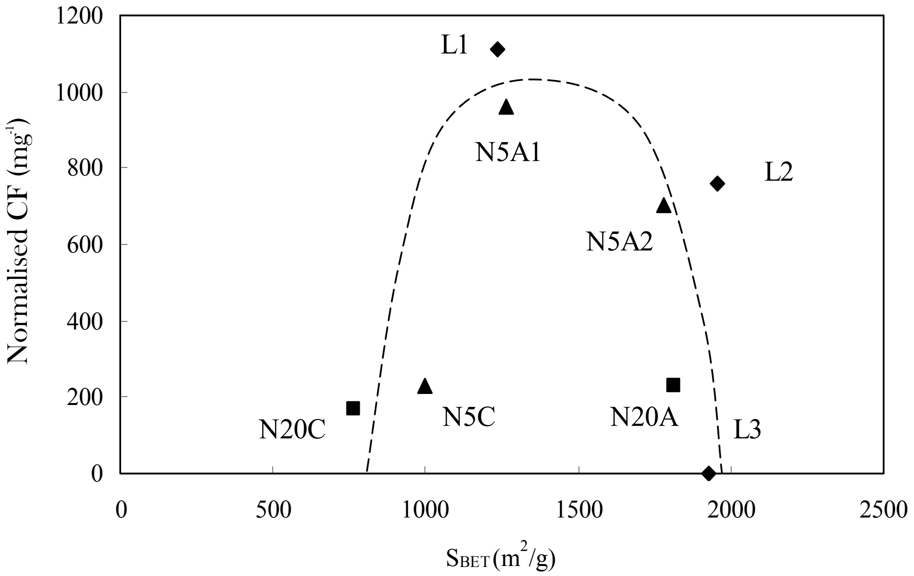


Figure 13: Study of concentration factor of benzene versus the BET surface area of the different AC materials

c. Influence of the structure of the pre-concentrators on their performance

In Figure 14, the concentration performances of two adsorbents of similar microporous texture but from different origins, L1-d2 and N5A1, are compared at a fixed flow rate of 100 mL min^{-1} and similar adsorbent weight of 0.2 mg. The dependence of their corresponding concentration factor on the benzene content in the gas stream is presented as a function of adsorption time. Whatever is the material, no stabilization of the CF is observed when the cylinder containing 150 ppb of benzene is used, even after 60 min of adsorption time. For such a low concentration, no higher adsorption times have been studied, because the targeted application requires to be based on a rather short process, i.e., faster than 60 min. Lower concentration factors are obtained with higher benzene contents in the gas stream:

N5A1 approaches saturation beyond 60 min if 1 ppm of benzene is flowing (Fig. 14.b), whereas L1-d2 keeps adsorbing benzene in the same conditions (Fig. 14.a). At even higher concentration: 10 ppm of benzene in CO_2, the adsorbent is quickly saturated, and benzene breakthrough occurs from 10 min for both materials L1-d2 and N5A1. As expected from the previous discussion about pore size distribution, L1-d2 is seen to present slightly higher concentration performances than N5A1: all else being equal, L1-d2 indeed leads to higher absolute (and also normalized) concentration factor and requires higher adsorption time for being saturated.

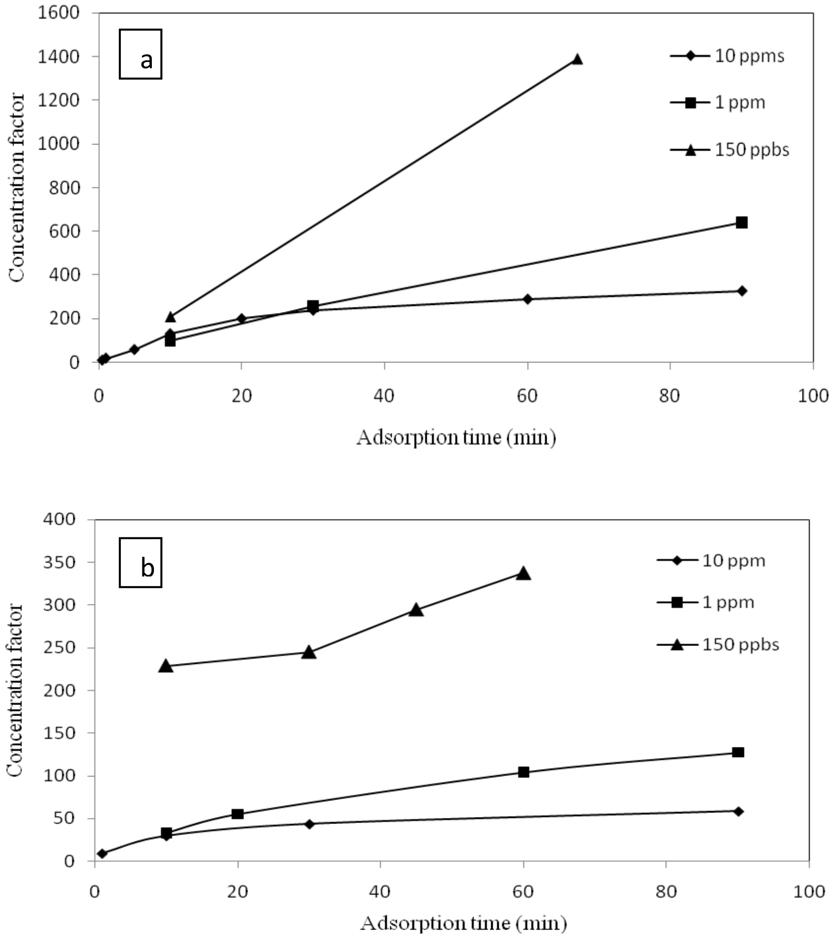


Figure 14: Breakthrough curves of benzene by (a) L1-d2 and (b) N5A1

From Figure 14, it could be easily observed that using this preconcentrator, lower concentrations of benzene in the gas stream lead to higher concentration factors. Since the amount of the adsorbent in this preconcentrator is low (0.2 mg). This effect could be then due to the breakthrough of the adsorbent.

2.2.2. Carbon nanotubes

We tried to tune the adsorption properties of carbon nanotubes to check the possibility of benzene concentration, using six different carbon nanotube samples. The adsorption capacity of either single walled, double walled or purified and unpurified multi-walled carbon nanotubes, and carbon nanotubes functionalized with tetrafluoromethane are also investigated. More details about the preparation and characterization of these materials are available in Annex I, section 1.1.2.

The CNT adsorbents tested were prepared from three different commercially available pristine CNTs provided by three different companies: Nanocyl, Mercorp and He Ji, SA:

✓ Three different pristine CNTs were produced by Chemical Vapor Deposition (CVD) from Nanocyl SA: single walled carbon nanotubes (NC1100), double walled carbon nanotubes (NC2100) or multi walled carbon nanotubes (NC3100), with a CNT purity grade of 90 %, apart from NC3100 the purity of which was higher than 95 %.

The NC3100 sample was functionalized using a radio-frequency CF_4 plasma and was called "NC3100-CF_4".

✓ MWCNTs were produced by Arc Discharge from Mercorp, SA Company and they were referred to as "MRGC".

✓ SWCNTs were provided by He Ji, SA company from China and were called "S4401".

- Adsorbent deposition

The deposition parameters were adjusted for the different CNT samples following the results presented in table 3. Acetone (CAS: 67-64-1, Scharlau) was used to disperse the pristine CNT samples, while N,N-Dimethylformamide (DMF) (CAS: 68-12-2, Alfa Aesar) was more suitable for 95 % purified MWCNT (NC3100) samples. Three substrates were deposited from each material, in order to set the reproducibility of the results.

Table 3: Airbrushing parameters of the different CNT sample

Adsorbent/ 16 mm^2	**Sample**	**Organic solvent**	**Suspension (mg/ml)**	**N_2 flow (ml/min)**	**Distancia Nozzle-substrate (cm)**	**Evaporating Temperature (°C)**	**deposited Volume (ml)**	**deposited Weight (mg)**
MWCNTs	NC3100	DMF	0.05	6	7-8	190-200	25	0.1
	MRGC	Acetone	0.2	6	5.5	120	30	0.1
	NC3100 -CF_4	Acetone	0,05	6	7	120	20	0.1
DWCNTs Nanocyl	NC2100	Acetone	0.1	6	5.5	120	20	0.4
SWCNTs	NC1100	Acetone	0.2	6	5.5	120	10	0.1
	S4401	Acetone	0.2	6	5.5	120	10	0.4

After their deposition, the adsorbing layers were subjected to a thermal treatment at 250ºC during 2 hours using a heating and cooling rate of 4ºC/min in a nitrogen ambient for not to further oxidize the samples. This thermal treatment was already adjusted by Leghrib et al. using DTA/TGA analysis [6].

- Characterization of the deposited layers

The ESEM images performed on the airbrushed CNT layers showed a homogeneous covering over the alumina substrate. However, the CNTs form a network of bundles due to tube-tube intermolecular forces, as can be observed in figure 15.b.

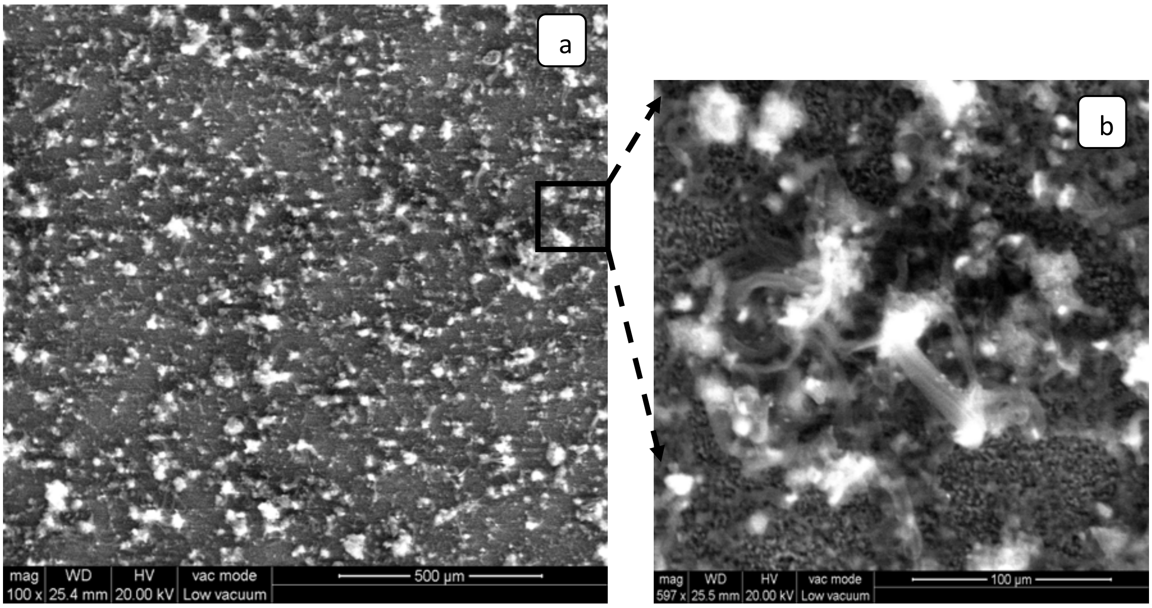


Figure 15: (a) ESEM image of MWCNTs (NC3100) airbrushed on alumina substrate (b) Zoom

- Adsorption capacity towards benzene

The different prepared concentrators were studied towards benzene adsorption. Figure 16 shows the plot of the concentration factor towards benzene normalized per milligram of adsorbent obtained with the different CNT samples.

From this figure, we could notice that the different materials adsorb benzene since their concentration factor is higher than 1. However the adsorption capacity of almost all the materials is too low to allow the pre-concentration of benzene. The "MRGC" sample is the lonely material which presents a quite good pre-concentration capacity compared to the other materials.

a. Effect of carbon nanotube structure

In fact, adsorption of benzene can occur on the external wall surface of the CNT through π- π interaction or through capillary condensation in its internal pores. In the case of MWCNTs, the layer-to-layer spacing of 0.34 nm is generally smaller than the radius of gyration of organic vapors, so most organic chemicals are too large to be adsorbed between the MWCNT layers, and this is also the case of benzene [7].

On what concerns the pristine materials from Nanocyl, all elaborated following CVD, although theoretically, SWCNTs were expected to better adsorb benzene than DWCNTs followed by MWCNTs, due to their higher surface area; however, the results obtained experimentally here show that MWCNTs presented the best concentration factor towards benzene, compared to SWCNTS or DWCNTs (Fig. 16). On the other hand, DWCNTs presented the worst concentration factor.

b. Effect of the CNT fabrication procedure

On the one hand, if we focus on the pristine MWCNTs prepared from Nanocyl and Mercorp company, it can be observed that Mercorp MRGC samples presented a higher adsorption capacity in comparison to pristine Nanocyl NC3100 samples (in fact, MRGC samples show the highest concentration factor). This behavior can be associated to the presence of impurities like graphitic particles in MRGC samples which remain after the CNTs fabrication process. This is in accordance with [8], which shows the higher adsorption affinity of graphite to benzene rather than CNTs.

On the other hand, if we focus on SWCNTs materials and we compare the samples NC1100 and S4401 provided by Nanocyl and He Ji companies respectively, we see, that the NC1100 samples presented a concentration factor lower by around three times than the one due to S4401 samples. Moreover, it was reported in literature that SWCNTs of lower diameter present higher adsorption capacity towards benzene [9]. In this case, the adsorbate molecules are subjected to a larger interaction potential from the delocalized electrons in the nanotube walls. Even if S4401 samples present a slightly lower diameter (1-2 nm) than NC1100 samples, we cannot confirm that the difference in their adsorption capacity is due to the difference in their diameter since this difference is too low. However, this can be explained by the much higher content of impurities present in He Ji samples (cf. Table 2, Annex I), as in the previous case.

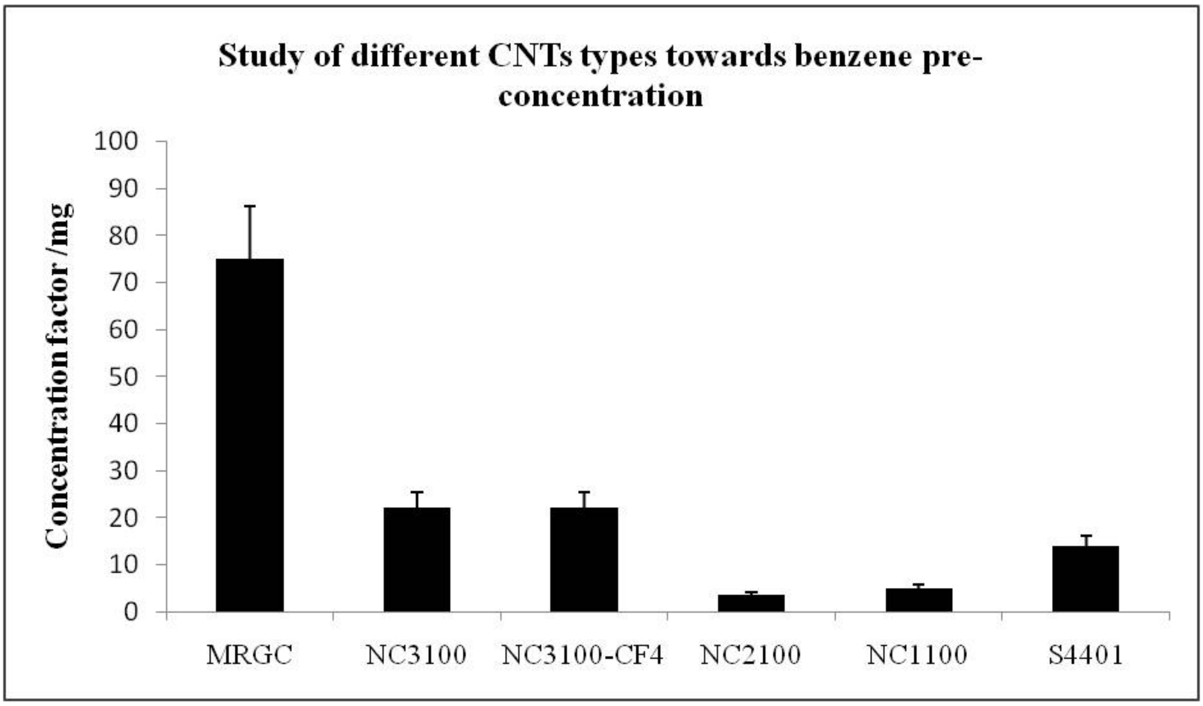


Figure 16: Adsorption capacity of the different CNT based adsorbents towards benzene

c. Effect of surface functionalization

The plasma treatment with CF_4 was performed in order to increase the hydrophobicity character of the CNTs [10-11]. However, when comparing pristine and CF_4 treated NC3100 MWCNTs, we did not notice any improvement in the concentration factor of CF_4 functionalized MWCNTs compared to the pristine MWCNTs. In fact, this can be due to the detachment of those groups during the heating process performed at 250ºC for benzene desorption or the annealing process performed on the deposited samples at 250ºC for completely removing acetone. In [12], it was suggested the occurrence of fluorine desorption from the CNT surface by performing a post fluorination annealing process of the samples. The largest fluorine loss occurred between 200 and 300ºC.

The experimental results obtained here suggested that the adsorption capacity of the CNTs towards benzene is very weak (too low concentration factors). And this can be due to the bundling effect of carbon nanotubes, which was reported to cause a significant reduction in surface area [13].

The previous study performed on activated carbon (section 2.2.1) presented concentration factors towards benzene which are at least ten times higher than the ones obtained with the CNT materials characterized in this section, even for those having similar surface area.

For CNTs, the adsorption mechanism seems to be different. From literature, it appears that the order of benzene adsorption is inconsistent with the order of surface area, pore volume and average pore diameter but is dependent on their surface chemical nature [14] rather than their porosity characteristics, in contrast to what was observed with activated carbon. In our case, the content of fluoric groups attached to the surface of the nanotubes is maybe too low, which explains the non improvement of the concentration factor of the treated samples to benzene. The treatment conditions must be then readapted so as to get a higher yield of functional groups attached to the nanotube surface.

This suggests that despite its raw granular structure, activated carbon is more suitable for benzene concentration than the different carbon nanotube based adsorbents tested here. However, those materials were reported to have a faster adsorption/desorption kinetics and to be less affected by humidity compared to conventional activated carbon. Nevertheless, they remain more suitable for the concentration of other molecules, such as hydrogen and methane [15-16].

2.3. Conclusion

- A characterization technique based on mass spectrometry has been set-up. This technique was demonstrated to be more suitable for the characterization of the optimal working conditions of the preconcentrator rather than the usual use of gas sensor systems.
- The "concentration factor" has been selected as criteria to estimate the pre-concentration capability of the pre-concentrator and the experimental pre-concentration conditions of benzene were successfully optimized using a planar testing support of alumina.
- Different adsorbent based on activated carbon and carbon nanotubes have been deposited by air-brushing and tested towards the adsorption of benzene:
    - ➢ Airbrushing technique is an excellent method for preparing homogeneous, adherent, adsorbent layers in a controlled way.
    - ➢ The results suggested the low adsorption capacity of intrinsic pure as well as functionalized CNTs.

The best adsorption capacity was attributed to activated carbon, especially, the L1 adsorbent, derived from Kraft lignin, which was the material presenting the most suitable microporous structure, thus leading to the best adsorption properties. Hence, concentrations factors up to 1000 were reached with this material. This material will be finally selected as adsorbent for the pre-concentrator and its performance will be more deeply studied in next chapters.

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Chapter 3. Study of the performance of the pre-concentrator towards benzene in presence of interfering species using mass spectrometry

Once the preconcentrator based on activated carbon is fabricated and its preconcentration conditions towards benzene are fixed, a deeper study will be performed by testing benzene adsorption and the interference from other compounds using the mass spectrometer. In fact, in real conditions, such as in industrial areas, other interfering compounds could coexist with benzene. Only a negligible interaction with common polar molecules, such as methane, is expected to take place in the selected activated carbon, owing to the low amount of oxygenated groups present in its surface. However, some non polar molecules are likely to interfere in the adsorption of benzene in the preconcentrator: the most common ones could be toluene and xylene due to their chemical resemblance with benzene.

The effect of humidity on the adsorption of benzene is also envisaged using a gas sensor instead of the mass spectrometer. In a real application, humidity of air may vary and cause the early breakthrough of the adsorbent, which will affect the preconcentration of benzene and the reliability of the analysis.

The selective desorption of benzene in presence of toluene using the preconcentrator is also tested during this chapter.

3.1. Experimental characterization set-up

3.1.1. Analysis of benzene in presence of toluene

The pre-concentrator consists of activated carbon airbrushed over the alumina support (see section 2.2.1 for details). The characterization of the preconcentrator was carried out by mass spectrometry, following the procedure and parameters fixed in chapter 2, using the chamber with wall: the collection of the analyte was performed at 100 ml/min during 10 min and the analyte injection started 0.5 min before analyte desorption. After, the desorption of the analyte was performed by heating the preconcentrator under 100 ml/min of helium.

Benzene, toluene are used as testing target vapors. The tests were performed using a calibrated cylinder of 1 ppm of benzene balanced with air, whereas toluene was generated from a permeation tube of liquid toluene. The concentration of this latter was calibrated by controlling the heating temperature and flow of synthetic air of the equipment in which the tube was introduced. Different concentrations of benzene were obtained by mixing the content of the 1 ppm benzene bottle with synthetic air, and adjusting the proportion using a system of mass flow controllers.

Mixtures of benzene and toluene were generated by connecting benzene at the inlet of the calibration system of the tube. This system acted at the same time as gas mixing system. The total flow at the system outlet was fixed at 100 ml/min using the internal mass flow controller (MFC) of the system. Figure 1 shows the experimental set-up including the spectrometer circuit with the new testing analytes.

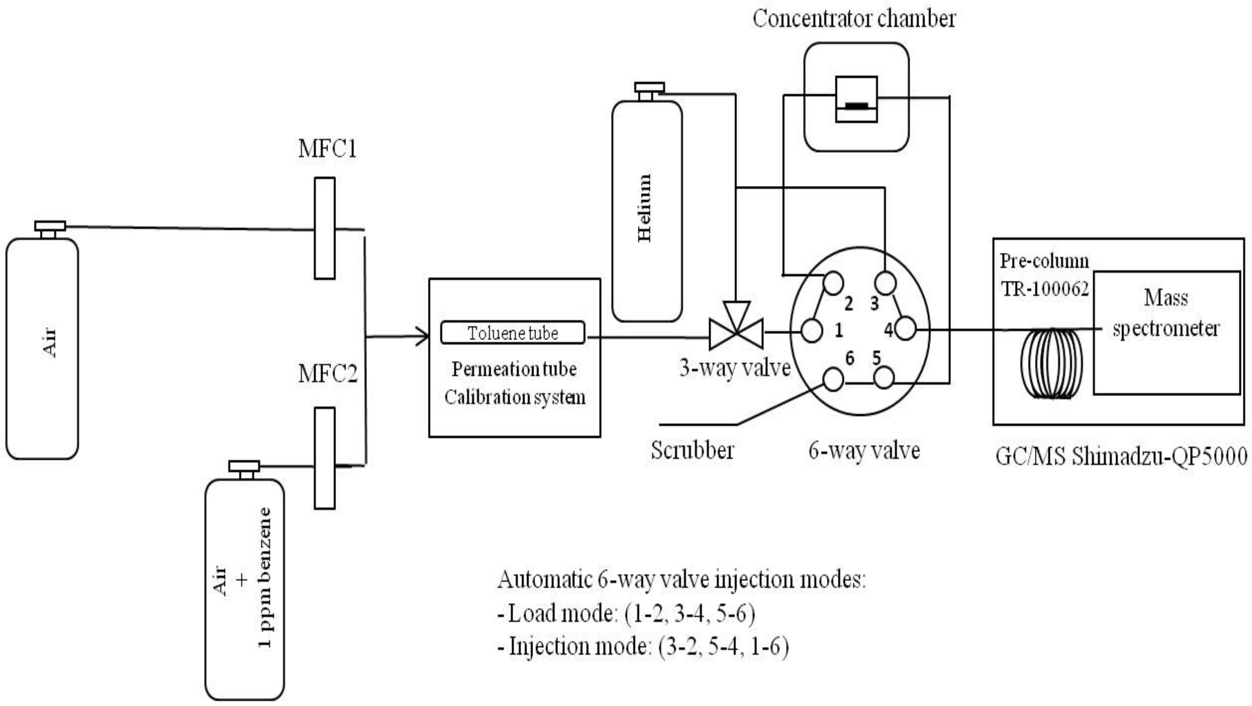


Figure 1: Experimental characterization set-up for the preconcentration of benzene in presence of other compounds

Benzene and toluene were identified using the MS system by their fingerprint characteristic peaks at m/z= 78 (The peaks 51, 52 and 39 are extra peaks belonging also to the spectra of benzene and can be ignored) and 91, respectively. The peak resulting from the sum of the different analyzed peaks in each experiment was called "TIC".

a. Adsorption interference tests

In order to study the mutual adsorption interference between benzene and toluene in the preconcentrator, the adsorption of the analytes was performed as before and their desorption was carried at 190ºC during 5 min. The concentration factors of both compounds were analyzed separately and next in a mixture.

Different concentrations of benzene, ranging from 150 and 1000 ppb were tested, while the concentrations of toluene tested were 150, 250 and 350 ppb.

In real conditions, the analytes can be either in equal or different proportions in air, and adsorption interference is likely to occur between benzene and toluene in the activated carbon, considering their similar characteristics. This interference is a serious drawback for gas preconcentration and may depend on the proportions of the vapors in the mixture to be adsorbed. As it is not easy to study all the different possible proportions, the investigation will be limited to two different cases. The mixture was at first studied in equal proportion of both vapors in the pre-concentrator. Then, the adsorption of one vapor was studied in presence of a fixed concentration of 150 ppb of the other one. 150 ppb is a quite high concentration in real conditions. This value was selected in order to evaluate the maximum effect of interference of one vapor in the presence of the other.

In order to make sure of the reproducibility of the results, each measurement was replicated 3 times for each tested analyte concentration.

b. Selective desorption tests

As already explained in chapter I (section 1.2), in some cases, temporal separation of vapor mixtures can be obtained by the preconcentrator as different compounds desorb at different rates. Then by adjusting the thermal desorption profile of the preconcentrator, a selective desorption of the analytes could be achieved.

The selective desorption of benzene in presence of toluene was then tested using different desorption temperature profiles either linear ramps or pulse steps. The separation tests were performed at an equal proportion of both analytes in a mixture, fixed at 150 ppb.

3.1.2. Analysis of benzene in presence of moisture

The effect of air humidity on the preconcentrator response towards benzene could not be studied with the mass spectrometer in order to avoid the possibility of saturating it with moisture. For this reason, the mass spectrometer was replaced by a commercial taguchi gas sensor TGS-822 from Figaro. An Agilent multimeter (Model 34970A) was used to monitor the sensor resistance as a function of time. The sensor was heated at 400ºC by applying 6.5 V to its heater resistor using an Agilent power supply (Model N5751A).

The adsorption conditions were fixed at 100 ml/min during 10 min, using a calibrated cylinder of 1 ppm of benzene diluted in air. Desorption was then performed at 260ºC during 5 min, at 100 ml/min. The concentration of benzene was controlled by means of an "Environics Model" automatic flow controller equipment. This system allowed working either in dry or humid controlled atmosphere.

To evaluate the effect of moisture on the preconcentrator response to benzene, the sensor response to 500 ppb of benzene with and without the concentrator was studied at different relative humidity (RH): "Dry" (In fact corresponds to 10 % RH), 50 and 75 % RH, and each measurement was repeated 3 times for testing the result reproducibility.

The sensor response without the preconcentrator was calculated as the difference between the steady state resistance, reached by the sensor while the analyte was flowing to the concentrator/sensor system in the adsorption stage, and the sensor baseline resistance. On the other hand, the response to the desorbed analyte was calculated as the difference between the resistance at the maximum of desorption peak and the baseline resistance.

3.2. Analysis of benzene in presence of toluene using the mass spectrometer

3.2.1. Study of the adsorption interference between benzene and toluene

- Calibration of the pre-concentrator towards single vapors

The calibration curves of the MS towards benzene and toluene show perfect linear behavior in the range of concentrations studied (Fig. 2). Then, the concentration factors for both compounds were plotted against their concentrations. The error bars represent the standard deviation derived from three repeated measurements and they demonstrate the quite acceptable reproducibility of the results.

