CIENCIA 22(4), 205 - 217, 2014
Maracaibo, Venezuela

The use of kaolin for passive sampling of volatile organic compounds in air

Christof Stönner[1]*, Daniel Gallart-Mateu*[2] *and Miguel de la Guardia*[2]*
[1]*Johannes Gutenberg-Universität Mainz, 21th Saarstraße St, 55122 Mainz, Germany.*
[2]*Universitat de València, 50th Dr. Moliner St, E-46100 Burjassot, Valencia, Spain*

Recibido: 12-12-13 Aceptado: 27-10-14

Abstract

The use of kaolin as adsorbent to fill semipermeable membrane devices (SPMDs) in order to catch volatile organic compounds (VOCs) from air has been evaluated. The quantification was performed by head-space sampling-gas chromatography (HS-GC-MS) using a multi-analyte calibration in spiked passive samplers in a range of 15 ng to 15 μg and providing a multi-residue analytical procedure. The omission of sample pre-treatment and the avoidance of deleterious solvents make possible a fast, direct and green determination of VOCs in air with limit of detection values of the order of 40ng per sampler.

Keywords: Volatile compounds, semipermeable membrane kaolin device.

Empleo de caolín en el muestreo pasivo de compuestos orgánicos en aire

Resumen

Se ha evaluado el uso de caolín como adsorbente para muestrear compuestos orgánicos volátiles (VOCs) en aire, empleando membranas semipermeables de polietileno (SPMDs) rellenas con caolín. Los análisis se llevaron a cabo por cromatografía de gases con detección por espectrometría de masas y volatilización directa de los analitos desde los muestreadores usando espacio de cabeza (HG-GC-MS). Los calibrados se prepararon con muestreadores aditivados con una mezcla de VOCs, en el intervalo de 15 ng a 15 μg, proporcionando un método de análisis multi residuo. La ausencia de pretratamiento de las muestras y del uso de disolventes nocivos permitió un análisis sostenible de VOCs en aire con límites de detección del orden de 40 ng por muestreador.

Palabras clave: compuestos volátiles, membrane semipermeable, kaolin device.

1. Introduction

Monitoring of air quality is important to detect pollutants and to assess their risks to human health and the environment. The main air pollutants are particles and gases, emitted by various anthropogenic and natural sources (1). Volatile organic compounds are widely distributed in solid and liquid materials in our daily life. They can be found in building materials, furnishings, cleaning and cosmetic products, as well as in industrially produced fuels and pesticides and can be found in industrial as well as in rural areas

---

* Autor para la correspondencia: Miguel.delaguardia@uv.es

(2). Examples, regarding the monitoring of different air pollutants, are the determination of VOCs in vehicles and petrol stations (3) as well as the investigation of pesticides indoor (4) and outdoor ambient air (5). Recent studies report the evaluation of VOCs as biomarkers in human breath, which results in monitoring tools to evaluate the physiological state of a person and may lead up to disease diagnosis (6).

This study focuses on the green analytical determination of VOCs and BTEX in air using passive samplers filled with kaolin. The group of VOCs comprises a wide range of molecules and some of them are known to be hazardous to human health. In this case, compounds studied were representative of this wide group, like chloroform, 1.1.1-trichloroethane, 1,2-dicholoethane, benzene, trichloroethylene, bromodichloroethane, toluene, dibromochloromethane, tetrachloroethene, ethylbenzene, *o,m,p*-xylene and bromoform. The effects on human health depend on the time of exposure and the level of concentration (2). Moreover, some VOCs show immediate symptoms when they are inhaled, whereas other ones provide long-term risks and are suspected of causing cancer (7).

Generally, VOCs are present in air at low concentration levels (for benzene, the maximum permissible concentration in Spanish legislation, as indicated in the RD 102/2011, is 5 $\mu g/m^3$ air) and the preconcentration of VOCs from ambient air is advantageous and can be done by the deployment of active or passive sampling. Both sampling techniques imply the enrichment of air contaminants on a solid or liquid adsorbent, and the choice of the adsorption medium has a strong influence on the determination of target molecules. Active samplers pump ambient air through a trap containing an adsorbent, such as activated carbon (8) or porous polymers (9). With this method it is possible to collect a high volume of air. In the case of passive sampler the accumulation of VOCs is based on their diffusion through a barrier or membrane and their accumulation in the filling material. The most commonly passive samplers are Radiello samplers, solid phase microextraction fibres, polyutethane foam disks (10) or semipermeable membrane devices (11, 12).