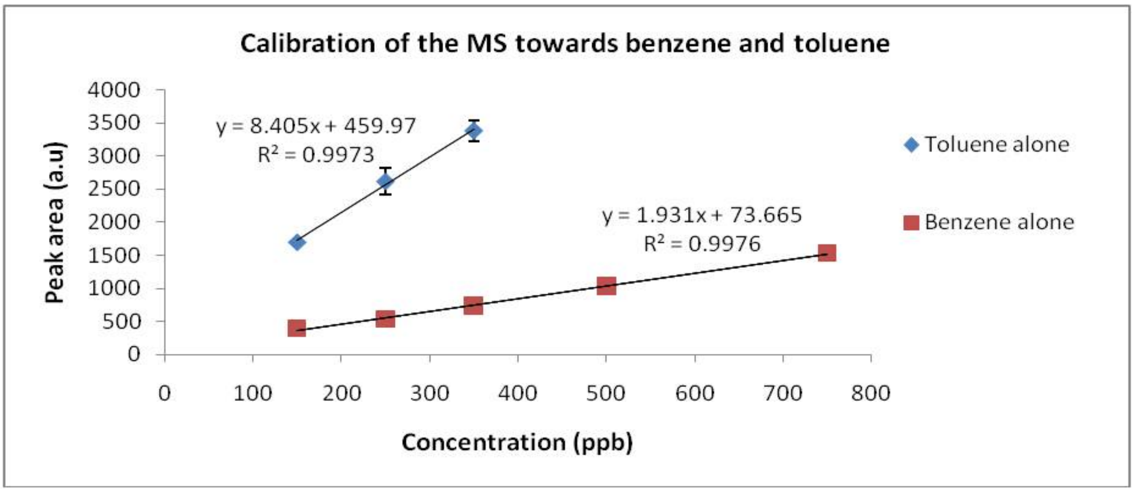


Figure 2: Calibration curve of the MS towards benzene and toluene

Figure 3 shows the average concentration factors obtained for different concentrations of benzene and toluene analyzed separately, using a pre-concentrator with 0.2 mg of activated carbon.

Very good adsorption capacities towards both vapors were obtained, reaching concentrations factors up to 250. These results agree with the those obtained in chapter 2. In fact, activated carbon L1 has narrow pores suitable for the adsorption of small molecules such as benzene and toluene. The concentration factors obtained for toluene are quite similar to the ones obtained for benzene due to their structure similarities.

For both compounds analyzed separately, the concentration factor is quite constant for concentrations up to 350 ppb. After, in the case of benzene, a slight drop of the concentration factor is observed, indicating the breakthrough of the adsorbent.

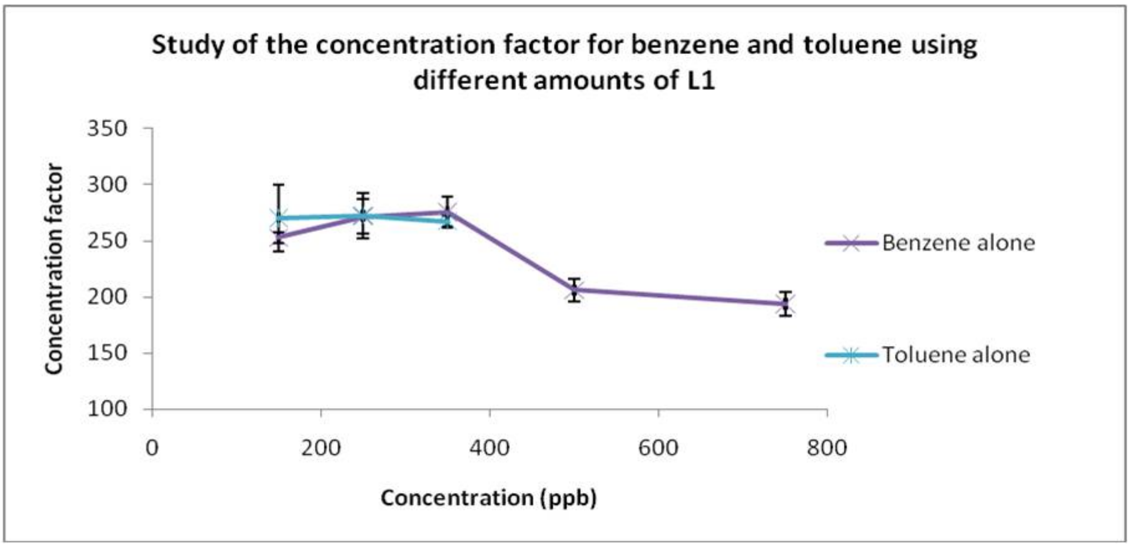


Figure 3: Calibration of the preconcentrator towards benzene and toluene analyzed separately at different initial concentrations in air

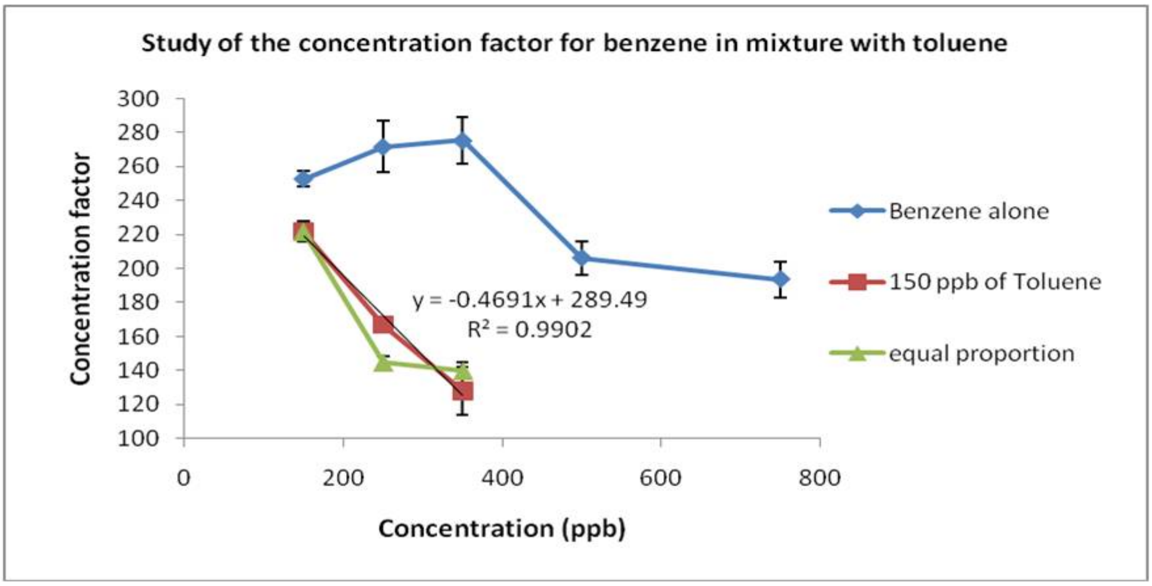
- Calibration of the pre-concentrator in the mixture

Figure 4.a shows the study of the adsorption capacity of benzene at different initial concentrations in presence of toluene, at equal proportion and at a fixed concentration of 150 ppb of toluene. It can be clearly seen that the adsorption capacity of benzene decreased in the presence of toluene. Also, the breakthrough of the adsorbent seems to occur earlier compared to when benzene is alone. This decrease is negligible for a concentration of 150 ppb of benzene, when the mixture is analyzed at equal proportion or when the concentration of toluene is maintained at 150 ppb.

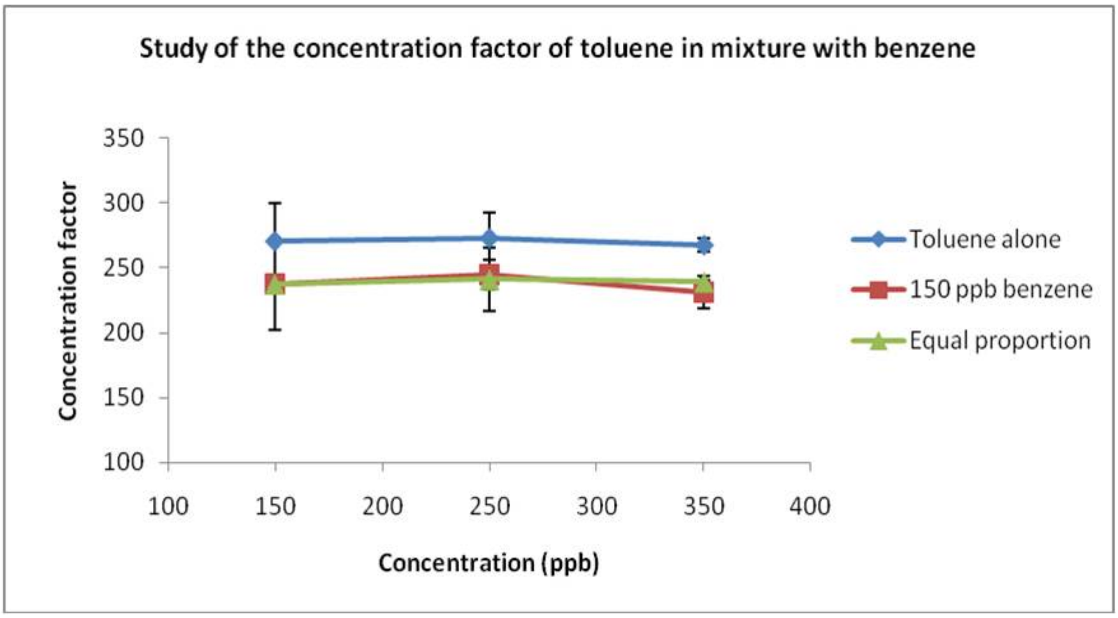
From the equation of the curve plotted in figure 4.a, the concentration factor drops by a rate of 0.47 per ppb, so this change is not expected to be significant in a real application, where the concentration of benzene should be lower than 100 ppb.

The same study was repeated with toluene in presence of benzene (Fig 4.b). The change of the concentration factor of toluene in the mixture is insignificant for concentrations below 250 ppb. The concentration factor of toluene in the mixture is constant with time and seems to be independent from the concentration.

Then, the pre-concentrator designed here could be used to concentrate either benzene or toluene or both compounds irrespective to the proportions of these vapors in real conditions (below 100 ppb).



(a)



(b)

Figure 4: Study of the concentration factor of the mixture of (a) benzene in presence of toluene (b) toluene in presence of benzene

In next section, we will study the selective desorption of benzene in presence toluene using the preconcentrator.

3.2.2. Study of thermal programmed selective desorption of benzene in presence of toluene

a. Benzene in presence of toluene

The separation of benzene and toluene during the desorption step is based on the difference in their boiling points: 80ºC and 110ºC respectively. When a linear temperature ramp is used, benzene is expected to be desorbed from the preconcentrator earlier than toluene.

The threshold desorption temperature of benzene was already determined in chapter 2 and was estimated at 60ºC. Figure 5 shows how the shape of the desorption peak of benzene changes when a pulse or a linear temperature profile is employed. In fact, the desorption is delayed as much as the heating rate is lowered. The rising time must be then adjusted so as not to enlarge excessively the desorption duration.

Different linear ramps from room temperature to a maximum of 150ºC were tested by changing the heating rate from 15 to 150ºC/min. No separation of the analytes was noticed in the TIC peak even at 15ºC/min (Fig. 6). Also, at this heating rate, the desorption cycle is enlarged to 20 min, which is an excessive duration for usual applications of gas analysis.

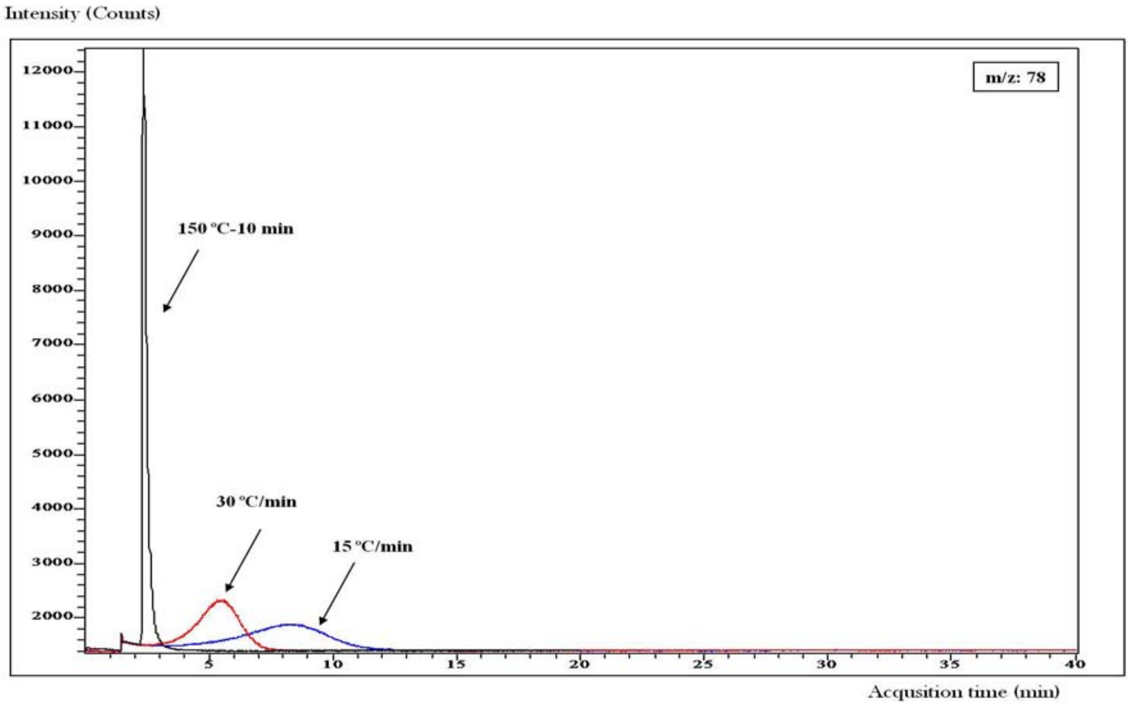


Figure 5: Study of desorption peaks of benzene versus different desorption temperature profiles

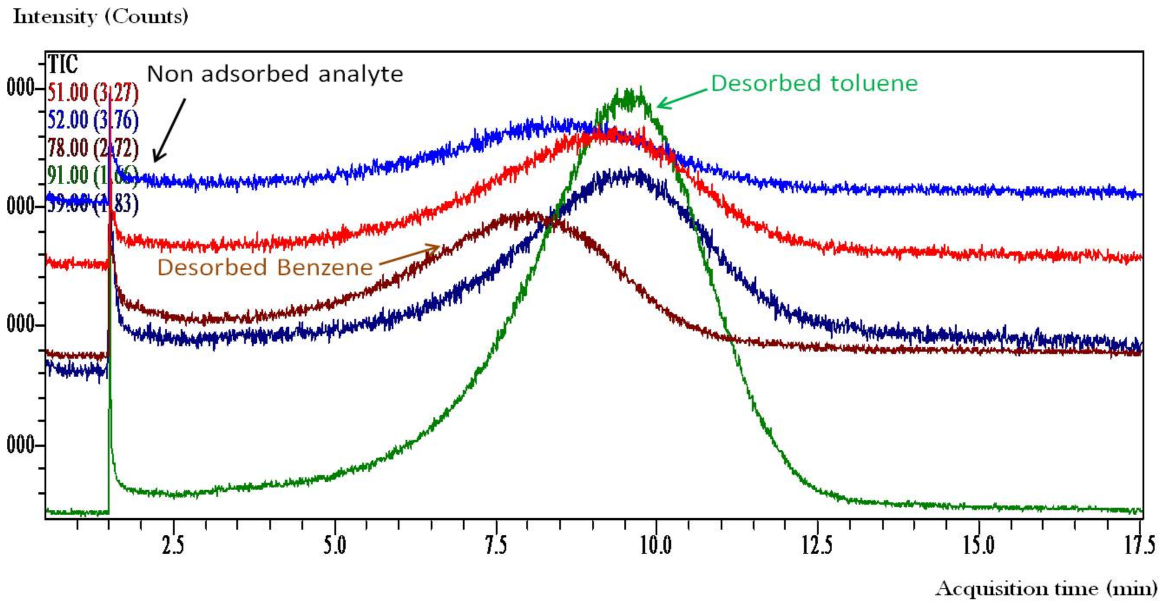


Figure 6: Study of the selective desorption of benzene (m/z: 78) in presence of toluene (m/z: 91) using a desorption linear ramp of 15ºC/min at 150ºC.

We tried then to separate both compounds using thermal heating steps. The first step must be as low as possible so as to desorb benzene without desorbing toluene. And then the duration of the first step could be then increased so as to eliminate completely benzene. After, the second step could be initiated at higher temperature to desorb toluene.

We have played with different temperature steps. However, toluene is desorbed in the first step together with benzene even if the temperature is lowered to 75ºC (Fig. 7).

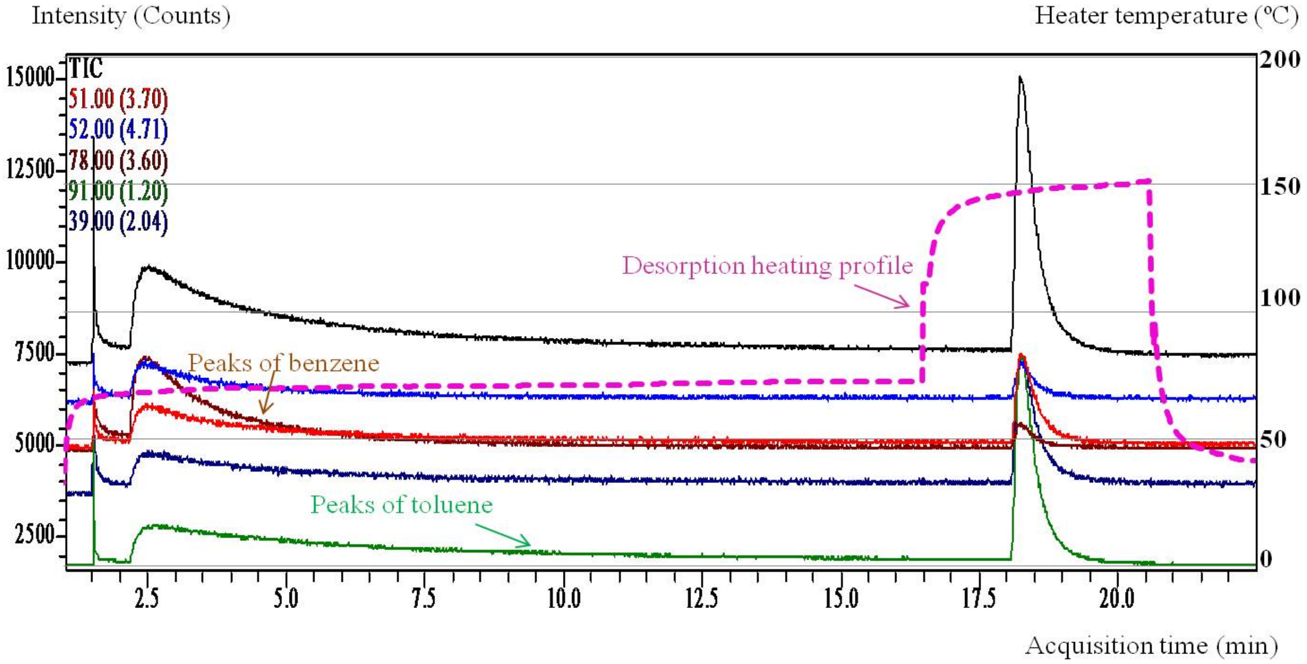


Figure 7: Study of the selective desorption of benzene (m/z: 78) in presence of toluene (m/z: 91) using a two-step desorption temperature of 75ºC and 150ºC. The discontinuous line represents the two step heating profile used for gas desorption.

No separation of benzene and toluene is then possible with the preconcentrator. This problem could be probably due to a non homogeneous distribution of the temperature in the alumina heating area. Then, the separation of those gases will be checked later with the micro-concentrator where the temperature distribution is expected to be more homogeneous.

We will then test the separation of benzene in presence of butadiene. In fact, the boiling point of butadiene is -4ºC, then the difference between both compounds is around 80ºC, much higher than the difference of temperature between benzene and toluene (30ºC).

b. Benzene in presence of butadiene

The selective desorption of benzene in presence of butadiene was studied with the mass spectrometer using the same experimental setup used before (Fig. 1). A calibrated cylinder of 100 ppm of butadiene balanced in air was then mixed with the benzene cylinder at different proportions using the mass flow controller system. A mixture of 0.5 ppm for benzene and 50 ppm of butadiene in air was fixed to perform the separation tests. In this case, the proportions analyzed were not the same because of the limitation imposed by the mass flow controller system.

Figure 8.a shows the desorption peaks of the mixture using a pulse of 175ºC during 10 min. Butadiene is represented in the spectra by its characteristic peak due to m/z= 54.

The desorption peaks of the mixture were studied using different heating steps: The first heating step was in the range of 50-60ºC maintained for 30 min and followed by a heating pulse at 175ºC during 5 min.

Since a temperature in the range of [50-60[ºC is applied, butadiene is desorbed alone and benzene doesn’t appear, however even after 30 min, the desorption of butadiene is not complete and a big amount of the gas is desorbed from the pre-concentrator, when the second heating step at 175ºC is initiated. Figure 8.b shows the desorption peaks of the mixture at a step of 55ºC. So, the separation of benzene and butadiene is possible, however we expect that the desorption duration will be excessively enlarged.

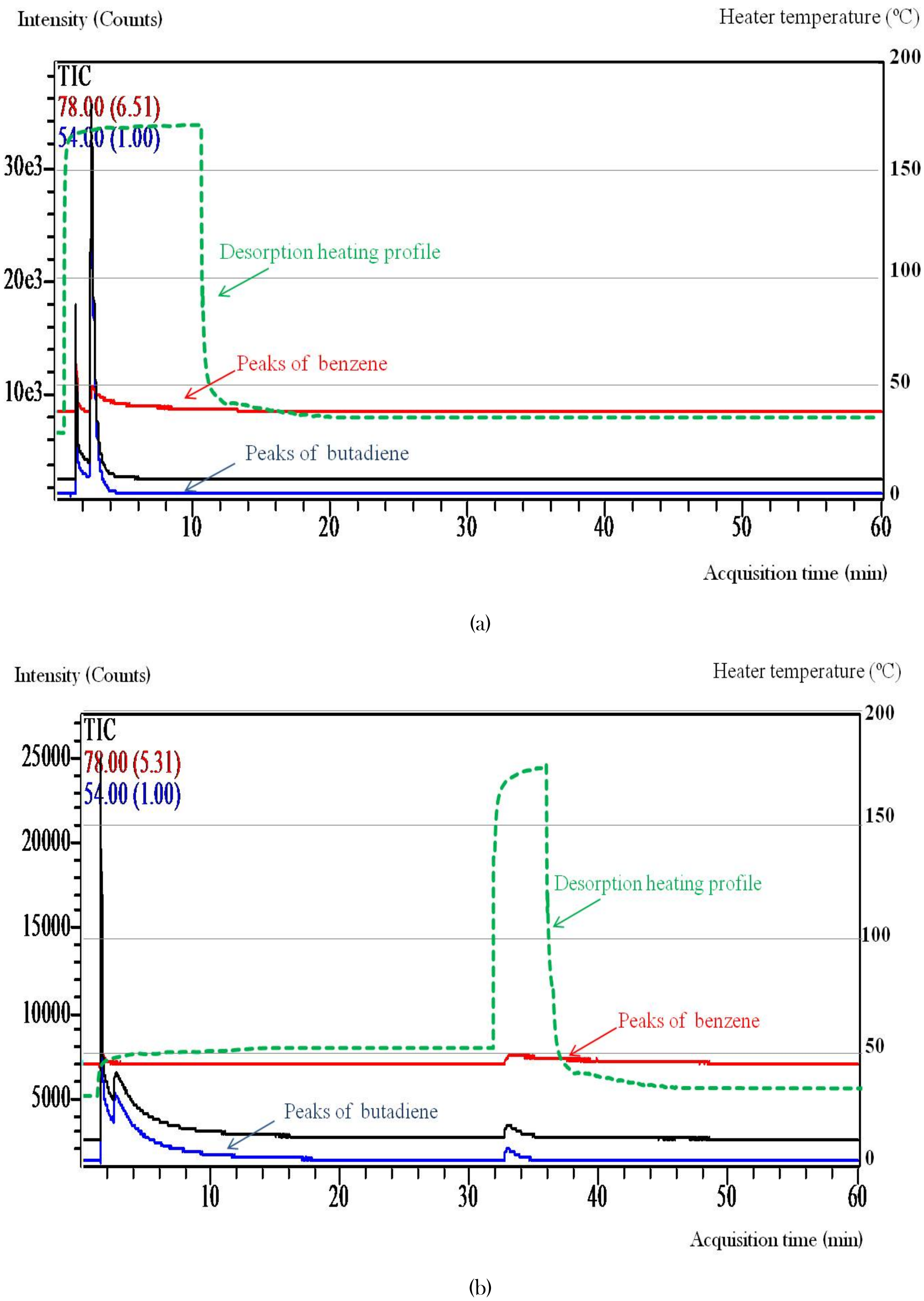


Figure 8: Study of the selective desorption of benzene (m/z= 78) in presence of butadiene (m/z= 54) using (a) A pulse of 175ºC (b) a two-step desorption temperature at 55ºC and 175ºC. The discontinuous line represents the two step heating profile used for gas desorption.

3.3. Study of humidity effect on benzene preconcentration

Figure 9 shows the plot of the sensor resistance in presence of 500 ppb of benzene, with and without the preconcentator, versus relative humidity (Fig. 9). Moisture seems to have no effect on the behavior of the preconcentrator towards benzene, since the drop in the sensor caused by the presence of humidity is the same with and without the preconcentrator. This response decrease corresponds to 4.7 and 10.1 % in 50 and 75 % RH respectively, compared to the response in "dry" air (10 % RH).

This is an excellent result which confirms the validity of the concentrator based on activated carbon to be operated in ambient air independently from the presence of humidity. This result is explained by the experimental conditions and the extremely low amount of oxygenated surface groups of the selected activated carbons. Highly functionalized carbons are indeed known to be much more affected by the presence of moisture [1]. When mixed with a VOC, water competes with it so as the adsorbed amount of VOC is lower than in the absence of humidity [2]. However, aromatic vapors of low molecular weight are preferentially adsorbed in the narrow micropores and, at such low concentration of VOCs and such low number of surface functions, interference with water is negligible as observed here [3]

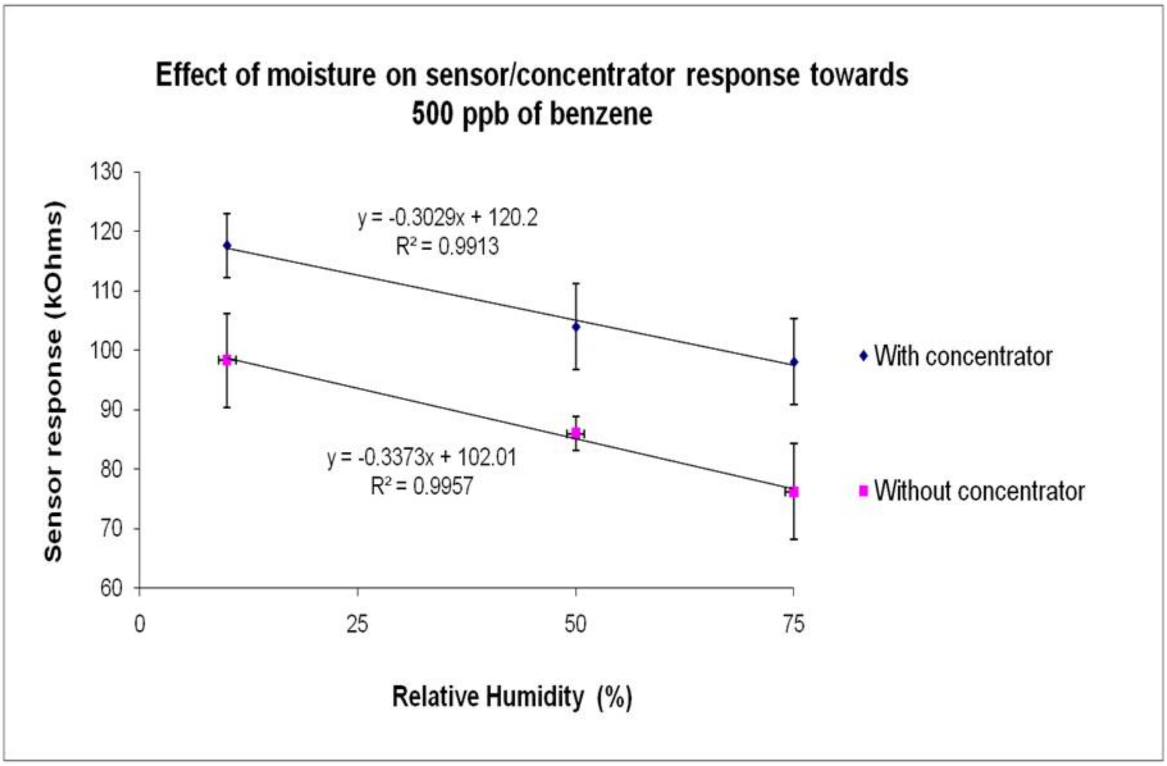


Figure 9: Effect of humidity in the system response towards benzene

3.4. Conclusion

The performance of the preconcentrator was tested for benzene in presence of toluene. As expected, the activated carbon is able to concentrate both compounds with quite similar performances. Surprisingly, only a small interference between both compounds occurs, which will not be a limitation for the quantification of the concentrations of both gases in a real application.

The selective desorption of benzene in presence of toluene using the preconcentrator based on alumina wasn't possible and could be due to the non homogeneous temperature distribution in the heater area. The separation was possible when using an analyte with a boiling point very far from the one of benzene, such as butadiene. However, the desorption cycle will be excessively enlarged. This problem will be probably avoided when using the micro-concentrator, which is expected to have more homogeneous temperature distribution with an optimal heater design.

Concerning the effect of moisture on the preconcentration of benzene, the preconcentrator was shown to be unaffected by humidity, thanks to the nature of the selected activated carbon and to the low concentrations of VOCs to be detected. This is an excellent result that confirms the applicability of the preconcentrator in real application where the humidity may vary.

After the characterization and optimization of the preconcentrator performance towards benzene and in presence of other interfering species, the preconcentrator will be then coupled with a detection system to check the possibility to improve its response and thereby lower its detection limit towards benzene.

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Chapter 4. Study of the preconcentrator coupled to a MOx gas sensor for a sensitive and selective analysis of benzene

After the gas preconcentrator fabrication and characterization towards benzene alone and in presence of its main interfering species, the aim of the present study is to validate its use as injection unit in front a detection microsystem.

In the previous chapter, the preconcentrator was tested as a separation unit using a mass spectrometer. Regarding the complexity of such application, the selective detection of benzene will be carried out by the detection unit itself. In this case, we proposed to couple our preconcentrator either with a gas sensor or a chromatographic system composed by a GC column and a gas sensor. In both cases, a tin oxide gas sensor is used, because of its high sensitivity to different compounds, low production cost, and ease of use [1-3]. The role of the preconcentrator in such systems will consist in increasing the response of the system towards benzene, allowing by this way to lower the detection limit of the system towards that analyte.

4.1. Direct coupling of the preconcentrator with a gas microsensor

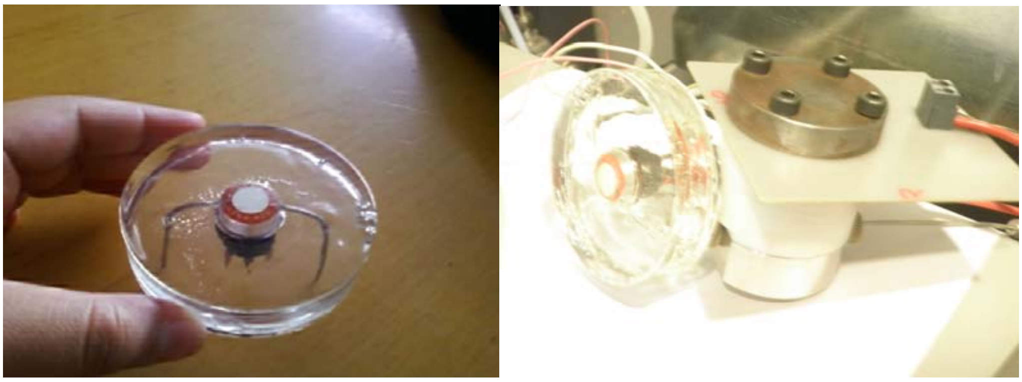
This time, the preconcentrator is coupled directly to a gas sensor array to check the possibility to improve the sensitivity and lower the detection limit of the detection system towards benzene. As simpler approach, we choose to make the first trials by coupling the preconcentrator with only one sensor. This sensor was a standard commercial taguchi tin oxide gas sensor TGS 822 from Figaro.

The idea is to check first the optimal detection conditions of the sensor alone towards benzene. The response of the sensor in these conditions will then serve as reference response. Then, the response due to the preconcentrator will be always compared to this reference.

4.1.1. Experimental characterization set-up

a. Characterization circuit

As said before, the sensor consists of TGS-822 from Figaro (Fig. 1a). In order to have a low dead volume, the TGS was sealed inside a resin block with 1/16 stainless steel connections for gas inlet and outlet. Then, the dead volume corresponds to the volume of the sensor package which is less than 1 cm^3.



(a) (b)

Figure 1: (a) Picture of the TGS embedded inside the sensing chamber with metallic inlet and outlet connections (b) picture of the concentrator chamber connected with the TGS.

The measurements were performed by connecting the pre-concentrator directly to the sensor chamber through stainless steel tubes (Fig. 1.b). This time, the preconcentrator used contains 0.4 mg of activated carbon, in order to avoid premature adsorption breakthrough already experienced in chapter 3 with the preconcentrator containing 0.2 mg of the adsorbent. The adsorption conditions were fixed at 100 ml/min during 10 min using two cylinders of either 1 or 10 ppm of benzene diluted in air. The desorption was performed at 260ºC during 5 min, while the desorption flow was adjusted during the experiments.

The concentration of benzene was controlled by an automatic flow controller system. An Agilent multimeter (Model 34970A) was used to monitor the sensor resistance over time. The sensor can be heated to different operating temperatures by applying to its heater resistor a given voltage using an Agilent power supply (Model N5751A). A calibration curve temperature of the sensor versus the applied voltage was previously obtained using a temperature sensor PT100.

4.1.2. Optimization of the sensor working conditions

a. Effect of sensor temperature

In order to evaluate the effect of the sensing temperature on the response of the sensor to benzene, the desorption flow was fixed at 100 ml/min, and the measurements were performed at a fixed concentration of 5 ppm of benzene, while the sensor temperature was varied between 270 and 450ºC by applying to the heater a voltage between 5 and 7 V.

The response with and without the concentrator are determined by the following procedure:

1- During the adsorption cycle, the analyte is passed to the concentrator at a fixed concentration during 10 min at 100 ml/min and is being detected in parallel by the sensor. The sensor response to the adsorbed analyte is then considered as the reference response.
2- When the adsorption cycle is finished, a flow of 100 ml/min of synthetic air during 5 min is passed to the system in order to recover the sensor baseline.
3- After that, the desorption is started by heating the concentrator to 260ºC during 5 min. By this way, the sensor response appears like a desorption peak.

✓ The sensor response without the preconcentrator was calculated as the difference between the steady state resistance, reached by the sensor while the analyte was flowed to the concentrator/sensor system in the adsorption stage, and the baseline resistance.

✓ The response to the desorbed analyte was calculated as the difference between the resistance at the maximum of the desorption peak and the baseline resistance.

✓ On the other hand, the effect of desorption temperature on the sensor response was estimated by heating the concentrator at 260ºC during 5 min without previous gas adsorption. The response of the sensor to the desorbed analyte is then corrected by cutting out the response due to the desorption temperature effect.

The effect of sensor operating temperature on the response of the system without and with the preconcentrator is evaluated. Figure 2 shows the electrical response of the sensor with and without preconcentrator to 5 ppm of benzene at different sensing temperatures. It could be seen clearly that the highest and fastest response is obtained at 400ºC.

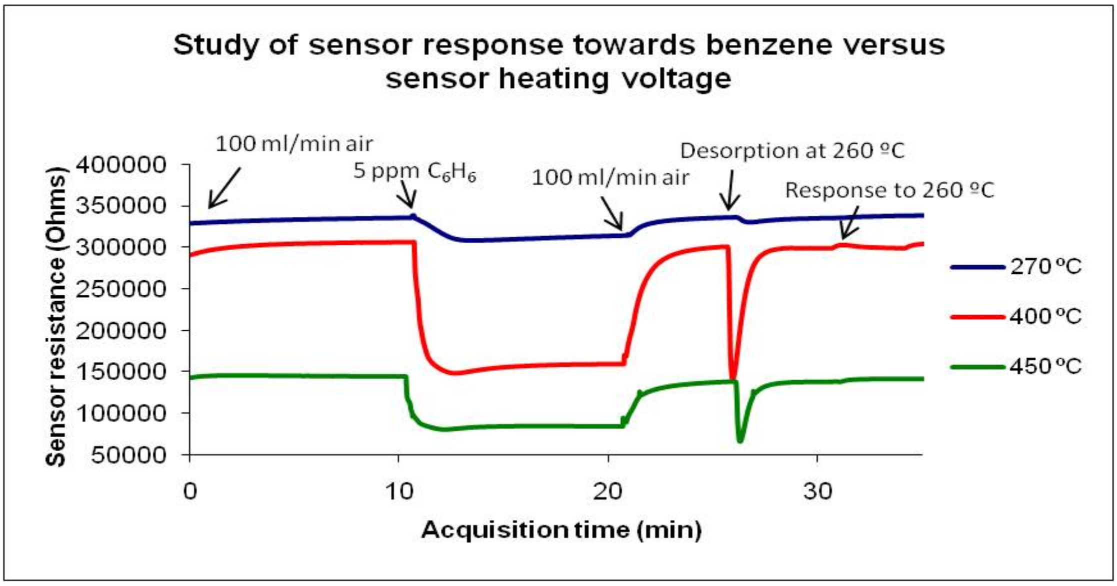


Figure 2: Sensor response at 100 ml/min and different sensing temperatures with and without preconcentrator towards 5 ppm of benzene

b. Effect of carrier gas flow

Then the sensor temperature was fixed at 400ºC and the effect of desorption flow on the sensor response was evaluated using flows of 25, 50 and 100 ml/min.

Figure 3 shows the variation of sensor response to 5 ppm of benzene without and with the preconcentrator at 400 ºC and different desorption flows.

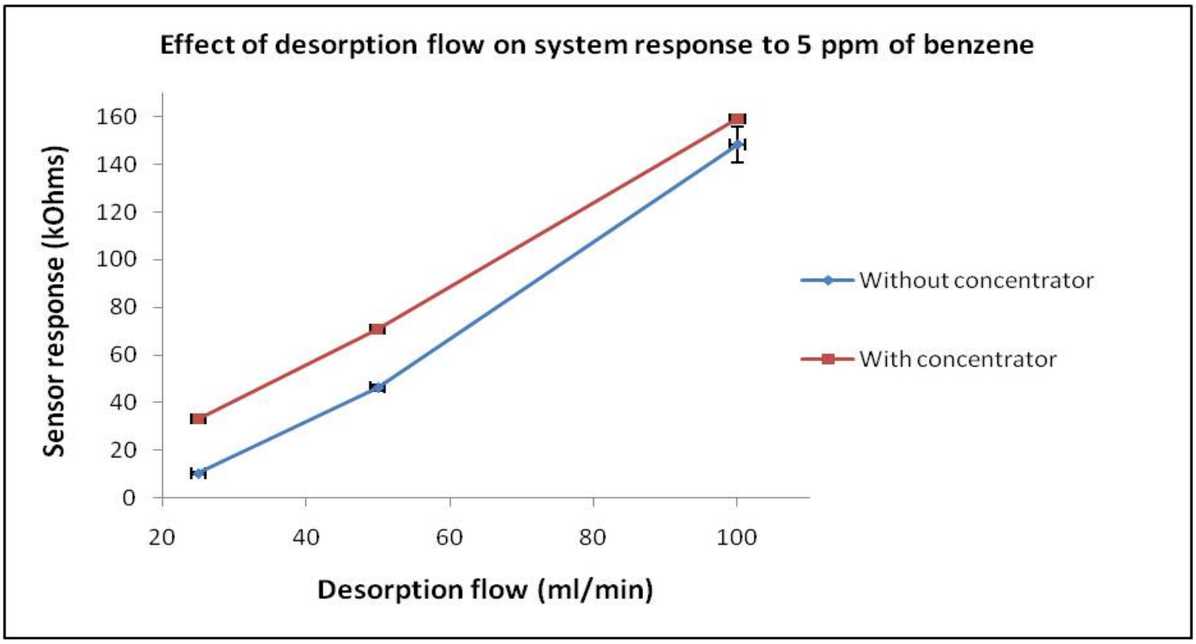


Figure 3: Effect of desorption flow on system response towards 5 ppm of benzene

It could be clearly seen that higher flow rate gave higher response to benzene. Then the best response of the sensor was obtained at 100 ml/min. It's difficult to explain this observation, as no paper was reported about such effect.

In next studies, the response of the sensor with preconcentrator in whatever conditions will be then always compared to the sensor response without preconcentrator evaluated in its optimal working conditions: 400ºC and a desorption flow of 100 ml/min.

By calculating the ratio between the sensor response with the concentrator in the different conditions and the sensor reference response at 100 ml/min and 400ºC, we will get what we defined as the "Improvement factor (IF)" which represents the improvement of the sensor response due to the pre-concentration step.

It must be pointed out that the response of the sensor to the effect of desorption temperature (Fig. 2) is less than 4 % and was cut off from the sensor response with the preconcentrator in each case.

From figure 3, it could be clearly seen that the response of the sensor to the desorbed vapor increases as much as the desorption flow increases. Normally, the contrary effect would be expected, as the higher flow rate may induce a dilution of the desorbed analyte and can consequently result in a lower detected concentration, as was explained in a reported model implemented by E.H.M. Camara et al. [4]. However, in our case, the behavior of the sensor response versus the carrier gas flow rate is the same, with and without preconcentrator.

However, even in these optimal conditions, the best improvement factor remained very low (1.2) whatever is the concentration of benzene. When the adsorption time was increased to 30 min, the improvement factor was increased from 1.2 to 3.

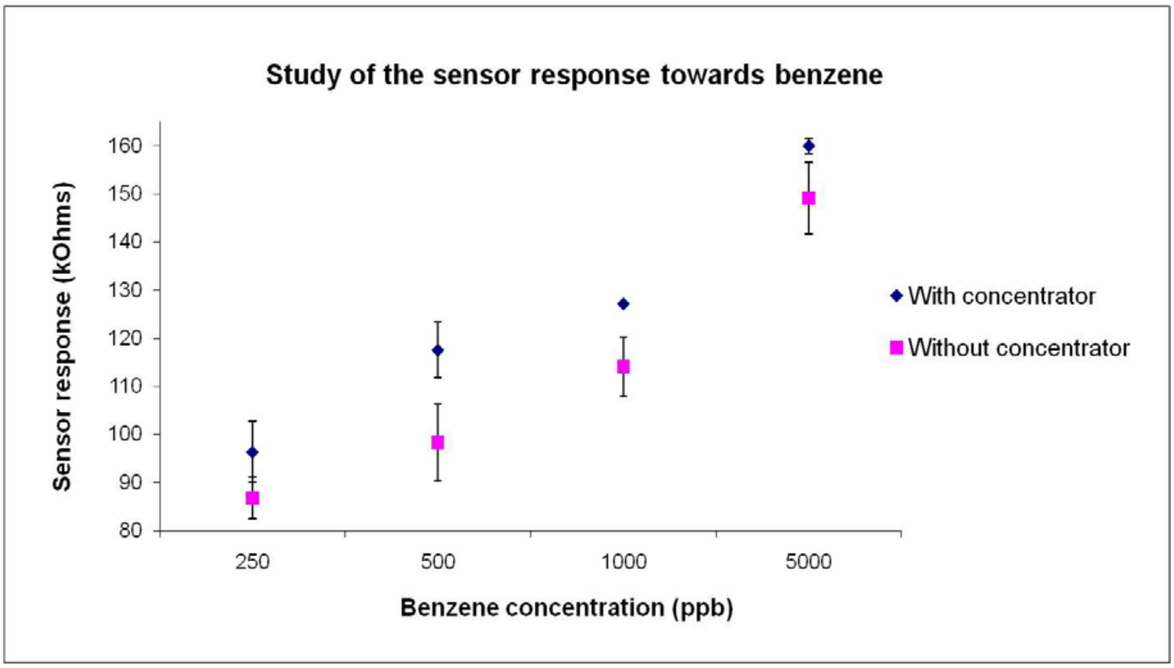


Figure 4: Study of the system response at different concentrations of benzene in air

The dilution conditions of the desorbed analyte at the inlet of the sensor must not be ignored, as the volume of the connections and the sensor chamber acts as low-pass filter reducing considerably the response of the sensor [4]. It must be pointed out that the configuration of the gas entrance at the sensor chamber in our case, is laminar, so maybe only a proportion of the desorbed analyte reacts with the sensor surface and the other proportion is being diluted in the dead volume of the sensor chamber and evacuated under the air flow.

These problems could be overcome by integrating the preconcentrator and the sensor on the same substrate or maybe putting the preconcentrator in front of the sensor on the same chamber. In this case, the dead volume will be considerably reduced and the sensor can be in closer contact with the desorbed analyte. Despite the slow response of the gas sensor, one possible solution is to close the gas chamber during analyte desorption, by this way, the desorbed analyte will be confined in front the sensor, so as this latter can have more time to react with the analyte.

Regarding the time needed to build the proposed solutions, we decided to test the preconcentrator with a gas microchromatographic system. In this case, the microcolumn separation capability allows the selective detection of more complex mixtures than usual sensor array systems. And regarding the problems already experienced with the laminar configuration of the sensor inlet, presented in section 4.1, the microcolumn outlet is placed perpendicular to the sensor inlet.

4.2. Study of the preconcentrator in front of a gas chromatograhic detection system: Application to the analysis of benzene in presence of butadiene

The aim of this study is to build a microsystem based on the coupling of three miniaturised units: our micro-concentrator with a chromatographic micro-column in front of a micro-tin oxide gas sensor for the selective and sensitive detection of atmospheric pollutants. The first trials will be made with the alumina substrate and in the next chapter, we will show the final results obtained with the microconcentrator based on the silicon microhotplate membrane.Herein, this study will be performed step by step and will deal with the selective detection of benzene vapor in presence of 1,3 butadiene vapor. This latter compound is also known as a human carcinogen which can be emitted in the environment from the exhaust of automotive engines, biomass combustion and industrial on-site uses or during various steps of the petrochemical production [4].

- The pre-concentrator is first characterized using a classical gas chromatographic (GC) column connected to a flame ionization detector system. By this way, the preconcentration conditions of both vapors are adjusted and their adsorption interference is studied.

  The FID detector is then replaced by a commercial metal oxide gas sensor TGS-800, by this way, the detection conditions of the analytes are fixed and the efficiency of the preconcentrator, as injection unit in front of the chromatographic system, can be checked towards the analysis of benzene in presence of butadiene.

4.2.1. Step 1: Preconcentrator characterization with classical GC/FID

a. Description of the characterization set-up

The preconcentrator used contains 0.4 mg of activated carbon. It was connected to a characterization circuit similar to the one described in chapter 2 and 3, by replacing the mass spectrometer by a FID detector (Varian Star 3400 CX) and the pre-column with a GC capillary column (Chrompack capillary column CP-SIL 8CB LOW BLEED/MS 30 m-0.25 mm-0.25 µm). The detection measurements of the system were performed using calibrated cylinders containing 10 ppm of the analyte (benzene or 1,3 butadiene) diluted in air. When necessary, the vapors were diluted in air and/or mixed using an automatic mass flow system, as reflected in Figure 5.

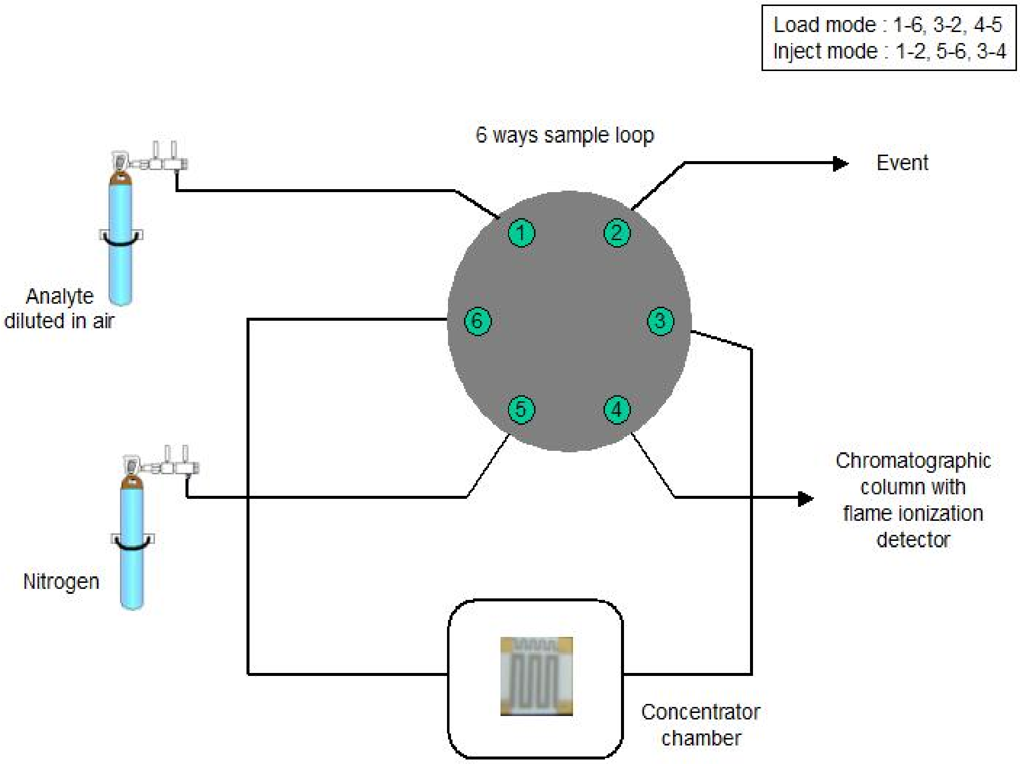


Figure 5: Experimental set-up used for the analysis of benzene and butadiene

The collection of the analytes is performed at 100 mL.min^{-1} during 10 min, while the desorption was made at 20 ml/min under nitrogen. The desorption temperature and time were adjusted depending on the analyte to be concentrated.

The detection limit was estimated as the lowest concentration of the vapor detected by the detector and which response was higher than around three times the response of the signal noise. In order to check the reproducibility of the results, each experiment was replicated 3 times.

b. Optimization of the desorption conditions of single analytes

The characterization of the pre-concentrator performance towards benzene and 1,3 butadiene separately was carried out to adjust the optimal desorption conditions (temperature and time).

First of all, we plotted the calibration curve of the FID response towards benzene and 1,3 butadiene at different concentrations without pre-concentration stage for a column temperature of 80ºC (Figure 6). The FID lowest detection limit for these compounds was evaluated to be 3 ppm. From this figure, we noticed that the FID response was linear within the range 3-10 ppm.

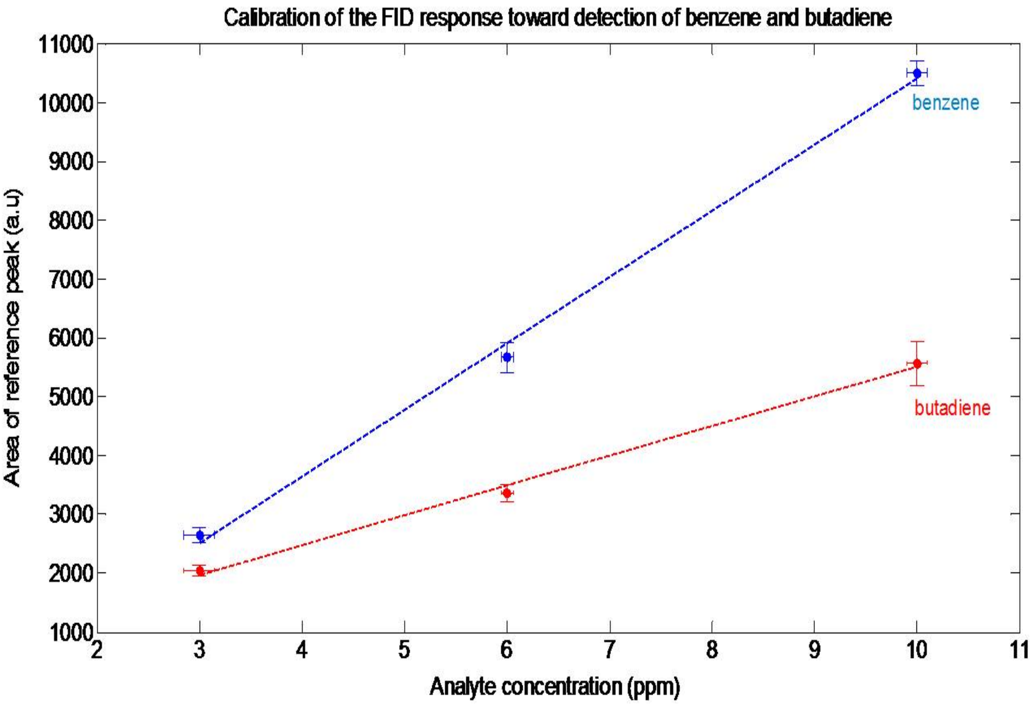


Figure 6: Evolution of the integrated area of the FID reference peaks of each analyte versus its concentration.

The desorption conditions for benzene in the pre-concentrator (desorption temperature of 260ºC during 5 min) had been adjusted previously, in chapter 2 in order to get the narrowest desorption peak of the concentrator using a minimum heating time, without affecting the chemical stability of the benzene molecule [5]. The same procedure was also tried for 1,3 butadiene.

As could be seen from Figure 7, in these experimental conditions, a second desorption peak was found. This observation suggested some temperature-induced reaction of the 1,3-butadiene molecule (thermal degradation), which was expected at such a high working desorption temperature. Previous studies confirmed the butadiene polymerization at high temperatures [6]. Such a reaction may even be promoted in our conditions, due to the presence of oxygen that can catalyze the formation of peroxides, subsequently leading to the formation of butadiene polymers. So, it was necessary to readjust the optimal desorption temperature and time for an efficient desorption of 1,3 butadiene, without any thermal degradation of the molecule.

For that reason, we studied the desorption conditions in order to obtain only one chromatographic peak. Finally, the best conditions found were a heating temperature of about 175°C with a desorption time equal to 10 minutes. Figure 3 shows an example of a 1,3 butadiene desorption peak obtained in these optimal conditions. These conditions were tested in the case of benzene, and we noticed that only 1 % of benzene remained in the concentrator. This value does not affect the measurement.

These new experimental conditions for the desorption of pollutants were applied for the analysis of both pollutants.

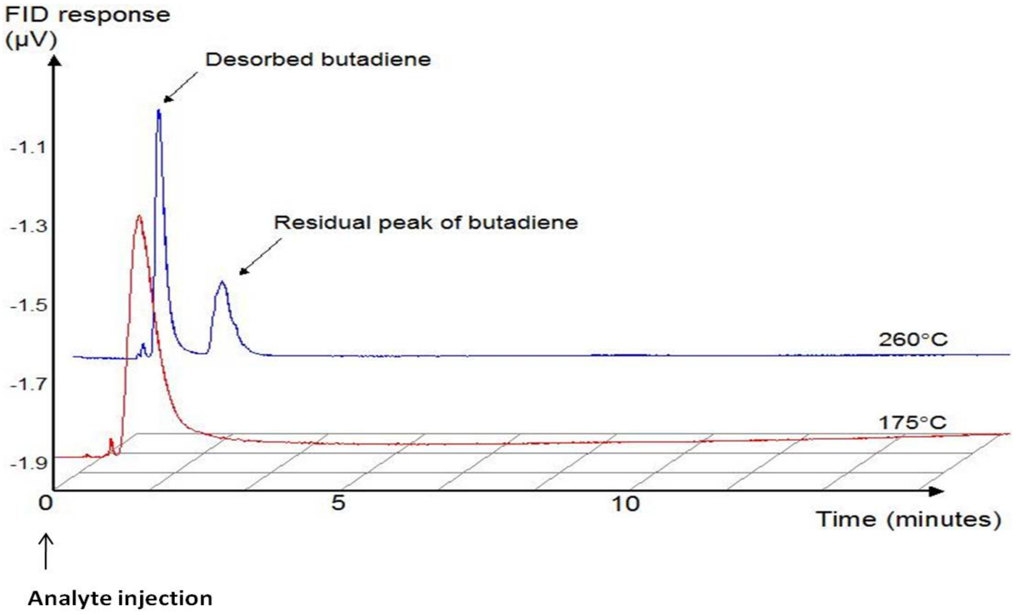


Figure 7. Influence of the heating temperature on the FID desorption peak of butadiene

- Analysis of single analytes

Figure 8 shows the plot of the integrated area of benzene and 1,3 butadiene desorption peaks obtained separately at different concentrations. From this figure, we noticed that the use of the pre-concentrator allowed detecting both vapors at levels as low as 500 ppb, corresponding to an increase of sensitivity of at least 5 times. Nevertheless, for both vapors, we observed a change in the slope of the response curve when concentrations up to 3 ppm for benzene and 6 ppm for butadiene are reached. This effect was attributed to the fact that the pre-concentration sites of the adsorbent began to breakthrough, in agreement with the results previously presented in chapter 2 [5].

Finally, we plotted the concentration factor evaluated for benzene and butadiene in the range of 0.5 to 10 ppm (cf. Figure 8). For analyte concentrations less than 3 ppm, the values were deduced by extrapolation from the equation of the calibration curves of the analytes (cf. Figure 6), given that it was not possible to evaluate the areas of the reference peaks for both vapors at these low concentration values.

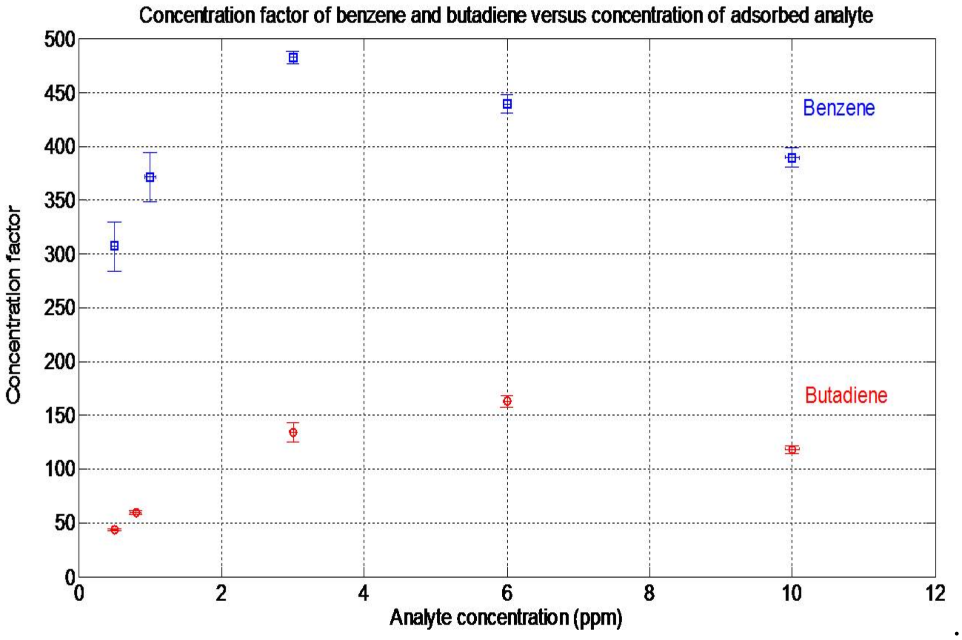


Figure 8: Evolution of the concentration factor of each analyte versus its concentration (empty squares: benzene, empty circles: butadiene)

By comparing the concentration factor obtained separately with benzene and 1,3 butadiene, it was observed that the concentration factor for benzene was much higher than that of 1,3 butadiene. This should be due to the higher affinity of benzene with activated carbon.

In order to check any possible adsorption interferences between both analytes, the adsorption capacity for each individual compound was compared to that obtained for their mixture. The evaluation of the concentration factor has been obtained from the peaks once separated by the chromatographic column.

c. Study of the adsorption interference between benzene and butadiene

The first separation test was performed using a concentration of the mixture fixed at 5 ppm for each analyte. Adsorption (100 mL.min^{-1} during 10 min.) and desorption conditions (175 ºC during 10 min using N_2 at 20 mL.min^{-1}) have been fixed according to the previous results.

- Optimization of column separation temperature

The column temperature has been fixed to 80ºC as before. At such temperature, we observed a partial separation of the two analytes. In order to evaluate the best experimental conditions for separating both pollutants in the chromatographic column, we studied the influence of the column's temperature. Chromatograms thus obtained are represented in Figure 9. The first chromatographic peak corresponds to the elution of 1,3 butadiene and the second one to the elution of benzene. From this figure, the best separation was achieved at a low temperature (30°C), but the elution of both compounds was excessively long. A temperature of 60ºC gave a good compromise between complete peak separation and short time analysis.

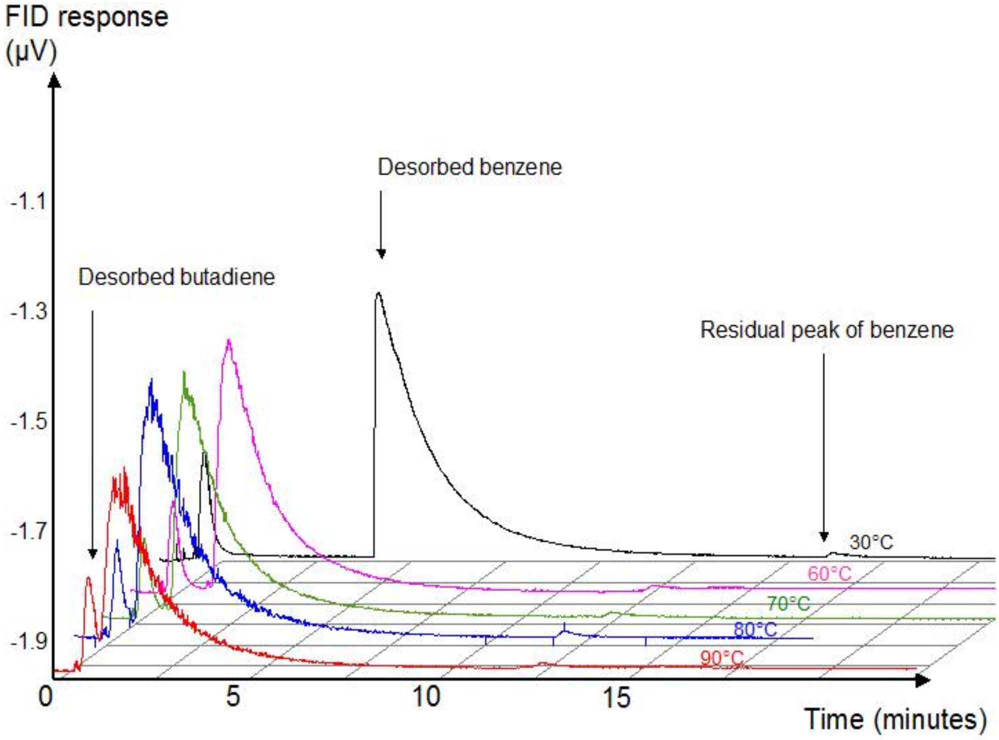
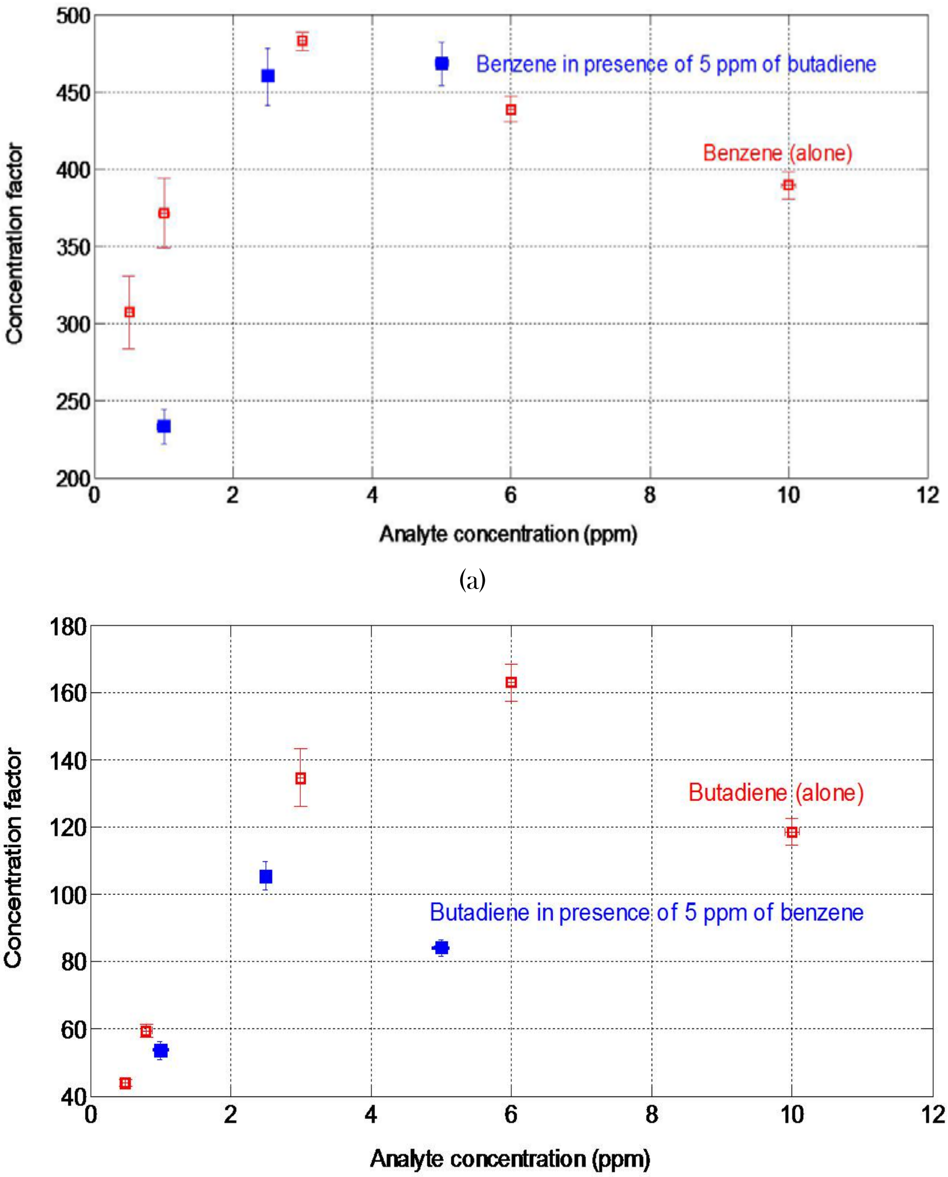


Figure 9: Chromatograms of the desorbed benzene and butadiene formerly mixed together, at different column temperatures.

Once the optimal column temperature was selected at 60ºC, the response of the system was studied towards different concentrations of the analytes in the mixture. For example, we fixed one concentration of an analyte (5 ppm) and we changed the concentration of the other. Concentration factors evaluated from these experiments are shown in Figure 10. When comparing the concentration factor curves of benzene (Figure 10.a) and 1,3 butadiene (Figure 10.b) separately and then in a mixture, we can notice a decrease of the adsorption capacity for both compounds when mixed. Looking at Figure 10, the system seems to be more adapted for concentrating benzene than 1,3 butadiene, due to an important decrease of the concentration factor for the latter compound. Also, the breakthrough for benzene occurs more or less at the same concentration (around 3 ppm), either when it's analyzed alone or in mixture with butadiene. However, for butadiene, the breakthrough took place earlier when this latter is mixed with benzene (around 3 ppm) compared to when it's alone (6 ppm).



(a)

(b)

Figure 10: (a): Evolution of the benzene concentration factor for various concentrations of benzene (empty squares: alone, full squares: in the mixture). (b): Same as (a) but for butadiene.

Once the optimal conditions for the simultaneous desorption of benzene and butadiene are fixed with the GC/FID system. The next study deals with the replacement of the FID detector by a metal oxide based gas sensor (TGS).

4.2.2. Step 2: Preconcentrator characterization with a classical GC and gas sensor

a. Description of the characterization set-up

The characterization setup was the same as in section 4.2.1 by replacing the FID detector with a commercial Figaro TGS-800 tin oxide-based gas sensor. In this case, the nitrogen carrier gas was replaced by synthetic air. The adsorption and desorption conditions are the ones adjusted before (section 4.2.1).

The effect of vapors on the sensor's electrical properties was recorded by monitoring the variation of the sensor's instantaneous conductance versus time, for a fixed temperature of the sensitive element (SnO_2). The electrical conductance of the layer corresponded both to the gas concentration and to the physical-chemical properties of the detected compound.

The response of the system was then calculated as the height at the maximum of the chromatographic peaks (By calculating the difference between the conductance value at the maximum of the chromatographic peak and the conductance at the position of the baseline). The effect of desorption temperature on the sensor response was also estimated by making a heating of the preconcentrator at 175ºC without previous gas adsorption.

The detection limit of the system was estimated as described in section 4.2.1. And again, in order to check the reproducibility of the results, each experiment was replicated 3 times.

b. Optimization of the system conditions

- Optimization of TGS sensing temperature

At first, we studied the response of the TGS at different sensing temperatures in order to have the shape of the TGS electrical response as close as possible to a chromatographic peak. For that, the concentration of benzene was maintained at 10 ppm, then the sensing temperature of the TGS was varied in the range from 270 ºC to 450 ºC. The highest and fastest response was achieved at 400 ºC.

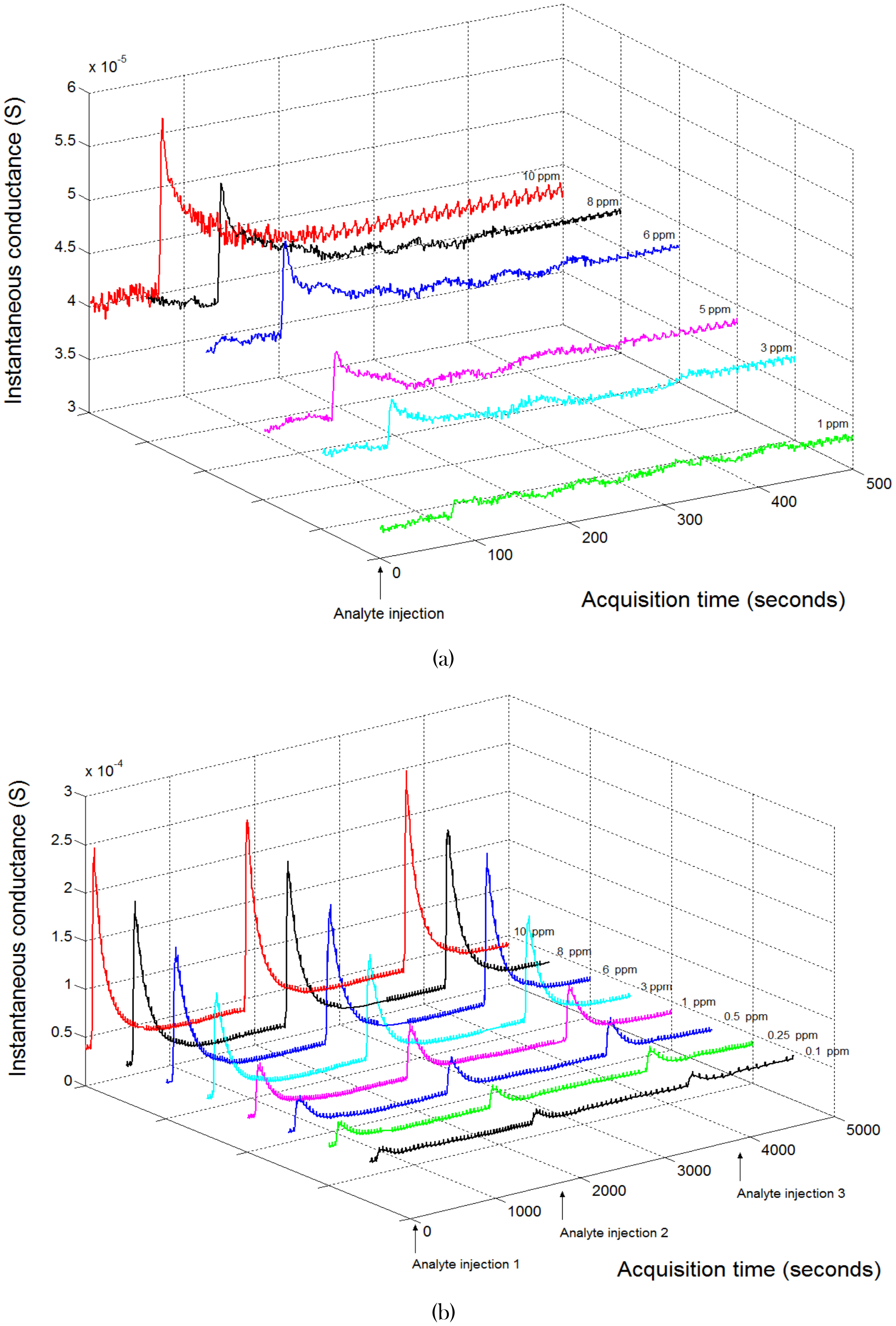
In fact, a previous work made by Sanchez et al., showed that the coupling between a chromatographic column and a SnO_2 gas sensor generates some experimental restrictions in order to have an electrical signal representative of each chemical compound contained in the gas sample [7]. Especially, this study showed that the sensor operating temperature must be high (400°C) in order to allow the successive detection of all compounds flowing outside the chromatographic column, and the carrier gas has to be rich in oxygen (synthetic air).

Then in the following study, the sensing temperature of the TGS will be maintained at 400ºC.

- Analysis of single analytes

Figure 11 shows the sensor's electrical response obtained for benzene detection: (a) without and (b) with the concentrator, at different concentrations, at a sensing temperature of 400ºC.

According to Figure 11 (a), the detection limit for benzene without the pre-concentrator is about 1 ppm. When the pre-concentrator was involved in the circuit (Figure 11(b)), the detection limit of benzene was lowered by at least 10 times. Besides, as can be seen in Figure 11 (b), the response of the system was quite repeatable with time. And the effect of desorption temperature on the sensor response was lower than 1 %.



(a)

(b)

Figure 11: (a) SnO_2-based detector reference peaks of benzene at different concentrations. (b) SnO_2-based detector desorption peaks of benzene at different concentrations, repeated 3 times

Once the system including the pre-concentrator, the GC column and the chemical gas sensor have been validated for benzene detection, the system has been studied for mixtures of 1,3 butadiene and benzene at equal proportion of both vapors in the mixture from 0.1 to 5 ppm in air.

For a GC column's temperature of 60ºC, the chromatographic peaks obtained were not clearly separated. This result may be due to the response time of the SnO_2-based gas sensor which is lower than the FID chromatographic detector. These new experimental conditions induced a new adjustment of the column temperature.

- Optimization of column separation temperature

So, we decided to study the influence of the GC column's temperature on the electrical responses of the TGS. From Figure 12, the separation was found to be better at lower temperature. Finally, a complete separation of the two peaks was achieved at 25ºC.

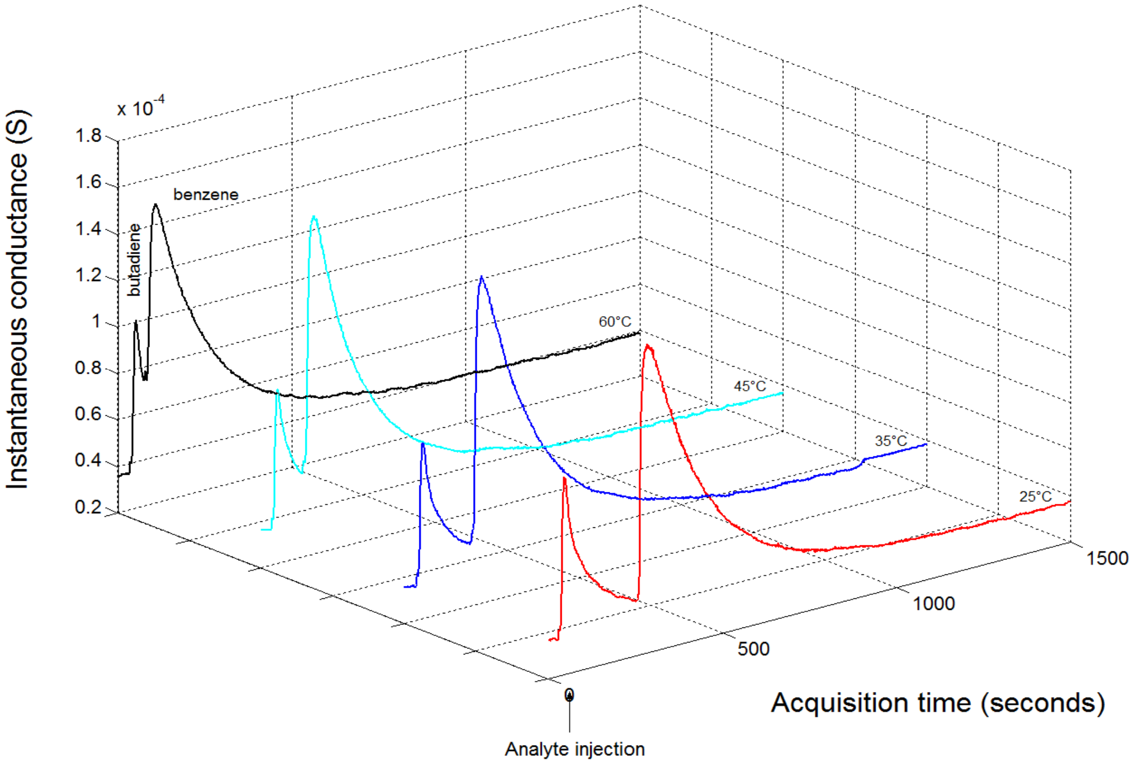
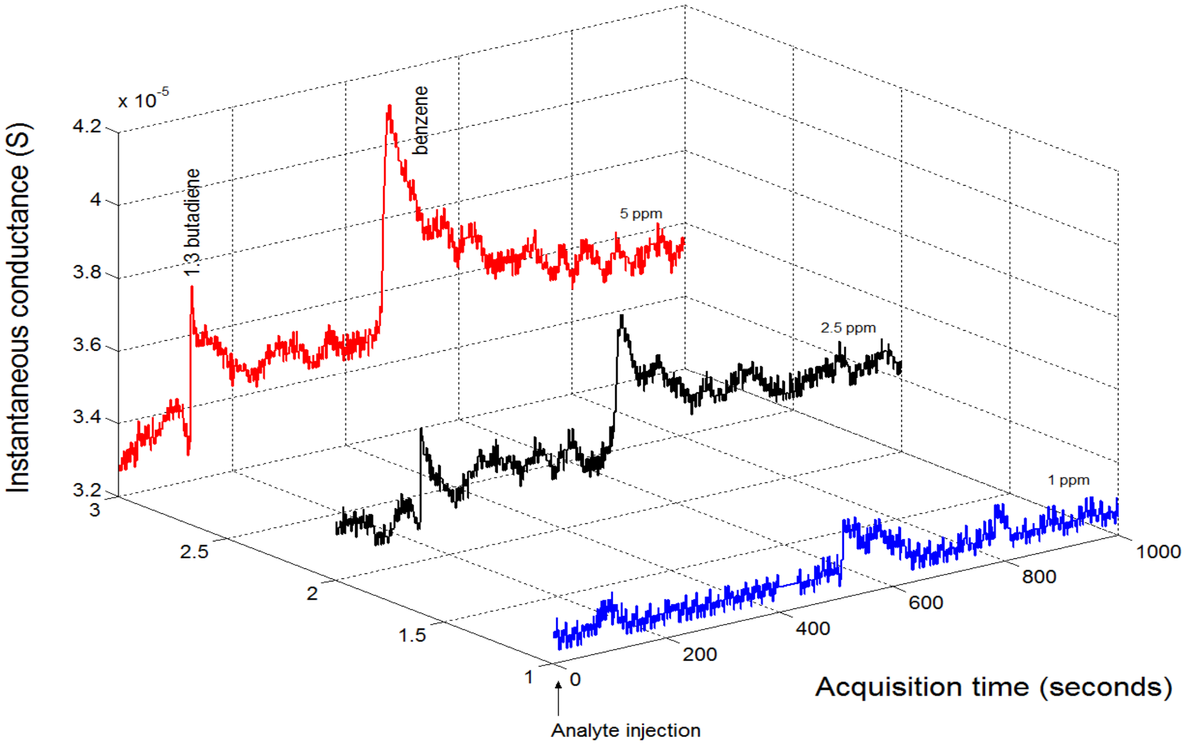


Figure 12: Desorption electrical responses of SnO_2-based gas sensor for benzene and butadiene at different column temperatures

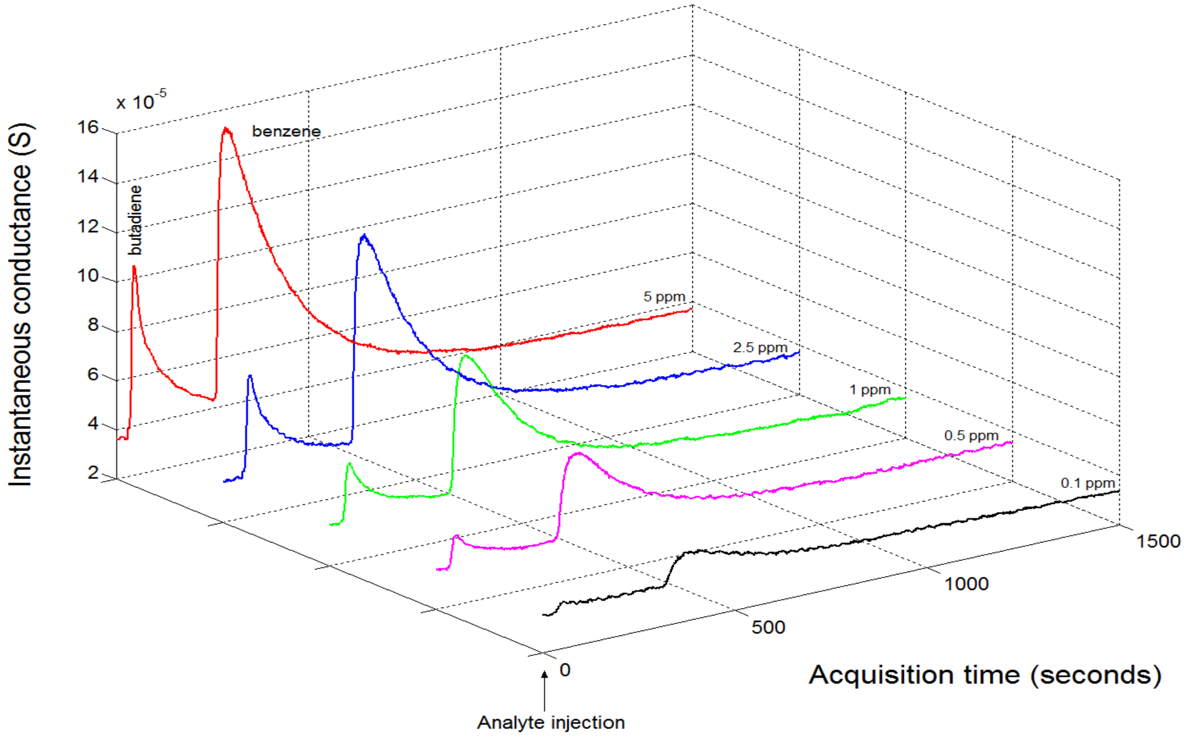
c. Analysis of benzene in presence of butadiene

So, we kept the column at 25ºC and then we studied the performance of the system towards the selective detection of benzene in the presence of 1,3 butadiene. Figure 13 (a) and (b) represent respectively the electrical response of the metal oxide gas sensor obtained for different concentrations of the analyte in the mixture, with and without pre-concentrator. From figure 13 (a), we noticed the selective detection of benzene and 1,3 butadiene with a detection limit about 1 ppm for benzene and 2.5 ppm for 1,3 butadiene.

With the use of the pre-concentrator unit, we can notice that the detection limit of the system was lowered by at least 5 times for butadiene and 10 times for benzene (0.5 ppm for the 1,3 butadiene and 0.1 ppm for benzene). We also notice well defined electrical responses with a small noise due the height of the chromatographic peaks. With the coupling of these three elements, it is possible to obtain the selective and sensitive detection of benzene and 1,3 butadiene. Each experiment was repeated with time using the same gas sensor and we did not observe any shift and variation in the electrical response of the SnO_2 gas sensor.



(a)



(b)

Figure 13: Electrical response of SnO_2-based sensor for the two analytes diluted in equal proportions, using a chromatographic column at 25°C (a) Reference peaks (b) Desorption peaks

From this study, we could notice the successful coupling of the preconcentrator with the GC column connected to the gas sensor.

4.3. Conclusion

In our working conditions, the direct coupling of the preconcentrator with the gas sensor didn't allow to well improve the response of the sensor towards benzene. Practically, an improvement factor of about three was obtained. This result is due to the too much rapid desorption kinetics of the preconcentrator which don't match with the slow response of the sensor and don't allow this latter to react sufficiently with the concentrated analyte, especially when a laminar configuration of the gas entrance into the sensor chamber is used.

By exchange, a successful coupling of a gas pre-concentrator, a gas chromatographic column and a commercial tin oxide based gas sensor was achieved for the analysis of benzene in presence of 1,3 butadiene:

- ✓ The preconcentration conditions for both analytes were optimized and selected step by step.

- ✓ We also showed that the pre-concentrator used in this study had more affinity for benzene than 1,3 butadiene.
- ✓ The results showed that it is possible to selectively detect benzene in presence of 1,3 butadiene with low power consumption by operating the column at 25 ºC. Moreover, the system based on SnO_2 gas sensor is cheaper and easier to be manipulated and seemed to be more performing in terms of detection limit and sensitivity than the FID towards benzene.
- ✓ Thanks to the use of the gas preconcentration unit, we were able to lower considerably the detection limit of the system, by at least 10 times. In particular, the detection limit of the system towards benzene and butadiene was lower than 100 ppb and 500 ppb, respectively.
- ✓ Moreover, we did not observe any shift in the response with time (after several experiments).

The present study clearly encourages pursuing the development of a miniaturized analytical platform composed by a pre-concentration unit coupled with a GC microcolumn and a miniaturized metal oxide-based gas sensor. Next chapter will deal with the development of the silicon microconcentrator and its testing with a spiral silicon microcolumn in front the TGS tin oxide gas sensor for the analysis of benzene in presence of butadiene.

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Chapter 5. Development of the silicon microhotplate based pre-concentrator and its application with a microchromatographic system for benzene monitoring

In this chapter, we present the development of the microconcentrator, including the adjustment of the deposition conditions of activated carbon and the check out of its preconcentration capability towards benzene.

Finally, the microconcentrator performance is validated as injection unit in front of a silicon micro-column connected to a metal oxide (MOx) gas sensor for the sensitive and selective analysis of the mixture of benzene in presence of butadiene, on the basis of the previous optimization of the system presented in the chapter 4.

5.1. Adsorbent deposition

The microfabricated device is based on a planar membrane of a total area of 2 mm x 4.5 mm and a heater active area of 1.5 mm x 4 mm. Details about the fabrication and thermo-electrical characterisation of the membrane are available in Annex I, section 1.2.2.

As already mentioned in chapter 1, this structure was selected for its simpler fabrication technology and better thermal isolation than the 3 D structures reported in the literature. The design of the heater was already optimized to have a homogeneous distribution of temperature in the heater active area with good electro-thermal features [1-3], allowing a low power consumption (1.02 mW/ºC).

Although this structure can't host as high amount of material as 3 D microconcentrators, good preconcentration capacity is expected to be achieved by taking profit from the high adsorption capacity of activated carbon, which was selected on the basis of the results presented in the previous chapters.

5.1.1. First deposition trials by airbrushing

On the basis of chapter 2, the activated carbon is to be deposited by air-brushing technique over the microhotplate membrane. The first deposition trials consisted of checking the mechanical resistance of the backetched membrane to the airbrushing conditions. These trials were made on a microfabricated backetched membrane of a total area of 3 mm x 3 mm (corresponding to an active area of 2.5 mm x 2.5 mm), with no heater deposited on the top and no silicon plug.

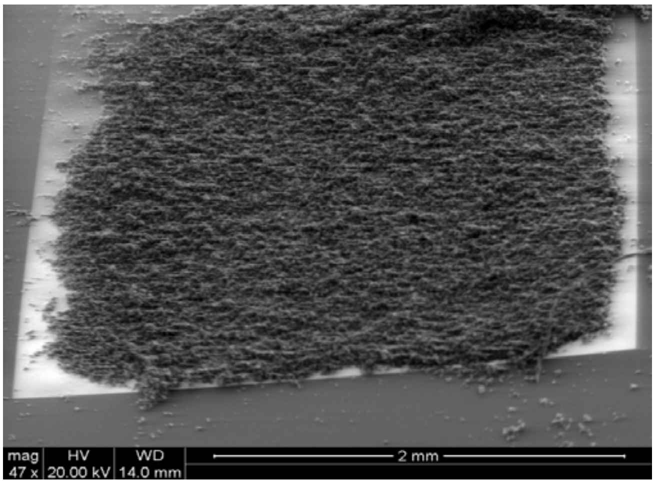


Figure 1: ESEM image of activated carbon airbrushed over a microfabricated membrane

By adjusting the airbrushing parameters (Table 1), we achieved a homogeneous layer of 0.2 mg of activated carbon well adhered to the membrane, as could be observed in figure 1. When this amount is overpassed, the adhesion of the material to the membrane starts to be affected.

The same parameters were then applied to airbrush the carbon over the microhotplate membrane. However, a mechanical lift off of the suspended membrane from the silicon substrate occurred during airbrushing. Figure 2 shows a picture of the membrane after the deposition trial. This problem is attributed to the stress induced by the silicon plug diffuser placed under the heater membrane. In fact, the high pressure imposed by the spray air flow used during the airbrushing process induced a mechanical lift off just in the plug frontier and no breakdown of the membrane was observed.

Table 1: Airbrushing parameters of activated carbon over the silicon microfabricated membrane

Suspension concentration	**Nitrogen flow (ml/min)**	**Distance nozzle-substrate (cm)**	**Evaporation temperature (ºC)**	**Airbrushed volume / deposited weight**
20 mg of carbon per millilitre of pentane	6	3 - 3.5	100	30 ml/ <0.1 mg 80 ml / 0.2 mg

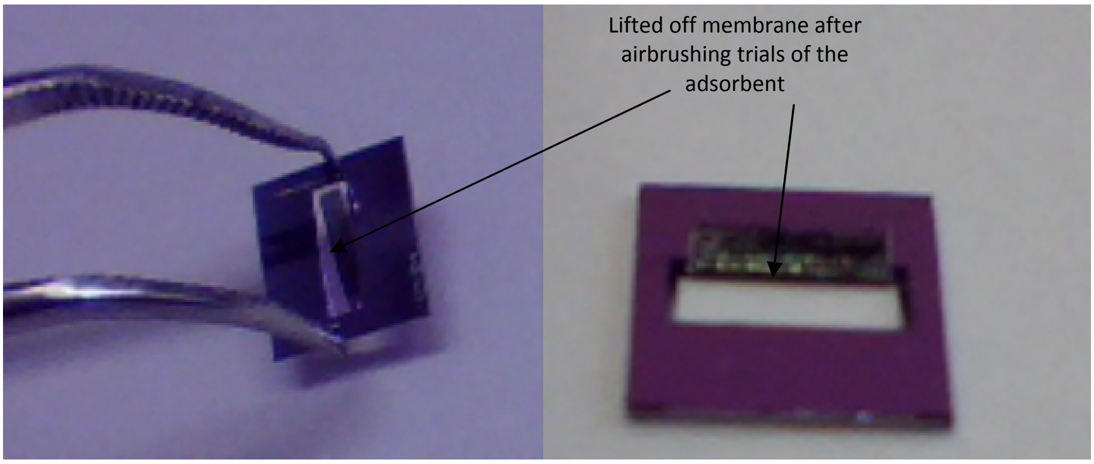


Figure 2: Picture of the lifted off layer after the trials of activated carbon deposition by air-brushing

5.1.2. Deposition by drop coating

In order to avoid this problem, the adsorbing layer was drop coated. Doing so, the quality of the deposition is not as high as that of airbrushing technique, but it is gentler and doesn't require any mechanical force to deposit the material over the membrane.

So, a suspension was prepared by mixing the activated carbon powder with glycerol by an optimized ratio of 0.5 mg per µL. Five microliters of the resulting paste were drop-coated over the heater area of the microhotplate membrane, previously encapsulated in a TO8 package, using an automatic drop coating system equipped with a dispenser. The total amount of adsorbent deposited was 0.25 mg.

Even if it would have been possible to use the airbrushing, the maximum amount of material which it could be deposited over the 6 mm^2 of the silicon membrane wouldn't be higher than 0.2 mg. Otherwise, the adhesion of the material starts to be affected, as was already confirmed in the initial trial of airbrushing performed on the membrane of an area of 3 x 3 mm^2. Therefore, in this case, the drop coating method allows depositing a higher amount of material than the airbrushing.

After the deposition, the layer was submitted to a thermal treatment which was carefully optimized in order to completely evaporate glycerol from the activated carbon pores as well as to promote the adhesion of the deposited area to the membrane. With this aim in view, two drying processes were performed. A first drying was carried out in air at 110ºC during 15 min, followed by a second drying at 300ºC during 2 hours. For both, a heating and cooling rate of 2.3ºC/min was used by application of a voltage ramp to the heater resistor using a Keithley source 2410. The rate was selected to be the slowest possible for avoiding cracks in the deposited layer. The second drying step was performed in an inert atmosphere by placing the microconcentrator inside a stainless steel chamber (Annex I, section 1.2.2) flushed by nitrogen at 50 ml/min.

5.2. Characterization of the preconcentrator towards benzene in presence of toluene

The adsorption capacity of the fabricated preconcentrator was tested first for benzene and then in presence of toluene using the same characterization procedure presented in chapter 3.
Also, the selective desorption of both vapors was again checked with this new preconcentrator in the same conditions as before.

5.2.1. Preconcentration performance towards benzene and toluene

Figure 3.a shows a picture of the adsorbing layer deposited over the microhotplate packaged support after being submitted to the thermal drying process.

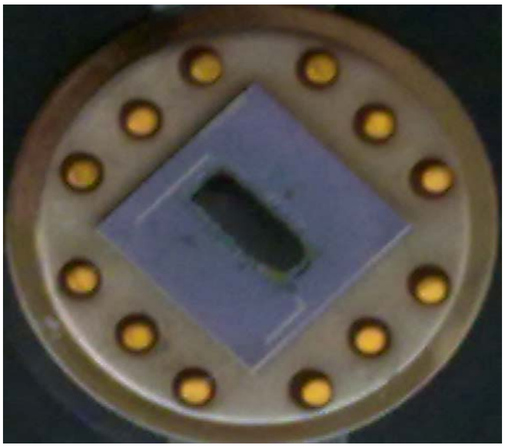


Figure 3: Picture of packaged microhotplate with a layer of activated carbon drop coated over the membrane after the thermal treatment

a. Study of the microconcentrator adsorption capacity towards benzene and toluene

The desorption peaks of benzene obtained at different concentrations are plotted in figure 4. A first small peak appears at 1.5 min, due to the injection of the analyte remaining in the preconcentrating chamber before starting analyte desorption. The second peak, which appears after the heating start, is not only due to the desorption of the analyte from the preconcentrator but also to its dilution in the dead volume of the gas chamber and the connections to the MS. Despite the dilution effect, it's clear that desorption of benzene from the preconcentrator is completed in less than 3 min, which is a quite narrow injection pulse that will be especially useful for applications with microchromatographic detection systems. The desorption duration can be even decreased to much less than 2 min. Using such conditions, almost all the adsorbed vapor will be released and less than 1 % of the analyte will remain in the preconcentrator (cf. Figure 4).

Figure 5 shows the calibration curve of the MS response towards the reference peaks of benzene and toluene versus their concentration, while figure 6 presents the concentration factors obtained for different initial concentrations of the analytes. As could be clearly seen from these figures, very good adsorption capacities towards both vapors were obtained, reaching concentration factors higher than 250 with no visible saturation of the adsorbent. The concentration factor increases linearly with a rate of 0.10 and 0.05 per ppb of benzene and toluene respectively. Then in real conditions, for which the concentration of VOCs should be less than 100 ppb, the error for the quantification of benzene from the preconcentrator calibration curve will be negligible.

In chapter 3, the same study was performed using 0.2 mg of the same adsorbent deposited by airbrushing onto 16 mm^2 of the alumina support [3]. If we compare the results obtained in figure 7 with the same results obtained in figure 3 of chapter 3, we can observe that at concentrations lower than 400 ppb, the concentration factors obtained with both concentrators towards benzene and toluene are quite similar, although the amount of the adsorbent used in both cases is not the same (0.2 mg for the alumina and 0.25 mg for the microhotplate). This observation is due to the higher dead volume of the microconcentrator chamber, compared to the alumina based preconcentrator chamber (cf. Annex I), which causes more dilution of the analytes, resulting in a concentration factor lower than expected.

However, at higher concentrations, a drop of the concentration factor for benzene is observed with the alumina preconcentrator (cf. Figure 3, chapter 3), indicating a saturation of the adsorbent (0.2 mg). By contrary, the concentration factor of the microconcentrator increases linearly with no visible saturation of the adsorbent, due to the higher amount of the adsorbent deposited (0.25 mg).

Figure 7.a and b, show a comparison of the desorption peaks obtained with the microconcentrator and the alumina based preconcentrator for 150 ppb of benzene and the corresponding desorption temperature profile at 190ºC used in both cases, respectively. It's clear from the figure, that the width at half maximum of the desorption peak obtained with the microconcentrator is much smaller than that of the alumina based preconcentrator. This difference is due to the faster thermal response (Fig 7.b) of the silicon microhotplate and the good temperature homogeneity in its active area, by contrast to the poor thermal insulation of the heater of the alumina based preconcentrator, and the thermal inertia of the alumina substrate, which slows the desorption kinetics of this latter.

For both concentrators, the total width of the desorption peak is less than 2 min. However, the higher dead volume of the micrconcentrator chamber causes the dilution of the desorbed analyte which results in a broader desoption peak. In the future, when the microconcentrator will be covered with the pyrex tape, the dead volumes will be much more reduced, the desorption peak will be much narrower and the concentration factors will be increased.

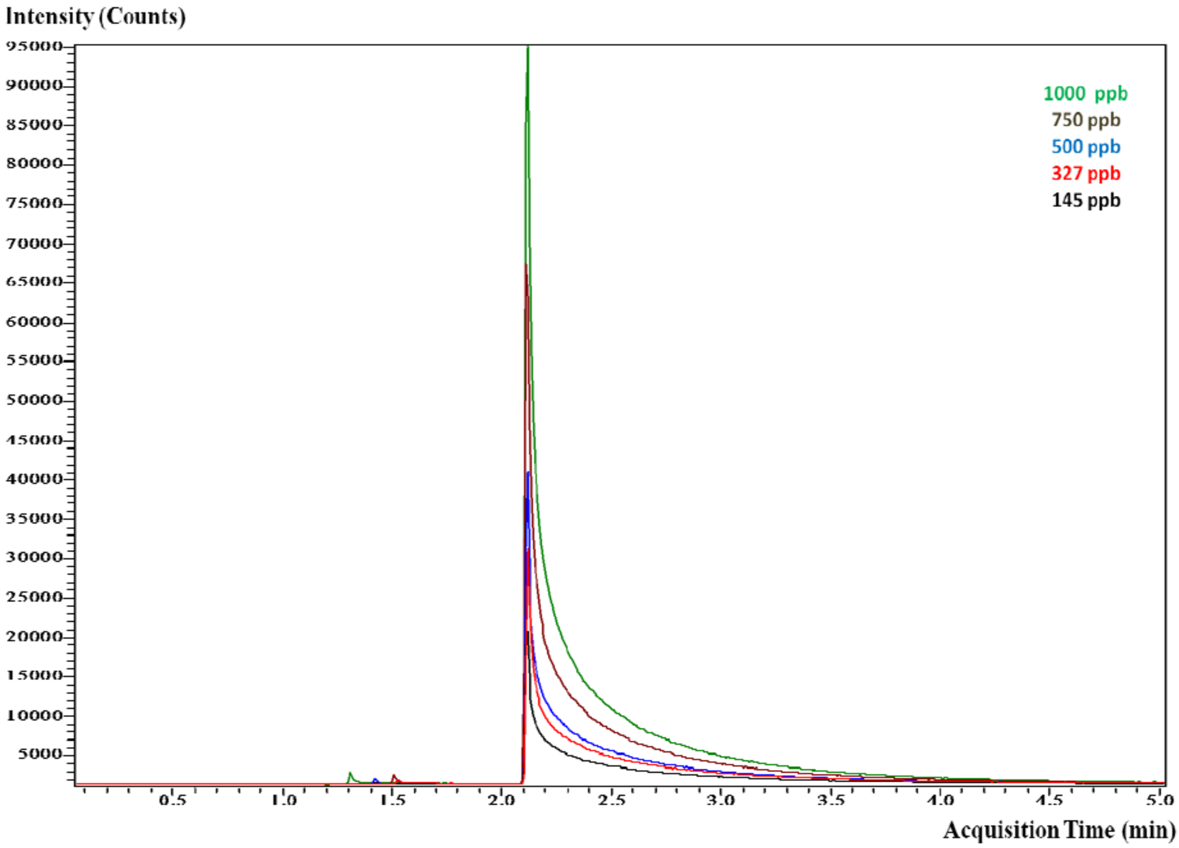


Figure 4: Desorption peaks of benzene at different initial concentrations

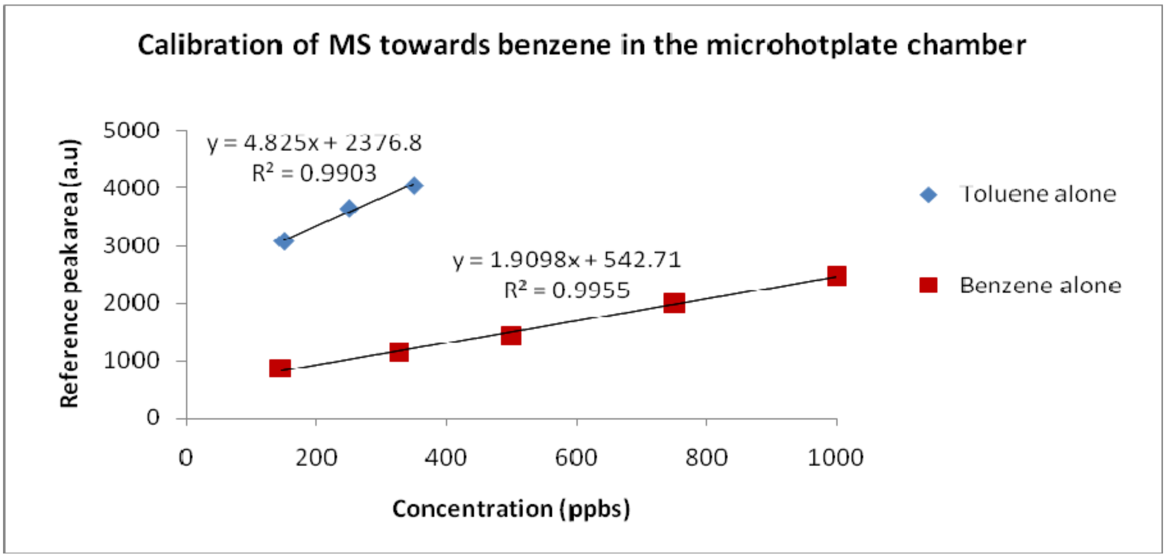


Figure 5: Calibration curve of the MS towards benzene and toluene analyzed separately

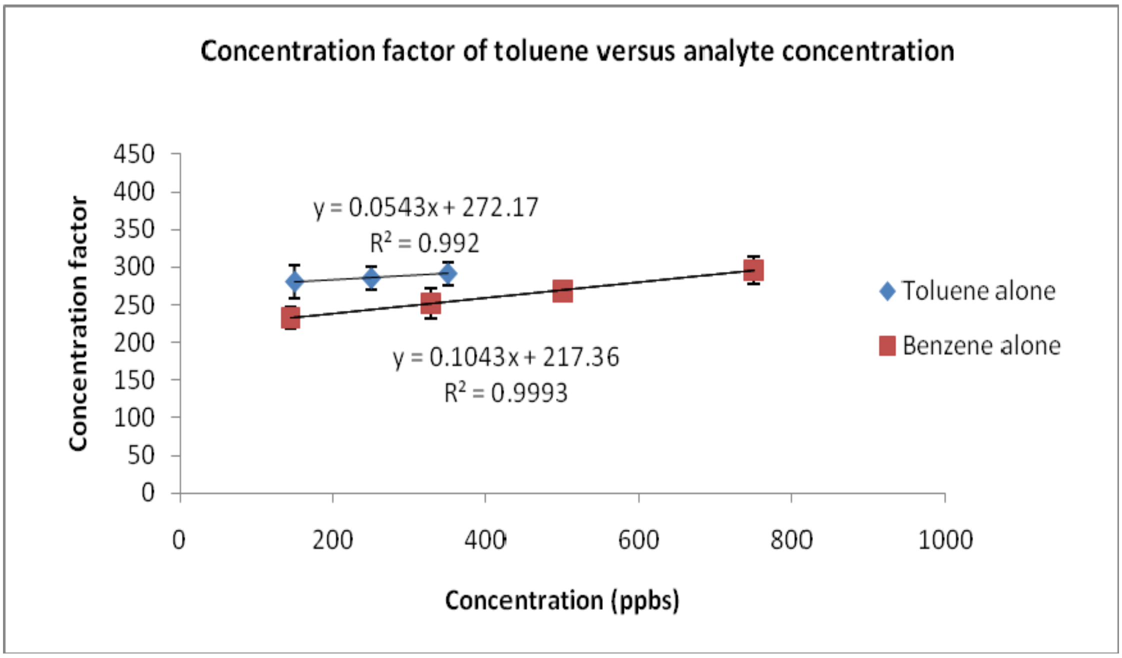
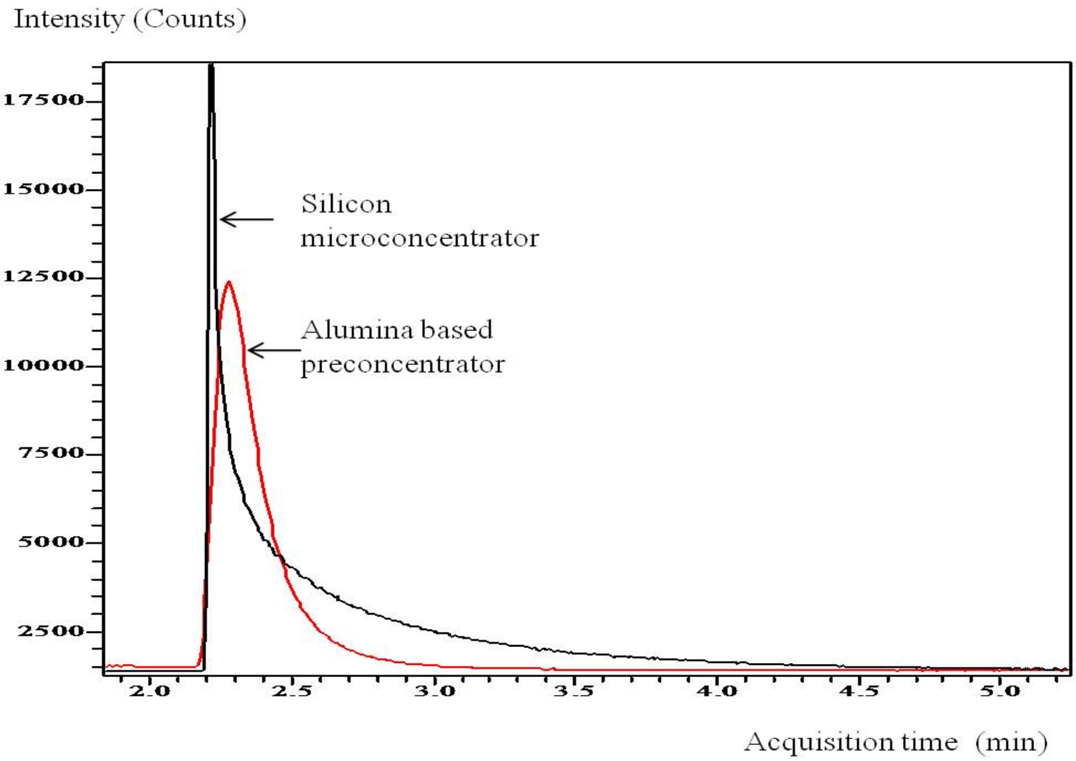
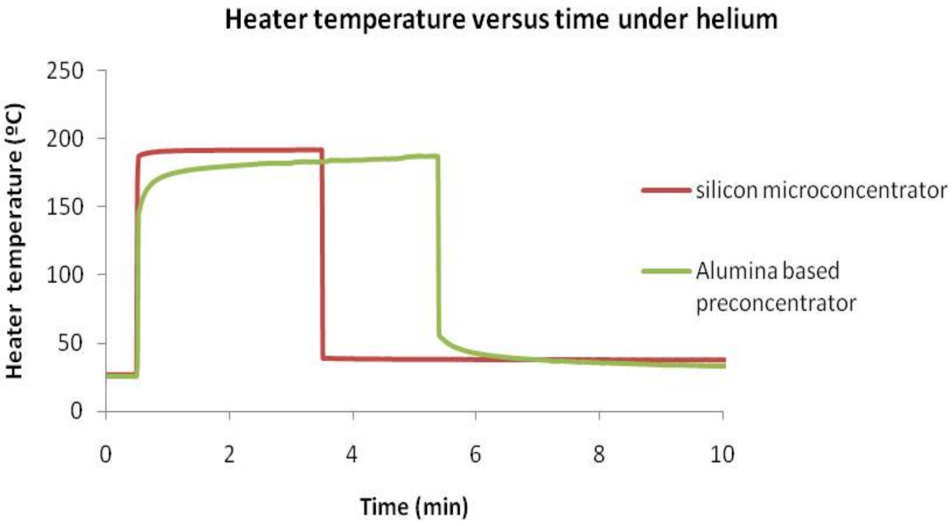


Figure 6: Concentration factors for benzene and toluene analyzed separately



(a)



(b)

Figure 7: (a) Desorption peaks of 150 ppb of benzene using the alumina based preconcentrator and the silicon microconcentrator (b) Corresponding desorption heating profiles

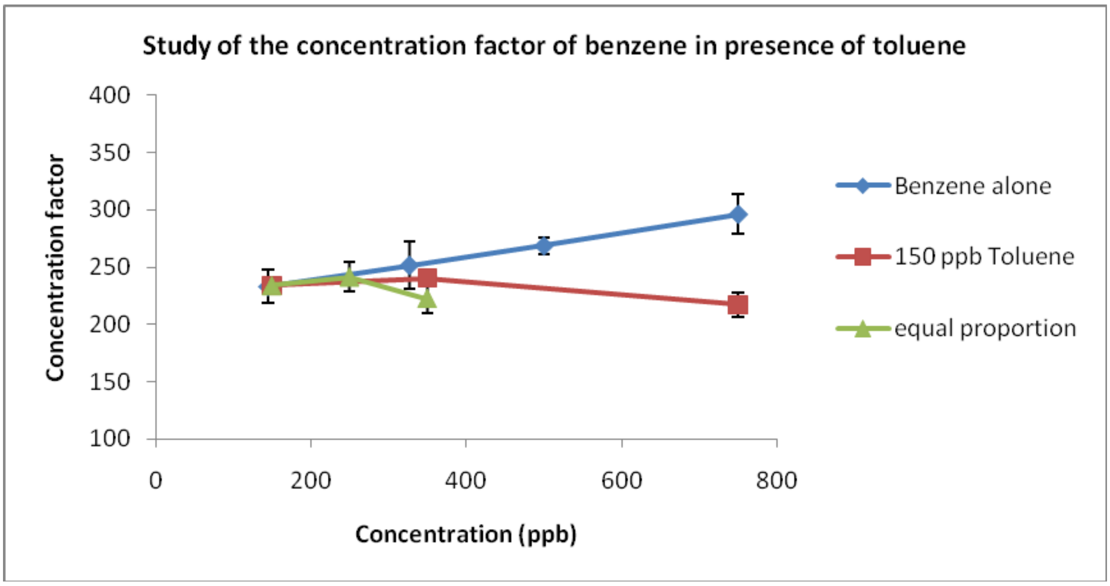
b. Study of the mutual adsorption interference between benzene and toluene

Figure 8.a shows the study of the adsorption capacity of benzene at different initial concentrations in presence of toluene, at equal proportion and at a fixed concentration of 150 ppb of toluene. It can be clearly seen that the adsorption capacity of benzene decreases in the presence of toluene. However, this decrease is insignificant for concentrations lower than 300 ppb, when the mixture is analysed at equal proportion or when the concentration of toluene is maintained at 150 ppb.

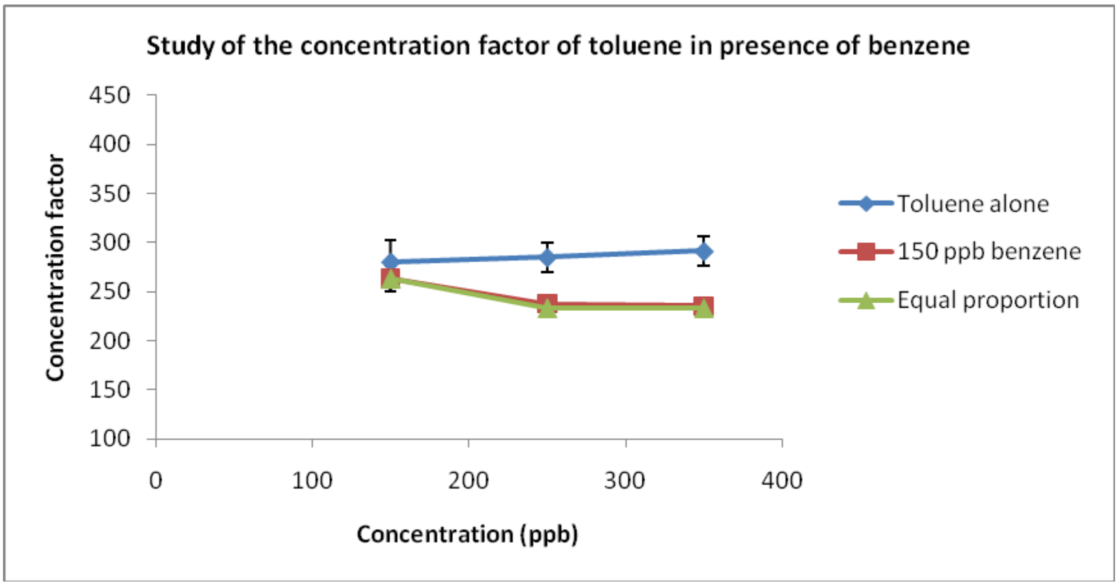
The same study was repeated with toluene in presence of benzene (Fig 8.b). The adsorption of toluene seems to be slightly more affected by the presence of benzene, than benzene in presence of toluene, for concentrations higher than 150 ppb.

It can be expected that the adsorption interference effect between benzene and toluene will be negligible, provided that the concentration of both vapors in a mixture remains lower than 100 ppb. The occurrence of such low concentrations is expected in real application.

Again, as in chapter 3, the micro-concentrator designed here could be used to concentrate either benzene or toluene or both, irrespective to the proportion of these vapors in real conditions. The quantification of both vapors could be predicted from the calibration curve of the pre-concentrator with an accuracy higher than 90 %.



(a)



(b)

Figure 8: Concentration factors of the mixture of (a) benzene in presence of toluene (b) toluene in presence of benzene

5.2.2. Selective desorption of benzene in presence of toluene

As in chapter 3, the separation of benzene in presence of toluene was tried using either linear ramps or two-step temperature desorption profiles.

When using linear ramps, different rising times to 190ºC were tested in the range of 0.5-120 min. Figure 9 shows an example of the desorption peaks of benzene and toluene obtained with a rising time of 60 min. As much as the rising times increases, the peaks are more separated. However, this separation is not enough for to be reflected in the total peak.

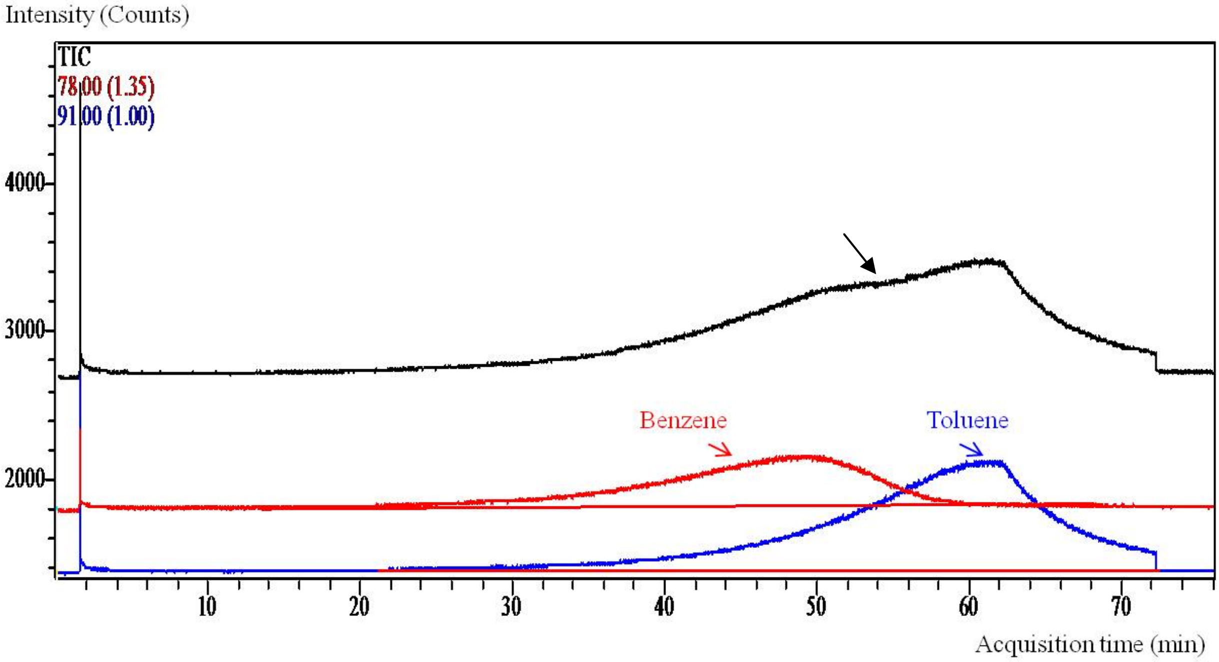


Figure 9: Desorption peaks of benzene and toluene obtained using a linear ramp desorption profile of 3.16 ºC/min to 190ºC

Then the two-step profile was tested, in this case, the first step was directly set at 60ºC and the second step at 110ºC, followed by a residual desorption at 190ºC to evaluate the remaining amount of benzene in the preconcentrator.

For the first step, we varied the heating duration from 10 to 60 min in order to evaluate the time needed to completely desorb benzene during the first step.

It was then observed that toluene desorbed also at 60ºC, together with benzene. This was not expected because 60ºC is the initial desorption temperature of benzene, and toluene having a boiling point 30ºC higher than benzene, mustn’t then desorb at this temperature.

With this profile, even by increasing the first step heating duration to 60 min, the desorption of benzene wasn’t complete (Fig. 10).

Consequently, lower temperature could perhaps help to separate the desorption peaks of both compounds, however, the separation will not be practical for the real application, since a time much higher than 60 min will be required to desorb completely the compounds.

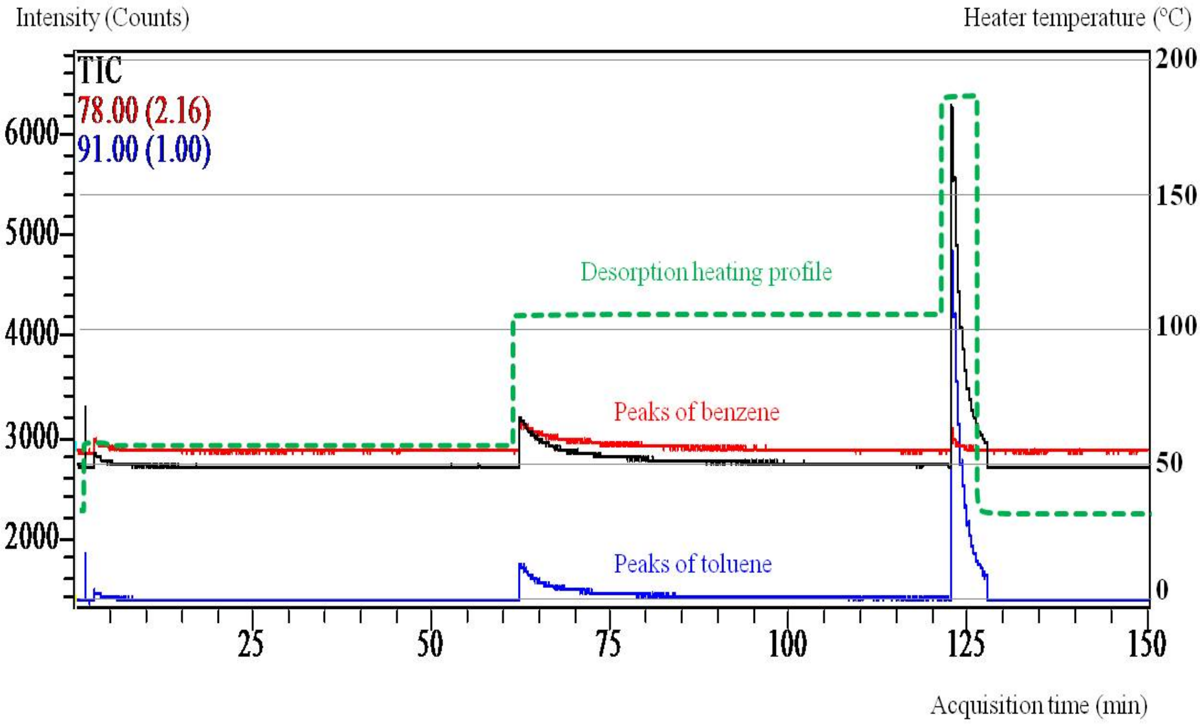


Figure 10: Desorption peaks of benzene and toluene obtained using a a two-step desorption profile at 60ºC during 60 min and 110ºC during 60 min

The selective desorption of benzene and toluene was expected to be ameliorated when the microhotplate microconcentrator is used, compared to the results obtained with alumina in chapter 3. In fact, following the results obtained by Inglés et al., an excellent temperature homogeneity was obtained using this microconcentrator thanks to the good design of the heater and the presence of the silicon plug under the membrane [1-3]. However, this homogeneity could be affected when the adsorbent is deposited on the top. In this case, if the delimitation of the adsorbing area above the heater area is perfect, then activated carbon seems to improve more the homogenisation of the temperature, since it's a good thermal conductive material. However, when the deposited area overpasses the heater area, the activated carbon outisde of the heater area remains at ambient temperature, then affects the heating temperature homogeneity of the remaining portion of the adsorbent in the active area.

To obtain a homogeneous heating of the adsorbent, the adsorbent deposition must be well adjusted over the active area. With drop coating, we don't unhopfully have such good control, since the deposited paste spreads after the thermal heating process. It would have been helpful to use the airbrushing technique to deposit the material, because the use of the shadow mask may allow a better control of the deposition. However the mechanical breakdown of the membrane remains an obstacle to achieve this goal.

Since no separation is possible with the microconcentrator, the separation will be achieved by connecting the microconcentrator in front of a silicon GC microcolumn connected to a metal oxide gas sensor.

5.3. Selective detection of benzene in presence of 1,3-butadiene using the gas micro-concentrator in front of a micro-GC column connected to a metal oxide gas sensor

As already explained in chapter 4, the aim of this coupling is to build a miniaturized system able to selectively detect traces of volatile organic compounds in air. In particular, this study was applied to the detection of benzene in presence of 1,3 butadiene vapor. The optimization of the preconcentrator working parameters was presented step y step. And the successful role of the preconcentrator based an alumina, when coupled to a classical capillary column connected to a gas sensor, was demonstrated by lowering considerably the detection limit of the system towards benzene.

With this aim in view, the preconcentrator and the chromatographic column will be replaced by their miniaturized version based on silicon microtechnology, which are respectively the microhotplate preconcentrator presented in this chapter and a silicon microcolumn developped in the "Laboratoire de Physique, Chimie et Rayonnements-Alain Chambaudet", in France. This microcolumn was already demonstrated to eluate selectively benzene in a mixture with other VOCs at a temperature near the ambient [4]. Now, we will check the performance of the preconcentrator and its effect on the operation of the microcolumn in these new conditions.

5.3.1. Description of the characterization set-up

The system studied in the present work is composed by the microhotplate preconcentrator, a GC silicon micro-column and the commercial metal oxide Taguchi gas sensor TGS-800 (Fig. 11). The three units were connected to each other using the characterization circuit already presented in chapter 4, section 4.2.2. .

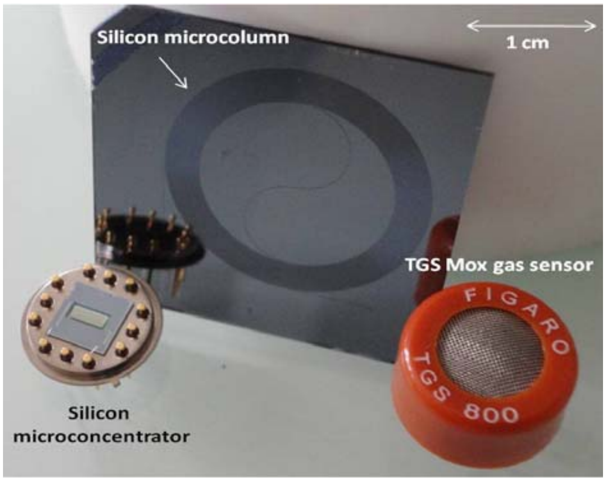


Figure 11: picture of a commercially available metal oxide gas sensor (TGS gas sensor from Figaro) in front of a GC micro-column and the gas micrconcentrator realized in this study.

The general geometry selected for the microcolumn is a circular spiral with a 50 µm-wide, 50 µm -deep and 2 m-long channel (Fig. 11). For this study, a Polydimethylsiloxane (PDMS) stationary phase was selected on the basis of a previous work reported by Sanchez et al., where it showed the best elution and separation performances for the analyis of VOCs in a mixture [4]. More details about the fabrication of the microcolumn are available in Annex II.

The characterization measurements of the system were carried out following the same protocol described in chapter 4, section 4.2.2. Just to remind, the adsorption conditions were fixed at a flow of 100 ml/min and a duration of 10 min. And the desorption was performed at 175ºC during 5 min. The microcolumn temperature was kept at 25ºC and the sensor temperature at 400ºC, in order to have a best elution of the analytes and a response of the system as close as possible to a chromatographic peak, respectively [5].

The response of the system and its detection limit were evaluated with and without the pre-concentrator, towards each analyte separately and then in a mixture of both analytes in air. To check the result reproducibility, each measurement was replicated three times for each analyte concentration.

5.3.2. Analysis of single vapors

a. Calibration of the system

Following [6], the efficiency of the microcolumn depends on two main parameters, the column temperature and inlet pressure. As said before, the microcolumn temperature was kept at 25ºC. In order to select the optimal elution pressure of benzene, the system response to the desorbed analyte, at a fixed initial concentration of 10 ppm of benzene was studied for different column inlet pressures.

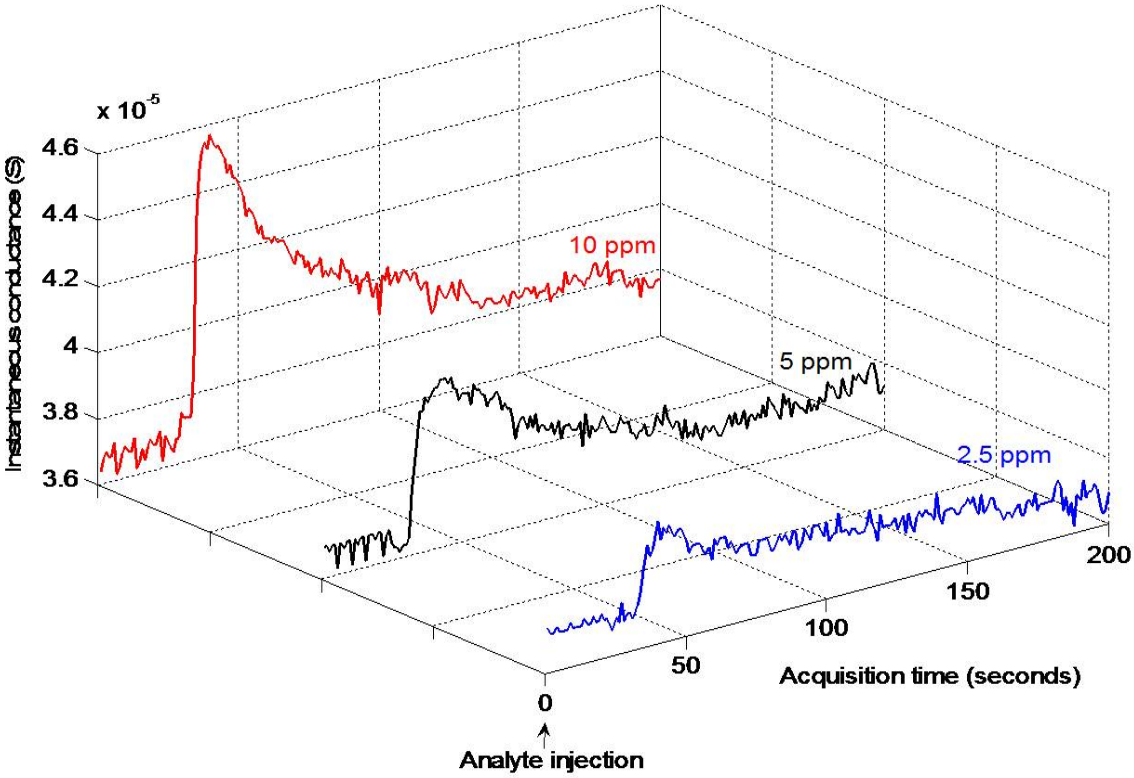
The optimal column elution pressure for benzene was found to be 4.5 bar, corresponding to a column flow of 0.9 ml/min. At this pressure, we noticed the appearance of the corresponding peak of benzene at a retention time of 30 seconds.

This pressure was then kept constant for the analysis of benzene and butadiene at different concentrations.

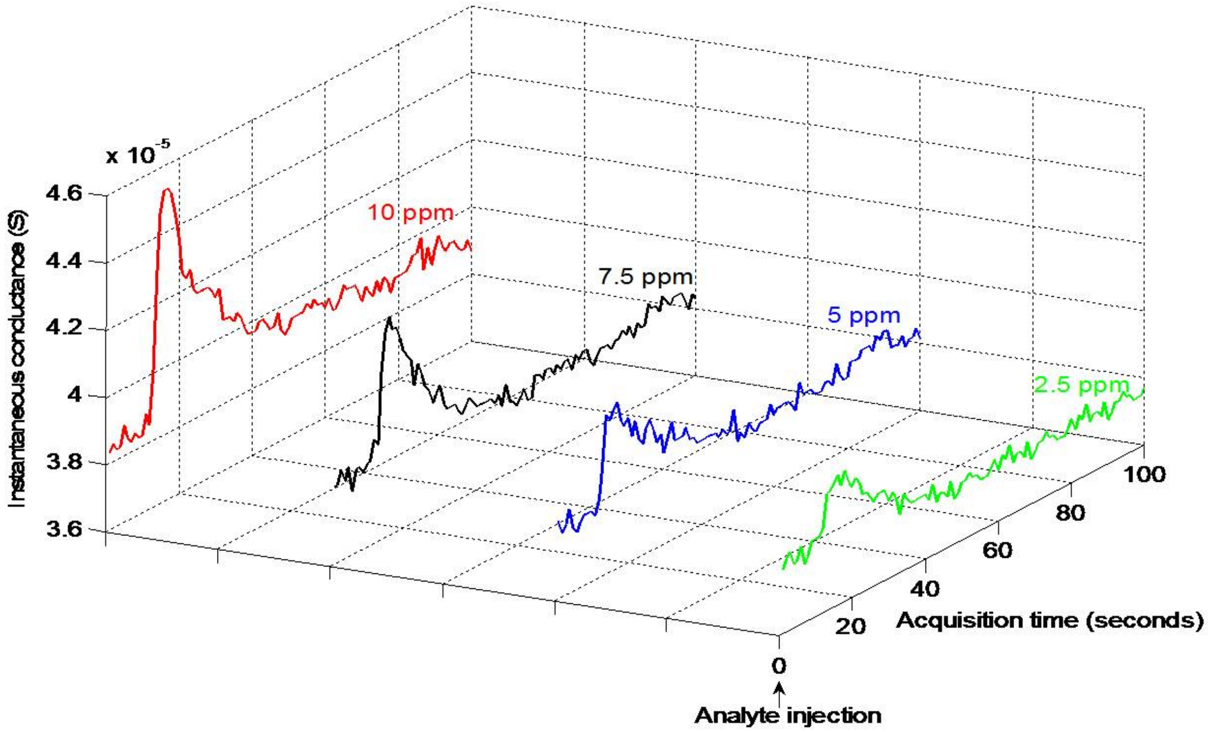
This consisted in analyzing each chemical compound separately with and without the use of the pre-concentrator. In the case of the reference benzene (without preconcentrator), no response of the system was noticed in our working conditions for concentrations of benzene up to 10 ppm. By contrast, when using the preconcentrator, the detection of this compound became possible. Figure 12.a represents an example of the chromatographic peaks obtained for the analysis of desorbed benzene at different initial concentrations ranging from 2.5 to 10 ppm.

By analyzing butadiene in the same conditions, no response of the system was noticed towards reference butadiene. Thanks to the preconcentrator, the detection of this compound was again possible. Figure 12.b shows the chromatographic peaks obtained for the analysis of desorbed butadiene at different concentrations ranging from 2.5 to 10 ppm. From this figure, we noticed the appearance of butadiene at a retention time of about 10 sec.

We can observe that for both analytes, the analysis of butadiene and benzene was completed in less than 1 min and 3 min respectively, which are quite short time analysis.



(a)



(b)

Figure 12: Chromatographic peaks of desorbed benzene (a) and desorbed 1,3 butadiene (b) analyzed separately

The calibration curves (height of the peak) of desorbed benzene and 1,3 butadiene, analyzed separately, versus their concentrations in air, were then plotted and represented in figure 13 . From these graphs, we can observe the linear behavior of the system response versus the concentration of the analytes analyzed separately with detection limits of 2.5 ppm for butadiene and under 2.5 ppm for benzene. Also, the system seems more sensitive for benzene than for butadiene, which agrees with the results the derived from chapter 4. This is due, on one side, to the more affinity of the adsorbent for benzene than for butadiene and on the other side, to the higher sensitivity of the TGS for benzene than for butadiene.

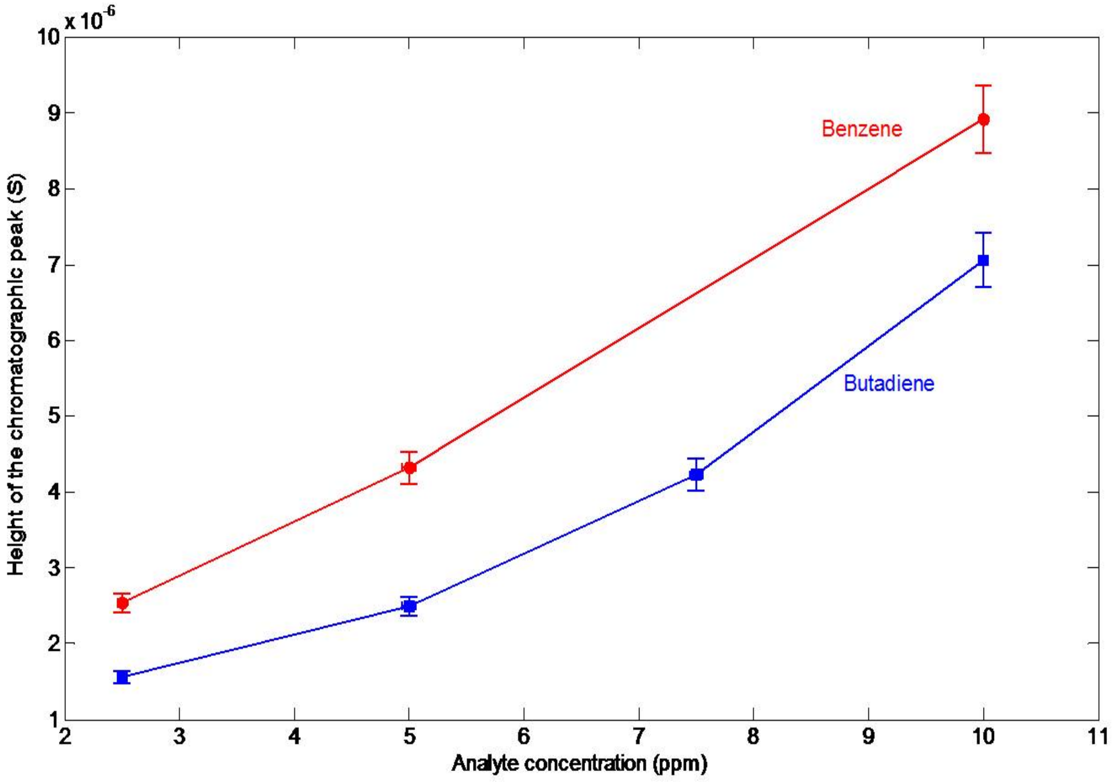


Figure 13: calibration curves for benzene and 1,3 butadiene analyzed separately

5.3.3. Selective detection of benzene in presence of butadiene

After checking the elution of each analyte separately, we analysed both analytes present simultaneously in the sample with a concentration equal to 5 ppm for each compound. The influence of the inlet column pressure on the separation of each analyte is represented in figure 14. Following this figure, the optimal separation of the analytes is again obtained at 4.5 bar.

This pressure is then fixed for the analysis of the mixture of both analytes at different concentrations in equal proportion. Figure 15 represents the chromatograms of separation of benzene and butadiene at different concentrations. From these chromatograms, we evaluated the detection limit of 1,3 butadiene at about 2.5 ppm, while the detection limit of benzene seems to be under 2.5 ppm.

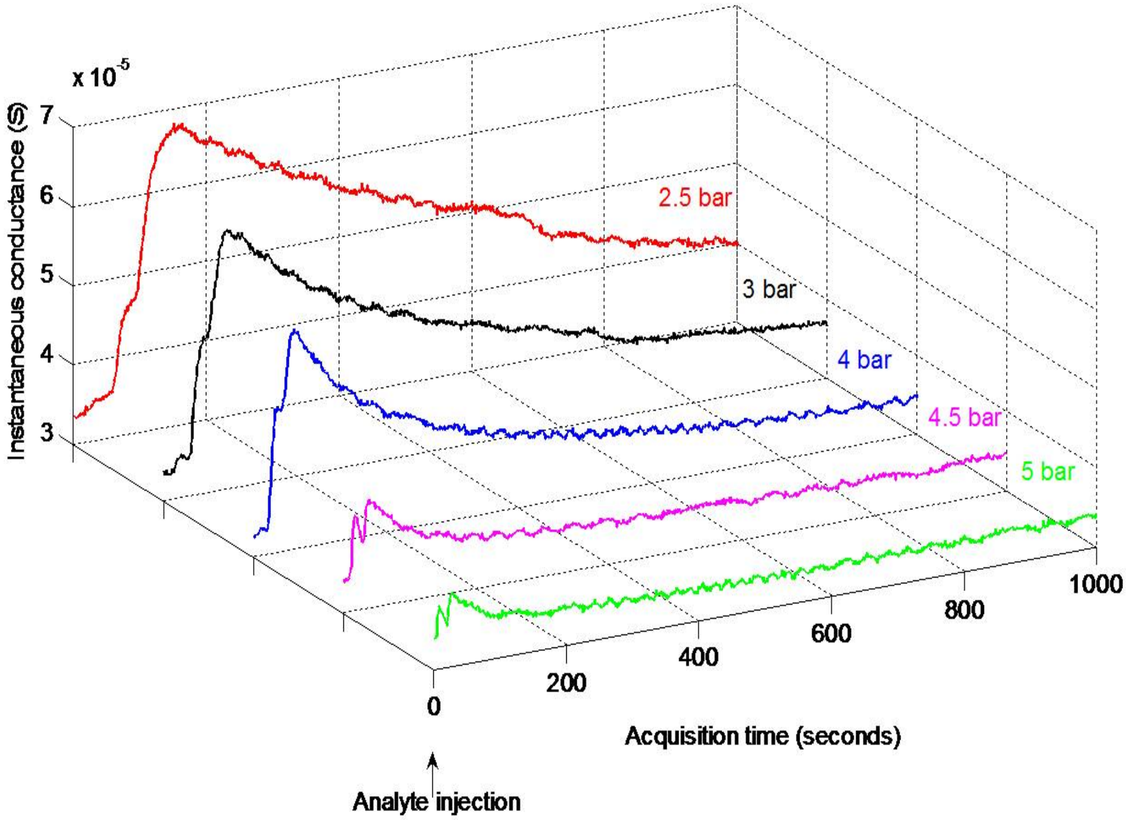


Figure 14: Chromatograms of the separation of 5 ppm of the mixture of benzene and butadiene at different column inlet pressures

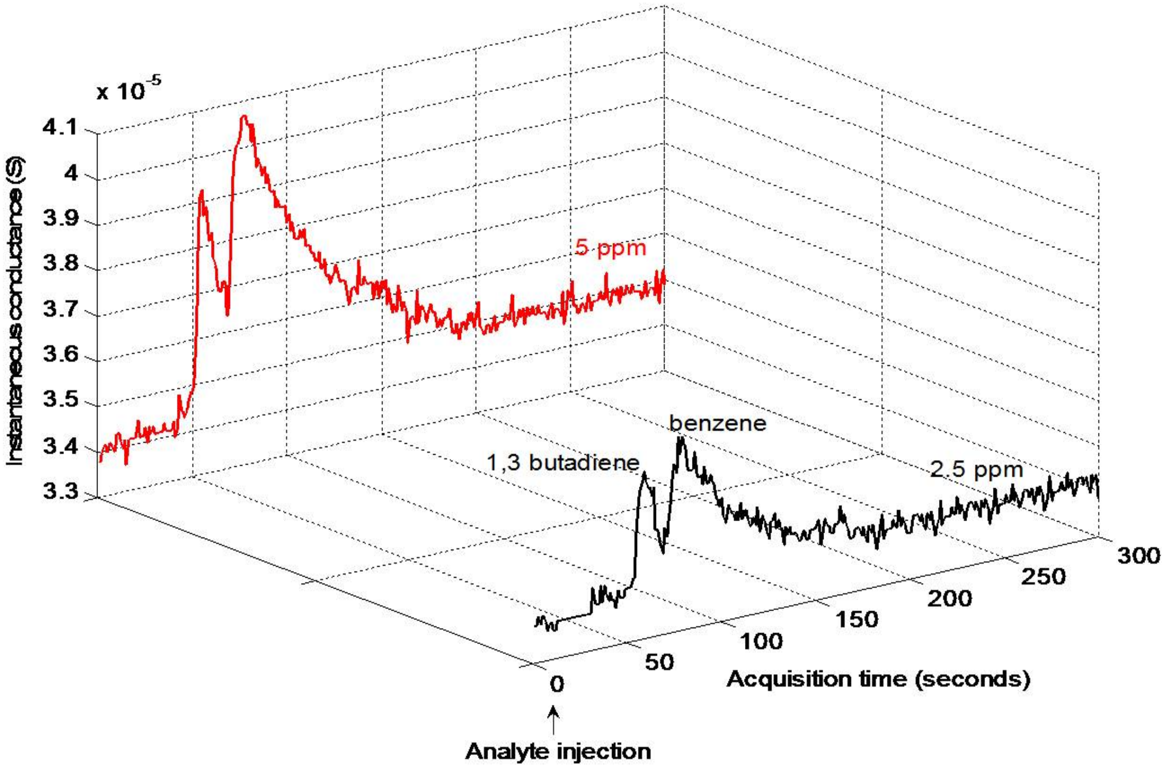


Figure 15: Chromatograms of the separation of the mixture of benzene and butadiene at different initial concentrations in equal proportion, at a column inlet pressure of 4.5 bar

5.3.4. Performance of the future GC microsystem

From these results, we can confirm the interest in using the preconcentrator in front the microcolumn and metal oxide gas sensor system. In fact, without the preconcentrator, the detection of benzene and butadiene wouldn't be possible in our working conditions. The detection limit for benzene was then decreased by at least 5 times. Also, the introduction of the preconcentrator in front the microcolumn, didn't alter the good operation of this latter.

By symmetry, the presence of the chromatographic column behind the preconcentrator is important as well, regarding its retention capability which allows avoiding the dilution of the desorbed analyte during its transport to the detection unit.

The performance of the preconcentrator and the microcolumn in such systems will change depending on the sensor to be used in the future. Starting from the evidence to use a silicon microsensor in the final integrated version of the system, some improvements can be then expected. However, the choice of the gas microsensor must rely on its intrinsic sensitivity to the tested analytes, independently from its detection limit.

On one side, taking as reference the Figaro gas sensor used during this study, the low dead volume of microsensors should allow to improve the concentration factor of the system. However, the final limit of detection of the system will be related to the initial detection limit of the selected microsensor. In order to have acceptable detection limits, the system without the preconcentrator must at least provide a detection limit of some ppm.

On what concerns the silicon microcolumn, its separation performance will depend on the response time of the microsensor to be used, the higher is the sensor response time, better is separation of the compounds.

5.4. Conclusion

A planar silicon microfabricated preconcentrator with high heated area and a low power consumption was fabricated. Activated carbon was used as adsorbing layer for its large, previously demonstrated, adsorption capacity and its deposition was adjusted. Thanks to this, to the well developed active area offered by the designed pre-concentrator, and the optimization of its preconcentration conditions, concentration factors as high as 250 have been achieved, which are among the highest reported in literature towards benzene, especially when a planar structure is used.

The advantage of the pre-concentrator presented here is its adaptability for the pre-concentration of either benzene or toluene, with the possibility to predict, with an accuracy higher than 90 %, the concentration of both vapors independently from their concentration, either alone or in a mixture. Unfortunately, the selective desorption of benzene in presence of toluene wasn't practically achieved by this microconcentrator due to the non enough control of the deposition area. However, this problem could be overcome by performing the deposition by airbrushing on a microconcentrator membrane with no silicon plug. However, in such case, the amount of material deposited will be lower, which will result in a slightly lower concentration factor than the one obtained with the drop coating method.

Compared to the alumina based preconcentrator, the microhotplate based microconcentrator has better thermal insulation, faster thermal response, which resulted in a narrower desorption pulse. This allowed its successful coupling with a microchromatographic detection system, for which the detection limit was lowered by at least 5 times.

The preconcentrator and the chromatographic column were demonstrated to play a complementary role between each other, without which the sensitive and selective detection of benzene in presence of butadiene wouldn't be possible. The good operation of the final system will require a good choice of the gas microsensor, as well.

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[6] http://www.cee.vt.edu/ewr/environmental/teach/smprimer/gc/gc.html

Conclusions

- The review of literature performed during this thesis, allows to highlight the efforts devoted by the scientists to develop miniaturized preconcentrating devices, regarding their interesting use as injection and/or separation unit in a detection microsystem, moreover, their ability to increase the signal to noise ratio and to reduce the detection limit of such systems.

  Different structures have been designed in literature starting from planar to 3D structures. The 3D structure seems the best in terms of preconcentration capacity, regarding the high amount of adsorbing material which it can host and the high concentration factors achieved. However, from other point of view, the planar structure, despite its smaller size, offers simpler fabrication technology, better thermal isolation in the case of being integrated with other units of the detection microsystem and faster desorption response.

- Regarding the above considerations, the planar microhotplate membrane was adopted in the present thesis. As solution for the limited collection efficiency of such structure, we proposed to use a high adsorption capacity adsorbent together with a big area preconcentrator able to compensate the small quantity of adsorbent that can be allocated in such 2 D structure and to optimize the experimental working conditions of the device. This device was then applied to the preconcentration of benzene, a cancerigenic compound involved in petrochemical industry and carbonated beverage production applications. Effectively, these solutions allowed us to obtain high preconcentration capability using a reasonably small size planar structure, reaching concentration factors among the best found in literature using 3D structures. In particular:

  - ✓ Mass spectrometry demonstrated its good adaptability as characterization technique for the preconcentrator, being a selective and fast response standard analytical technique, compared to usual gas sensing systems used in literature to optimize the device, which don't enable to separate the characterization of the preconcentrator in front of the sensor response. Also, using this technique, we were able to test correctly the selective desorption capability of the preconcentrator, which can't be tested for example with other analytical equipments such as FID or PID detectors regarding their non intrinsic selectivity.

  - ✓ We have pointed out the importance of such characterization prior to the coupling of the preconcentrator with a detection microdevice. In this way, the concentration factor of the device could be determined and the degradation of some unstable molecules, likely to occur during the preconcentration stage, such as butadiene can be diagnosed prematurely.

- ✓ Activated carbon and carbon nanotubes have tuneable adsorption properties; however, carbon nanotubes gave smaller adsorption capacity towards benzene. On the other hand, activated carbon and especially the material synthesized from Kraft lignin was the one presenting the most suitable microporous structure for retaining benzene, thus leading to the best adsorption capacity and presented low adsorption interference for benzene in presence of its most common interferents in air, such as butadiene and toluene, especially at low ppb level. In addition, this material is cheap, and has a low amount of oxygenated surface groups which explains its low affinity to moisture, in our preconcentrating conditions.
- ✓ The airbrushing deposition technique was proven to be an excellent technique for achieving homogeneous, adherent coating of the adsorbent on the device in a controlled way.
- ✓ This technique wasn't applied for depositing the adsorbent over the silicon hotplate based microconcentrator due to the mechanical fragility introduced by the silicon plug placed on the bottom of the membrane. So, this technique was replaced by the drop coating technique.
- ✓ The drop coating method doesn't achieve as high deposition quality as the airbrushing method, but it allows to deposit higher amount of adsorbing material on the top of small area membranes, as it's the case of our microconcentrator. In our case, this allowed to avoid the early breakthough of the adsorbent.

- ♦ Although the microconcentrator didn't give very good results as separation unit, however, we demonstrated its excellent performance as injection unit in front detection microsystems:

  - ✓ The microhotplate based microconcentrator has faster desorption kinetics than the alumina based preconcentrator, achieving a very narrow desorption pulse which is very useful for applications with microchromatographic detection systems. This advantage is due to the good design of the heater, the introduction of the silicon plug under the membrane and the good thermal insulation of this latter.

- ♦ When the preconcentrator was coupled directly with a gas sensor, it was noticed that the rapid desorption kinetics of the preconcentrator don't match with the slow sensor response and don't allow this latter to react sufficiently with the concentrated analyte. However, it was proven that the improvement of the sensor response depended on the configuration of the gas entrance to the sensor. In fact, the perpendicular configuration is preferred because it reduces the dilution effect of the desorbed analyte compared to the laminar configuration.Finally, a sensitive and selective detection of benzene in presence of butadiene was successfully achieved by placing the microconcentrator in front of a microchromatographic detection system developed in the LCPR-AC in France, consisting of a silicon microcolumn and a commercial tin oxide sensor, thanks to:

  - ✓ The step by step characterization and optimization dedicated to each unit of the detection system.
  - ✓ The efficiency of the microcolumn design and the good choice of the stationary phase, which allowed a successful separation of the analytes at ambient temperature. This is a very good result regarding the low power consumption of the future microsystem. Also the use of the microcolumn allows to reduce the effect of desorption temperature on the sensor response and to avoid the dilution of the desorbed analyte thanks to its retention capability.

- The preconcentration stage makes it possible the detection of the analytes by increasing the response of the system towards both by at least 5 times. The analysis cycle achieved in our case with the detection device is quite large cycle but it’s unavoidable, regarding:
  - ✓ The necessity to lower the desorption temperature for not to cause the degradation of butadiene.
  - ✓ Also, the operation of the microcolumn at ambient temperature induced the enlargement of the elution time of this latter.
  - ✓ This depends also on the response time of the gas sensor which is generally much slower than the analytical equipments, such as the mass spectrometer.
  - ✓ This is also due to the dead volume of the gas preconcentrator chamber and the connections of the system, which causes the dilution of the analytes and the broadening of the peaks. When the integrated version of the system will be implemented, the analysis time is expected to be reduced.

Future improvements

Very interesting results were achieved during this thesis, however, some future improvements could be beneficial to further improve them:

- The adsorbent deposition could be performed by airbrushing using a microconcentrator membrane with no silicon plug. By this way, a more homogeneous and adhered layer of the adsorbent could be obtained. Also, the deposition area could be limited, which will help to have more homogeneous temperature distribution in the membrane and which will allow the selective desorption of benzene in presence of other compounds.

- A pyrex tape must be used to seal the microconcentrator. This will help to reduce the dead volumes and thus increasing the concentrations factors. In this case, a perpendicular inlet with different outlet configurations could be tested to further increase the efficiency of analyte adsorption and desorption.

- In the case of slow gas sensors, the direct coupling of the preconcentrator with such devices could be envisaged and further improved by increasing the contact duration of the desorbed analyte with the sensor. This could be tested by closing the sensor outlet during analyte desorption or placing the sensor and the preconcentrator in the same chamber, stopping the gas flow during analyte desorption. However, in this case, the effect of gas pressure change and desorption temperature on the sensor response must be well studied.

- An integrated portable version of the microsystem, including the microconcentrator, the microcolumn and a tin oxide gas microsensor, must be envisaged by integrating all these units on the same silicon substrate.

- The system could be tested and optimized for the analysis of more complex mixtures, including toluene and xylene, for example.

Annex I. Materials: Adsorbents, Substrates and Preconcentrating chambers

1.1. Adsorbent preparation and characterization

1.1.1. Activated carbon

a. Preparation conditions

Different activated carbons (ACs) were prepared from commercial precursors: Kraft lignin on one hand, and Norit granular activated carbons, having two different granularities on the other hand. These materials were then activated and characterized in the department of "Chimie et Physique des Solides et des Surfaces" situated in Epinal (France).

- The commercial precursors

Three activated carbons have thus been prepared from Kraft lignin supplied by LignoTech Ibérica (Spain). The lignin was used as received; information about proximate and ultimate analysis can be found in [1], as well as details about chemical activation of lignin with alkaline hydroxides and resultant materials.
Five other adsorbents have been derived from commercial activated carbons supplied by Norit with two different grain sizes [2-3]. These materials are then referred to as N5C and N20C, 5 and 20 corresponding to the mean grain size expressed in µm.

- Chemical activation process

Kraft lignin and granular Norit carbons were physically mixed with ground KOH granules, using various KOH to precursor weight ratios, R, according to the procedure extensively detailed elsewhere [1,4]. The mixture was then heated at a fixed heating rate, r, up to various final temperatures that were maintained for 1h. After cooling under nitrogen flow, the materials were recovered, washed with distilled water, and dried. The experimental activation conditions, listed in table 1, have been chosen in order to obtain a wide range of sufficiently different adsorbents: a total of eleven ACs were thus evaluated as suitable materials for benzene pre-concentrator preparation.

- Material characterization

The pore texture parameters (surface area and pore volumes) of these materials were determined from the corresponding nitrogen adsorption-desorption isotherms obtained at -196°C with an automatic instrument (ASAP 2020, Micromeritics). For that purpose, samples were outgassed at 250 °C, and their adsorption data at relative pressures p/p_0 ranging from 10^{-5} to 0.99 were analyzed. The micropore volume, corresponding to pores narrower than 2 nm, was calculated according to the Dubinin–Radushkevitch method [5 and refs. therein]. The total pore volume, sometimes referred to as the so-called Gurvitch volume, was defined as the volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure $p/p_0 = 0.99$ [6]; the Gurvitch volume is assumed to be the sum micro + mesopore volumes. Finally, the pore size distributions (PSD) were calculated by application of the DFT model [7] supplied by Micromeritics software, considering slit-shaped pores. The mean micropore width, L_0, was calculated from the equation of Stoeckli et al. [8 and refs. therein]:

$$L_0 = \frac{10.8\ (\text{nm kJ mol}^{-1})}{E_0 - 11.4\ (\text{kJ mol}^{-1})} \qquad (1)$$

in which E_0 is the characteristic adsorption energy of nitrogen derived from the corresponding adsorption isotherms at -196 °C by application of the Dubinin–Radushkevich method [9].

Adsorption properties of ACs in the gas phase are controlled by their pore-size distribution (PSD). Given the extreme narrowness of a benzene ring (thickness 0.25 nm [10]), micropores are most suitable for adsorbing and hence concentrating benzene. Adsorption of carbon dioxide occurs in the same micropores but is very low, due to its supercritical nature in the present conditions. Moreover, benzene is a condensable vapor, so its affinity towards carbon is much higher than that of CO_2; the latter is then displaced by benzene as long as new C_6H_6 molecules arrive in the pre-concentrator.

The ACs used in this study have surface areas ranging from 765 to 1957 $m^2\ g^{-1}$. Figure 1.a shows adsorption-desorption isotherms of nitrogen at -196 °C for lignin – derived ACs. L1 typically is a microporous AC having a negligible amount of mesoporosity. Isotherms of L2 and L3 suggest a wider distribution of micropore sizes, hysteresis being related to mesopore volume. The corresponding pore texture parameters are reported in Table 1.

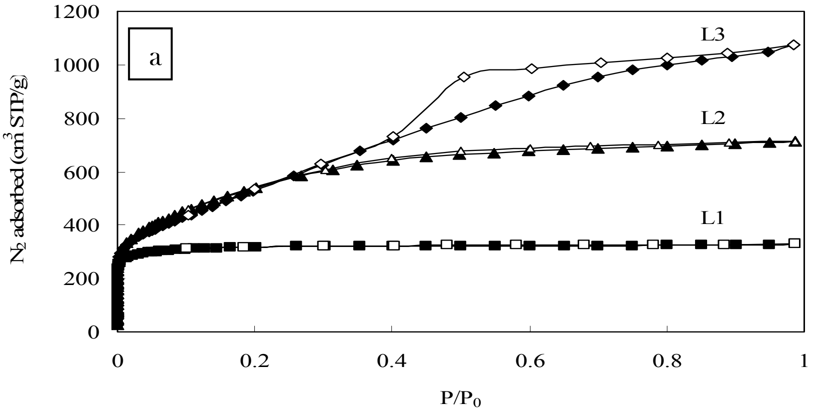
Figure 1.b shows the same kind of curves for N5C and its relatives: N5A1 and N5A2. The three ACs are again microporous. The efficiency of the additional activation by KOH is clearly evidenced by higher uptakes and related pore textures (see Table 1). The hysteresis loops being rather similar to each other, the mesopore volume may be assumed as roughly constant, whereas the micropore volume increases with an increasingly broadened micropore size distribution.

In agreement with the aforementioned findings, increasing the amount of activating agent (through R) and/or the activation temperature indeed leads to higher mean pore widths L_0 (Table 1). A value of L_0 as high as 2 nm is even found for L3, suggesting the presence of mesopores and justifying the wide hysteresis loop observed in Figure 1; lower benzene concentration performances are thus expected for pre-concentrators based on this material (see below). Provided that its microporosity is sufficiently developed, L1 may be assumed to lead to the best pre-concentrators, given that it is the AC presenting the narrowest pores, as suggested by its low value of L_0.

Table 1: Activation conditions and characteristics of the carbonaceous adsorbents

Adsorbent	Precursor	Grain size D(μm)	Activation conditions			BET surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	$V_{0.99}$ (cm^3 g^{-1})	Average pore width (nm)
			R	r (°C/min)	T (°C)				
L1-d1	Kraft lignin	10 <D< 20	1.1.	5	700	1057	-	-	-
L1-d2		D<40	1.1	5	700	1238	0.471	0.507	0.657
L1-d3		40 <D< 50	1.1	5	700	900	-	-	-
L1-d4		D> 100	1.1	5	700	1999	-	-	-
L2	Kraft lignin	D<40	6.1	5	700	1957	0.64	1.107	1.424
L3		D<40	3.6	5	770	1930	0.699	1.660	1.978
N5C	Norit N5C	5	-	-	-	996	0.374	0.613	0.825
N5A1			1	3	775	1267	0.472	0.748	0.885
N5A2			3	3	775	1779	0.661	1.037	1.016
N20C	Norit N20C	20	-	-	-	765	0.286	0.523	0.819
N20A			3	3	775	1816	0.67	1.097	1.031

L: “lignin”, N:“Norit”C: “commercial” (i.e., as received, without additional heat-treatment). A: “activated” (i.e., after chemical activation).



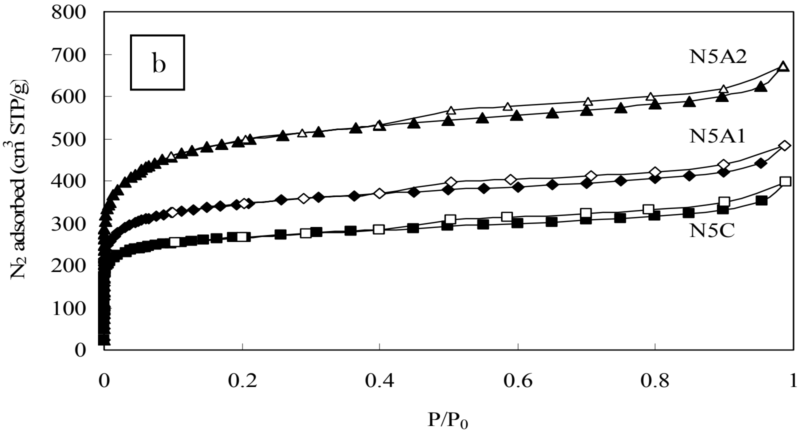


Figure 1: Adsorption-desorption nitrogen isotherms at -196°C of various adsorbents: (a) lignin-based materials L1, L2 and L3; (b) Norit-based materials N5C, N5A1 and N5A2. Full and empty symbols stand for adsorption and desorption, respectively.

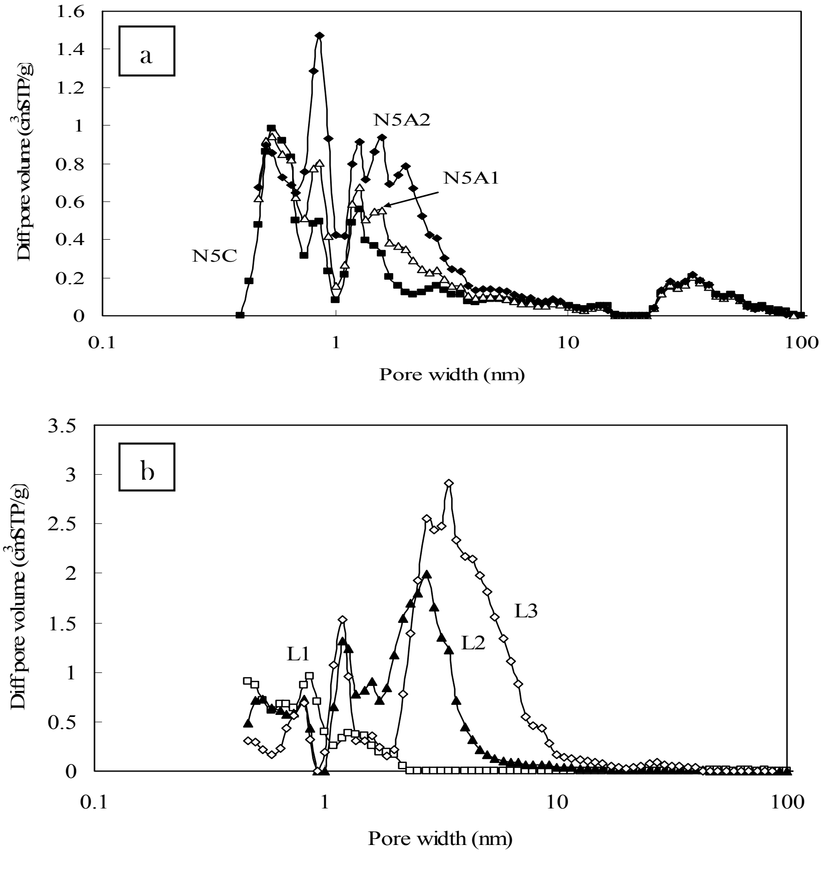


Figure 2: Pore-size distribution of activated carbons derived from: (a) Kraft lignin; (b) Norit commercial adsorbents

1.1.2. Carbon nanotubes

a. Preparation conditions

The CNT adsorbents tested here were prepared from three different commercially available pristine CNTs provided by three different companies: Nanocyl, Mercorp and He Ji, SA. The aim was to study the effect of CNT structure, purification and surface functionalization on their adsorption capacity towards benzene. The functionalization and surface characterization of these samples was performed in the "Université de Namur", in Belgium:

1- Three different pristine CNTs were produced by Catalytic Chemical Vapor Deposition (CCVD) from Nanocyl SA: single walled carbon nanotubes (NC1100), double walled carbon nanotubes (NC2100) or multi walled carbon nanotubes (NC3100). All the as produced samples had a CNT purity grade of 90 % apart from NC3100 the purity of which was higher than 95 %.
The NC3100 sample was functionalized using a radio-frequency CF_4 plasma during 5 min at a pressure of 0.1 Torr and a power of 50 W. The treatment using CF_4 is expected to graft fluorine groups to the CNTs [11] making their surface hydrophobic in order to increase their affinity towards benzene adsorption.
2- MWCNTs produced by arc discharge from Mercorp, SA Company: Those materials presented a CNT content from 30 to 40 % and the impurities found were mainly multi-layer polygonal structures ("Buckyonions") and graphitic particles.
3- SWCNTs were provided by He Ji, SA Company from China. Those presented a purity grade near 60 %.

The characteristics of the commercial pristine CNT samples were extracted from the product datasheet provided by the manufacturer and are presented below in table 2. From this table, we can see that the different samples presented different dimensions, different purity grades and different surface areas.

Table 2: Characteristics of the different commercial pristine carbon nanotubes

Commercial precursor from	**Nanocyl**			**Mercorp**	**He Ji**
Sample	MWCNTs (NC3100)	DWCNTs (NC2100)	SWCNTs (NC1100)	MWCNTs (MRGC)	SWCNTs (S4401)
Average diamete (nm)	9.5	3.5	2	6-20	1.1
Length (µm)	1.5	1-10	Several	1-5	10-20
Carbon nanotubes purity grade (%)	> 95	> 90	90	30-40	> 60
Specific surface area (m^2/g)	Not defined	> 500	> 1000	Non defined	> 400
Metal oxide and shell of carbon purity (%)	< 5	Non defined	< 30	60-70	(Ash < 1.5 wt%)
Amorphous carbon(%)	Pyrolytically deposited carbon on the CNT surface	< 1	Non defined		Non defined

b. Material characterization

SEM and XPS analysis

The morphology and structure of pristine samples together with the plasma treated samples were characterized by scanning electron microscopy (SEM; JEOL JSM 6100, apparatus at 10 kV). Their chemical composition was quantified by X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed with a system equipped with a hemispherical electron energy analyzer SSI-100. A monochromatized Al *Ka* line *hn* =1486.6 eV was used as photon source. The energy resolution of the system (source + analyzer) was 0.9 eV.

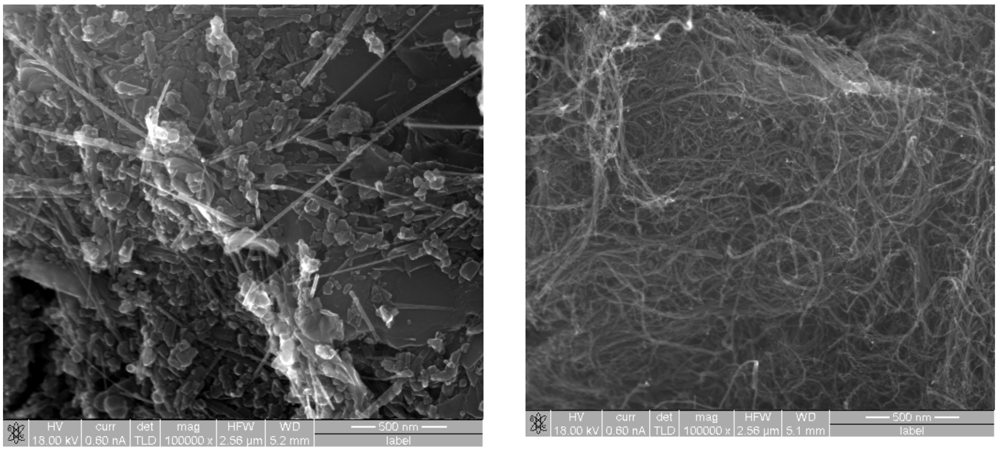


Figure 3: SEM images performed on pristine carbon nanotube samples: a) arc discharge and b) CVD samples

The SEM images presented in figure 3 show the difference between the MWCNT samples synthesized through CVD or arc-discharge (MRGC): the CNT powder resultant of arc-discharge synthesis is composed of straight CNTs and impurities can be easily observed while the CNTs synthesized through CVD are curved and form bundles due to van der Waals interaction between neighboring tubes.

Figure 4 shows the XPS spectra recorded on CF_4 RF-plasma functionalized NC3100/CNTs. The atomic concentration of fluorine was evaluated to be at 20 %. The survey spectrum shows the F1s peak at binding energy 686.7 eV, in addition to the C1s peak at 284.6 eV and the fluorine KLL auger transition near 830 eV. The reported primary binding energy BE shifts in the C 1s level of CFn groups (n=1–3) correspond to the following ranges: 3–4.8, 6–7.5, 7.5–10 eV, according to the number of fluorine atoms bound to the carbon concerned, that is, one, two or three, respectively [12]. In [11] it is suggested the formation of two different forms of C–F bonds, namely, semi-ionic and covalent C–F bonds.

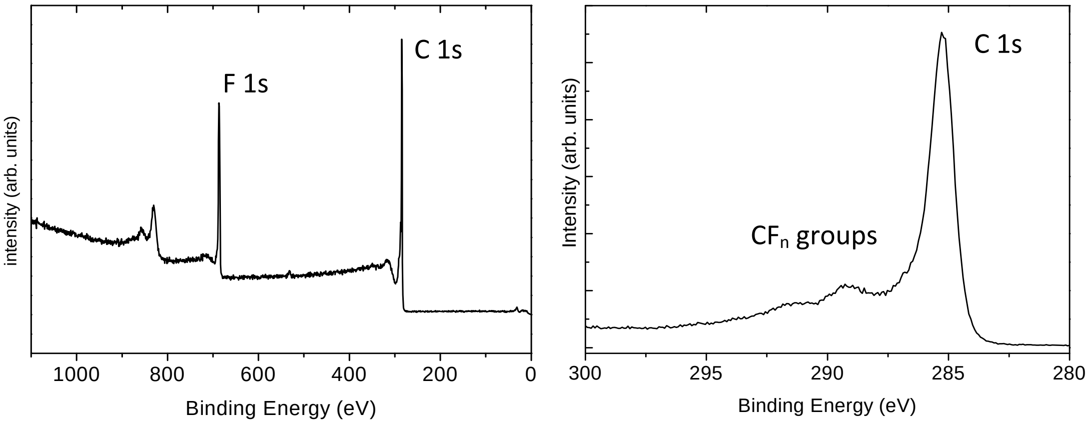


Figure 4: XPS spectra recorded on NC 3100 samples functionalized with CF_4 RF plasma (a) survey and (b) C 1s core level

1.2. Pre-concentrator fabrication

1.2.1. Alumina Substrate

An alumina pre-concentrator was home-fabricated so as to allow the first trials of adsorbent deposition and characterization. It consists of a self heated 1 cm^2 alumina substrate (Fig. 5) on which a platinum heater was screen printed on one side. And on the other side, the adsorbent is to be deposited.

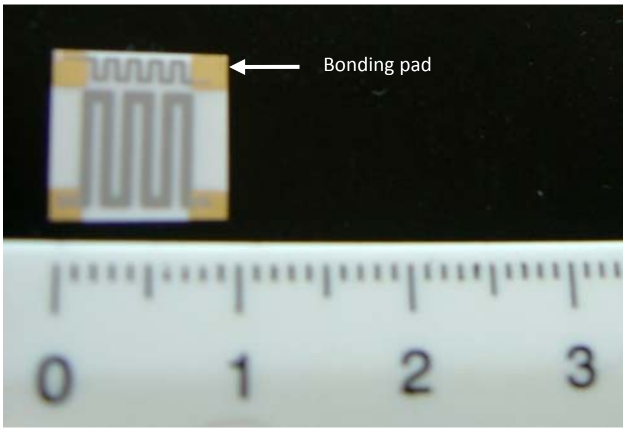


Figure 5: Top view of the alumina based testing support

a. Technological fabrication steps

The support is a commercially available alumina substrate with 2 cm^2 area and a thickness of 500 µm. The heater and pads were deposited from commercial pastes of platinum (LPA 88/11S, Heraeus) and gold (LPA 88/11S, Heraeus) respectively mixed with terpineol (Alpha terpineol, 95%, Alfa Aesar) at a ratio of 0.03 µL/mg. The heater paste was printed first onto the alumina substrate by using a high precision screen printing machine which allows one-side mask alignment (Fig. 6). The substrates were subsequently dried at ambient temperature for 20 min, then heated in an oven (Memmert Model) at

150 ºC for 15 min, for completely removing the organic vehicle, and then fired during 10 min in a belt furnace (Carbolite Model) to 900 ºC at a rate of 20 ºC/min. After substrate cooling, the pads were printed by the same process and then subjected to the same thermal treatment. The firing was performed at 950 ºC instead of 900 ºC used for the heater.

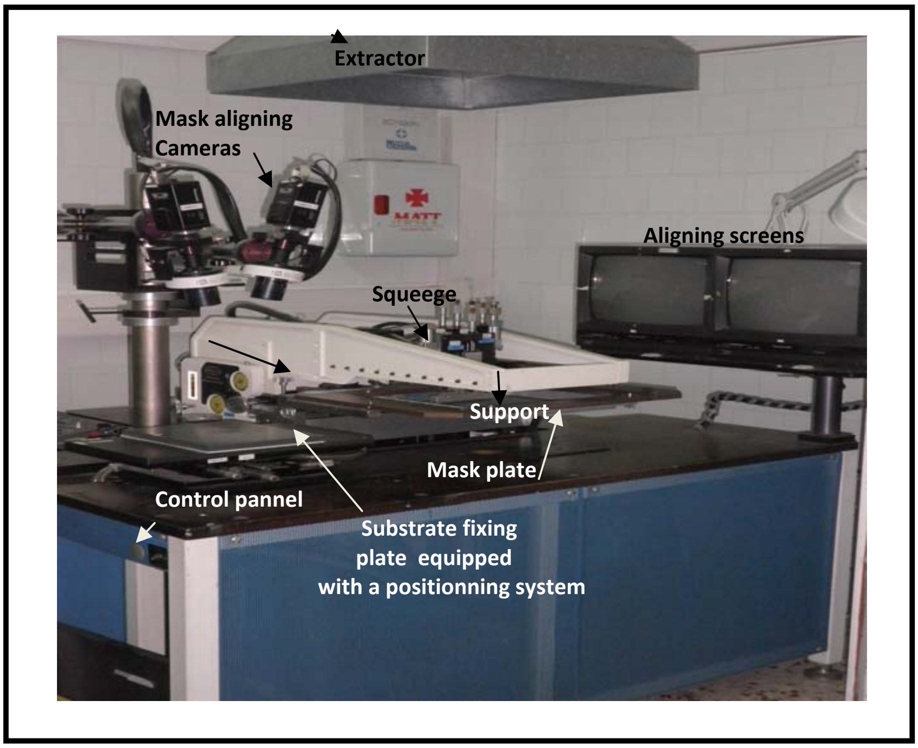


Figure 6: Picture of the screen printing machine

b. Thermo-electrical characterization

The substrate was heated by applying a fixed voltage pulse to the heater resistor pads by means of a Keithley source meter (model 2410) controlled by a Labview program . The resistance reached by the heater at each voltage was then measured by monitoring the current passing through the heater resistor. The temperature was then calculated using the formula:

$$T = T_0 + \frac{R - R_0}{R_0 \alpha} \qquad (2)$$

T: Heater temperature to be measured; To: Ambient temperature;
R=U/I: The resistance of the heater at each applied voltage U and measured current I;
Ro: The resistance of the heater at ambient temperature To, measured by applying 0.1 V to the heater resistor;
α: The temperature coefficient of resistance “TCR” of the platinum heater.

The TCR of the heater was determined by introducing the substrate inside an oven and subjecting it at different heating temperatures, while the heater resistance was monitored in parallel using the

Keithley source meter. Each temperature was maintained for 45 min, for that the heater resistor could be stabilized. The resistance at each temperature was then calculated by applying a voltage of 0.1 V to the heater and measuring the current. The TCR was calculated as the ratio of the slope of "the curve of heater resistance versus oven temperature" divided by Ro. The slope was extracted from the equation of the experimental curve. The mean TCR corresponding to the characterization of 5 substrates was 3.4 10-3 Ω-1 and the resistance at ambient temperature was 4.8 Ω at 22 ºC.

After the determination of the TCR, the temperature reached by the heater, for each fixed applied voltage was then plotted versus time using the formula (2) above. For that, the substrate was introduced inside a Teflon chamber equipped with electrical contacts connected to the heater pads and placed under 100 ml/min of helium.

Figure 7 shows the plot of the temperature reached by the heater after the application of a voltage pulse of 7.5 V at ambient air and under helium. The temperature reached the steady state at around 30 sec, due to thermal inertia of the alumina substrate. Even under the same applied voltage, the temperature reached under helium was at least 70 ºC lower than at ambient air. Helium comes from a cylinder where the gas is compressed, which explains this cooling effect.

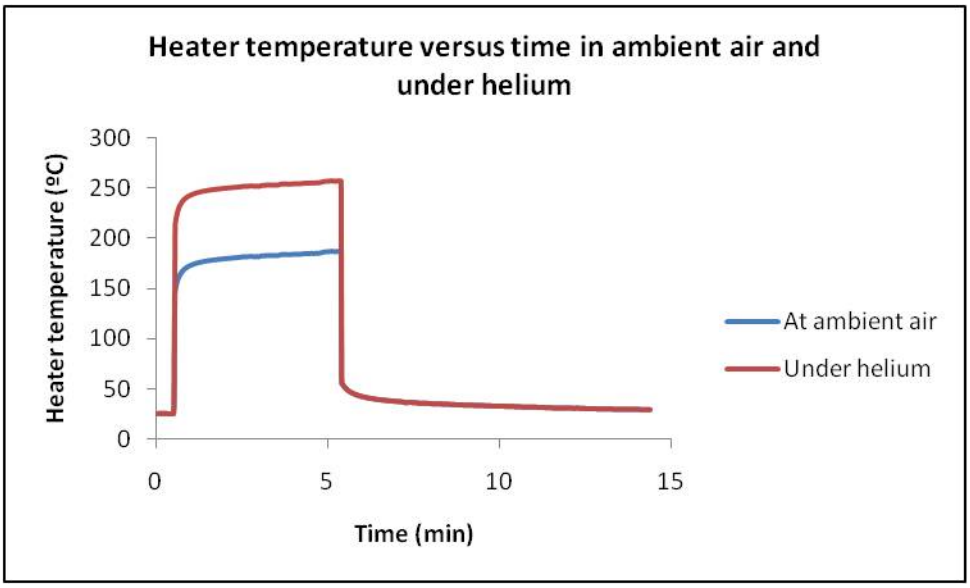


Figure 7: Comparison of the temperature reached by the heater under helium and ambient air

Figure 8 shows the dependence of the heater temperature, at the steady state, on the heater applied voltage. A perfect linear curve is obtained.

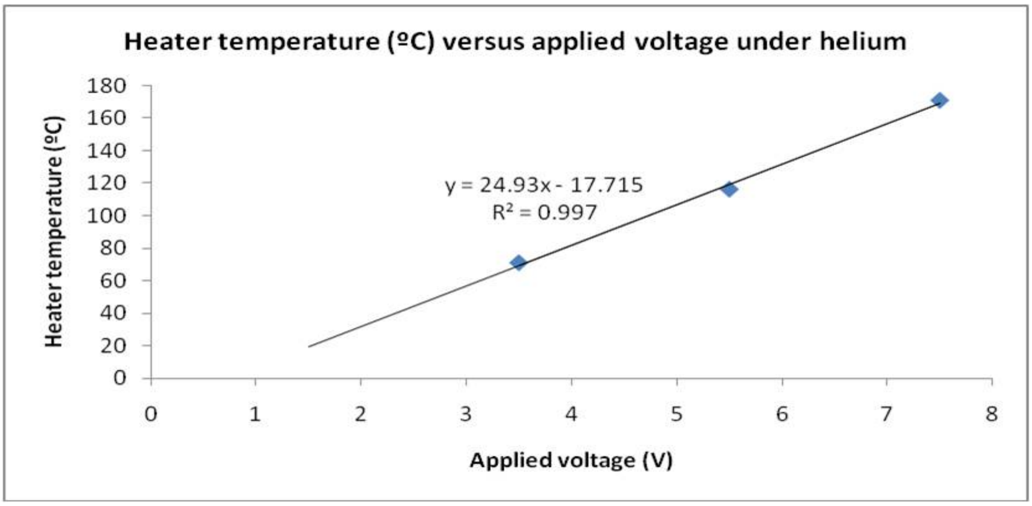
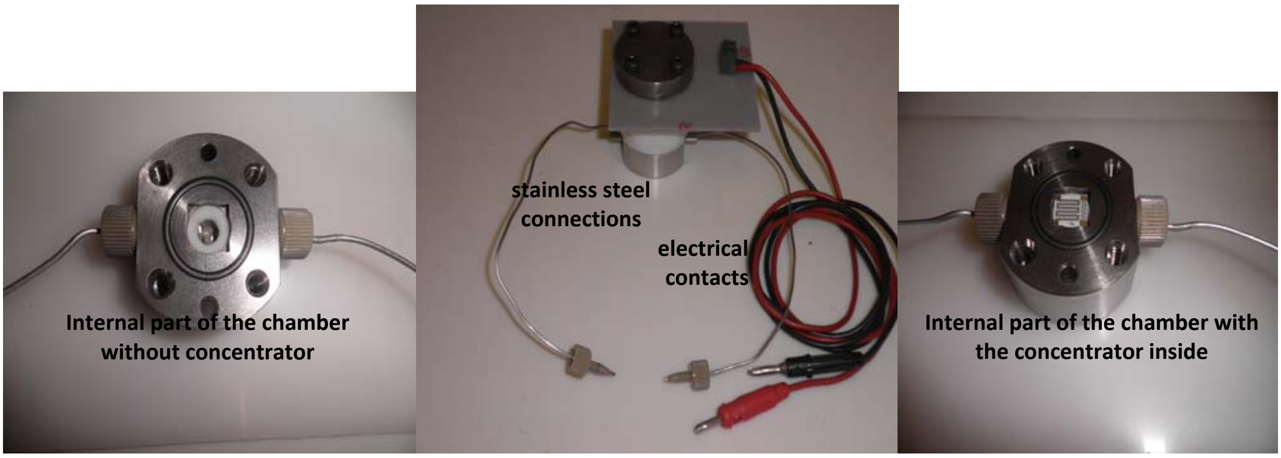


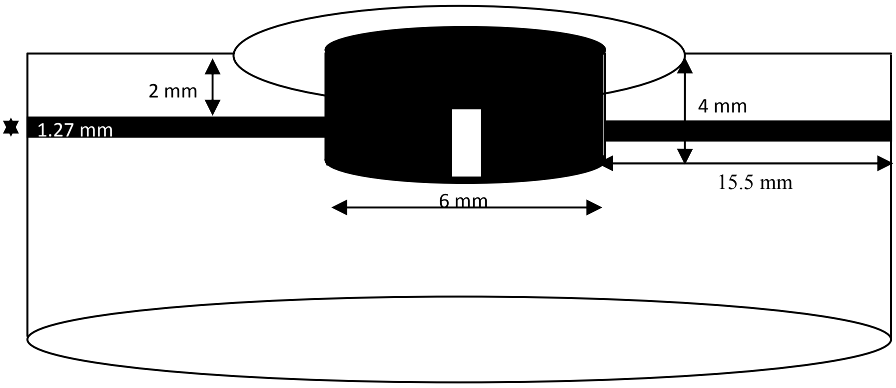
Figure 8: Curve of heater temperature versus the voltage applied to the heater resistor

c. Fabrication of the pre-concentrator chamber

A cylindrical teflon hermetic chamber is home designed for hosting the alumina pre-concentrator during the pre-concentration tests. Teflon is used for its chemical inertia and its resistance to temperatures as high as 280ºC. The chamber design is described below. The chamber is equipped with stainless steel tubes with a diameter of 1.27 mm, which allow to connect it to the gas characterization circuit (Fig. 9 a). The dimensions of the chamber are presented in figure 9 b. The internal volume of the chamber is estimated to 110 µL, and the total dead volume including the connections was 750 µL. This chamber is available in two configurations. The main difference between both, is the introduction of a teflon wall inside the internal volume of the chamber, in front of the adsorbent.



(a)



(b)

Figure 9: Pre-concentration teflon chamber adapted to the alumina substrate (a) Real picture with the different elements (b) Schematic vertical cross sectional view of the internal part of the chamber with the Teflon wall

1.2.2. Microhotplate membrane

a. Technological fabrication steps

The microfabricated device is based on planar membrane of a total area of 2 mm x 4.5 mm, as shown in figure 10. This membrane consisted of 1.2 µm deep dielectric SiO_2/Si_3N_4 layer which was backside anisotropically etched in a 300 µm silicon substrate. A 5 µm thick highly doped silicon plug diffuser is introduced under the membrane to further improve temperature homogenization in the heater area. A 0.25 µm thick platinum heater layer was deposited by sputtering over an area of 1.5 mm x 4 mm. It consists of three spiral shaped heaters which were defined by lift off. The track thicknesses and separation are described elsewhere [13]. A layer of titanium is deposited prior to platinum to promote the heater adhesion to the substrate [13]. The design of the heater was optimized to have a good homogeneous distribution of temperature in the heater active layer with good electro-thermal features [13].

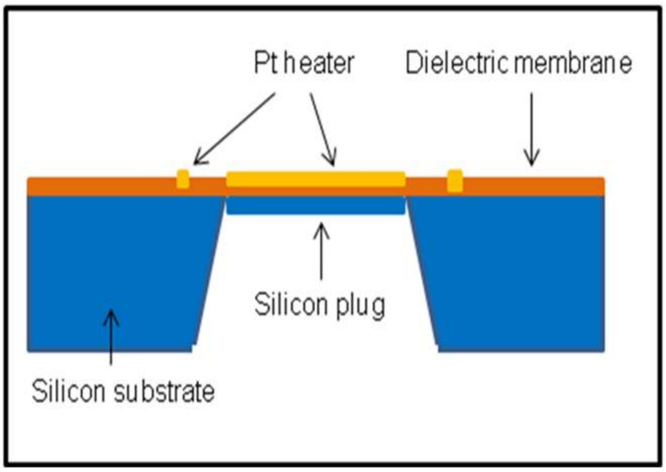


Figure 10: Schematic cross-view of the silicon micro-concentrator

b. Thermo-electrical characterization

The active layer of the membrane was heated by applying a fixed voltage pulse to the heater resistor pads, through the contacts of the TO8 package pins. The thermo-electrical characterization of the heater was performed as for the alumina preconcentratorbased heater (Section 1.2.1), by introducing the micro-concentrator inside an adapted stainless steel chamber with electrical connections and placing it under helium. The resistance at an ambient temperature of 28 ºC was estimated at 2180 Ω. The TCR was determined in [13] and was $2\ 10^{-3}\ \Omega^{-1}$

Figure 11 shows the variation of temperature versus time under the application of a pulse of 50 V under 100 ml/min of helium. While figure 12 shows the plot of the temperature reached by the heater after 1 min of voltage application versus the applied voltage under the same conditions. The curve is linear.

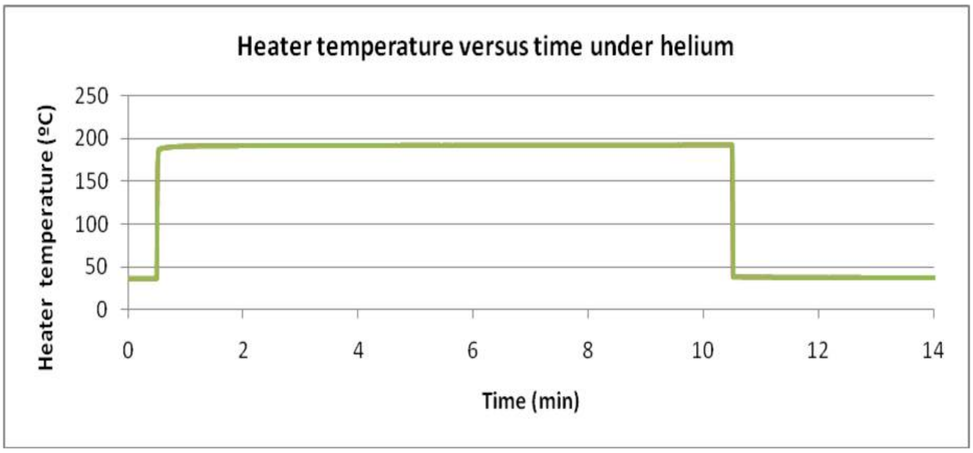


Figure 11: Heater temperature versus time under application of 50 V to the heater under helium

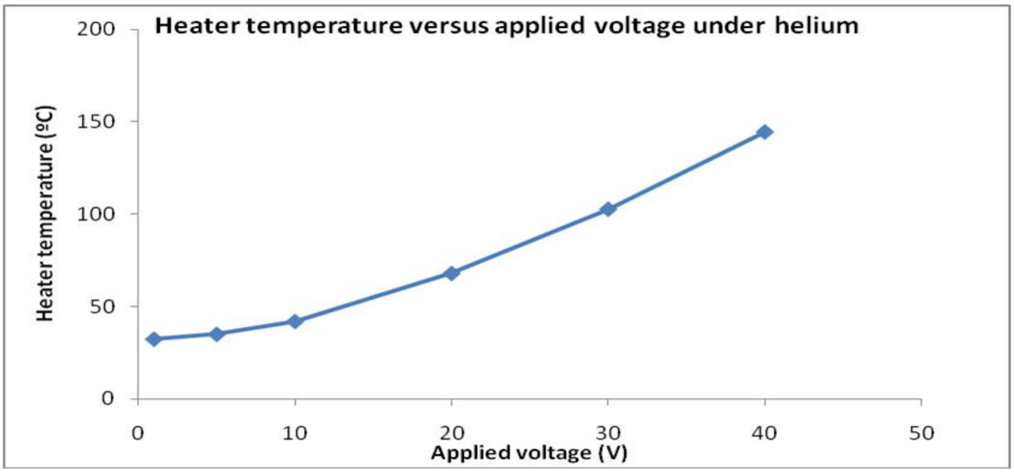


Figure 12: Curve of heater temperature versus the voltage applied to the heater resistor

c. Fabrication of the micro-concentrator chamber

The micro-concentrator chamber consists of a 310 µL stainless steel cylindrical cavity in which the TO8 packaged microconcentrator is introduced (Fig. 13). The gas inlet and outlet have a diameter of 1.27 mm and are connected to 1/16 stainless steel which allows the connection of the chamber to the characterization circuit. The total volume including the connections was 1600 µL. The TO8 pins are inserted in a PCB card with electrical contacts to heat the concentrator during thermal desorption.

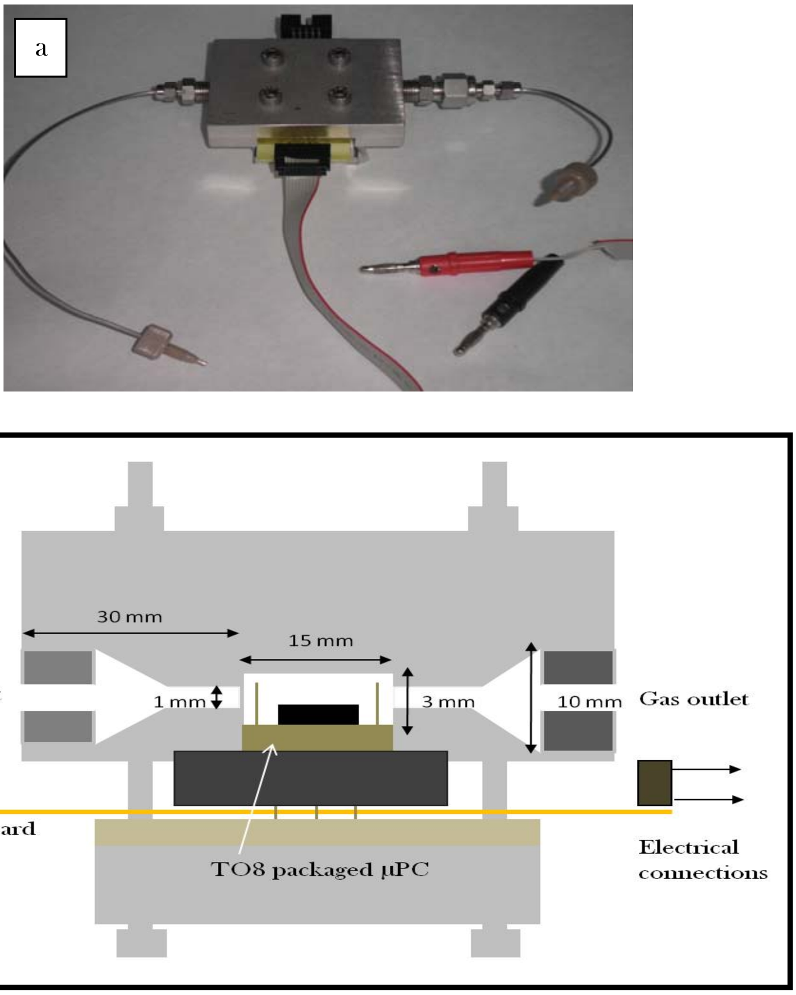


Figure 13: Home-made micro-concentrator stainless steel chamber (a) Real picture (b) Schematic cross sectional view of the chamber with the packaged micro-concentrator inside

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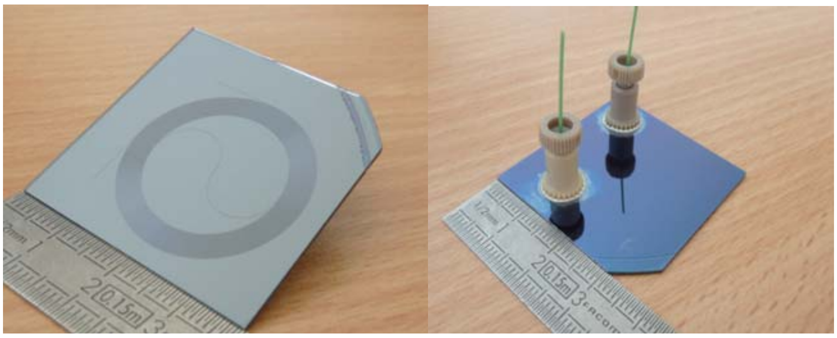
Annex II. Design and fabrication of the silicon microcolumns

The fabrication of the silicon microcolumn was carried out in the "Laboratoire de Chimie, Physique et Rayonnement- Alain chambaudet, Université Franche Comté, Besançon, France.

2.1. Structure design and fabrication

The general geometry selected for this micro-structure is a circular spiral configured like two interlocking structures in order to reduce the dimensions on the silicon wafer. This geometrical configuration makes it possible to dispose 4 GC microcolumns on a 4 inch silicon wafer [1]. This microcolumn consists of 50 µm-wide, 50 µm-deep and 2 m-long channel (Fig 1.a).



(a) Side of the etched micro-channel (b) Side of the fluidic connections

Figure 1: Silicon-micromachined gas chromatographic column [1].

In order to introduce the different gases and the appropriate stationary phase into the anodically sealed column, two capillary tubes are attached into the inlet and outlet holes defined by wet etching. Special fluidic connections are the used for chip based analysis from Upchurch Scientific® (Fig 1.b) [1-2].

2.2. Stationnary phase insertion

To complete the realization of the silicon micro-machined gas chromatographic column, a stationary phase should be introduced and put into the micro-channel. For this study, commercial Polydimethylsiloxane (PDMS)) was selected. This stationary phase has showed the best elution and separation performances for the analysis of VOCs in a mixture [1]. Given the very small size of the micro-channel, the easiest way to deposit the stationary phase is to use the so-called sol–gel technique. More details about the technological steps involved in the fabrication of the micro-columns are reported in [1].

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List of publications and conferences

o *Conference contributions*

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2. H. Lahlou, P. Ivanov, X. Vilanova, X. Correig, Improvement of The Gas Pre-concentrator characterization Procedure Using Mass Spectrometry, Workshop 'Graduated student meeting on electronic engineering', Tarragona (Spain), Poster, June 2008

3. H. Lahlou, R. Ferro, X. Vilanova, V. Fierro, A. Celzard, E. Llobet, P. Ivanov X. Correig, Fabrication and characterisation of a planar pre-concentrator based on air-brushed activated carbon for benzene, Eurosensors XXII, Dresden (Germany), Poster, September 2008

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