A semipermeable membrane device consists of a low density polyethylene (LDPE) layflat tube, which is heat-sealed on both ends and filled with liquid (12) or solid adsorbents (11). The transport of the target molecules through the membrane is possible, because of the random thermal motion of the polymer chains in the polymer network, resulting in small cavities of approximate 10 Å in diameter (13). The migration of molecules through the membrane is selective due to the special properties of LDPE. The nonpolar chemical composition of the LDPE membrane inhibits the sampling of ionized species, because of their hydrophilic behaviour and thus their insolubility in the nonpolar polymer. The intrinsic size limitation of the polymer network prevents the transport of very large molecules or molecules adsorbed on particulate matter through the gaps in the polymer network. These limitations enable the selective sampling of hydrophobic gases and vapours. The measurement of passive samplers provides time-weight-average (TWA) concentrations of pollutants, being useful to reflect daily or seasonal differences of air pollutants (14).

The standard configuration of SPMDs consists of membranes filled with absorbent materials. Solid filling materials reduce the costs for each sampler. The evaluation of adsorption and desorption properties, thermal stability and costs were performed for several solids such as graphitized carbon black, Tenax, silicates and activated carbon. A mixture of activated carbon and florisil was regarded as appropriate for the use as adsorbents for multianalyte sampling devices. These passive samplers are capable of retaining a large number of VOCs, which involve many compounds with different structures (15) (see table 1).

The main advantages of passive samplers as compared with active ones are

Table 1
Studied VOC's and their GC-MS measurement parameters

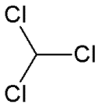
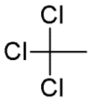
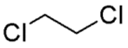
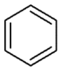
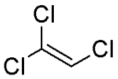
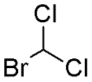
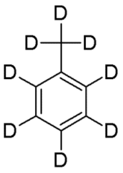
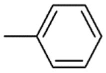
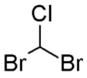
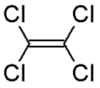
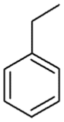
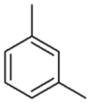
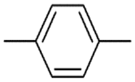
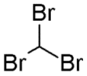
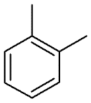
Compounds		Retention time (min)	Measured ions (m/z)
Chloroform		1.29	83+85
1,1,1-Trichloroethane		1.73	97+99
1,2-Dichloroethane		2.08	62+64
Benzene		2.17	78+77
Trichloroethylene		2.41	132+130
Bromodichloromethane		2.74	85+83+129
Toluene-d_8		3.63	98+100
Toluene		3.73	91+92
Dibromochloromethane		4.70	127
Tetrachloroethene		4.79	166+164
Ethylbenzene		7.21	91+106
m-Xylene		7.74	91+106

Tabla 1 (*Continuación*)

Compounds		Retention time (min)	Measured ions (m/z)
p-Xylene		7.84	91+106
Bromoform		8.78	173+175+171
o-Xylene		8.80	91+106

their ease of use and simplicity of deployment, because there is no need of power supplies (16). However, the accumulation of molecules is dependent on different environmental impacts, such as changing air temperatures and wind conditions (17). The determination of pollutants pre-concentrated in passive samplers can be done after an appropriate solvent extraction or directly by heating the samples and or without using head space.

In general, the headspace sensitivity can be enhanced by increasing the concentration of target analytes in the gas phase of the vial. This can be achieved by proper adjustment of the phase ratio (proportion by volume of the gas phase and the sample phase) and temperature. In the case of VOCs the headspace sensitivity is mainly governed by changes in temperature, since temperature affects the vapour pressures of the compounds and determines their amount in the gas phase (18). The degradation of compounds and the achievement of maximum response, due to attaining equilibrium, are some reasons limiting the use of a high vaporization temperature in headspace vials (19).

The ability of clays to adsorb VOCs and their deposit in the Earth's crust brought them into focus as cheap alternatives for the application of filling materials for SPMDs. Natural clays represent a group of soils, which are considered to be porous materials with high specific surface. Their adsorption capacities are based on intermolecular forces between the molecules and the surface of the solid and can consist of hydrophobic or polar interactions at various degrees. The type of interaction depends mainly on the physical properties of the adsorbent, as well as on those of the adsorbed species (20). In the case of VOCs, it is expected that the molecules could be mainly bound to the adsorbent by weak physical van der Waals bonding forces (21). Kaolin is common clay being kaolinite its main component, which is a hydrated aluminium silicate with a layered structure (22).

The aim of this study was the development of a SPMD's filled with kaolin to monitor pollutants in ambient air. Therefore several calibration studies were performed with various VOCs, which can be found in working environments, to evaluate the sorption behaviour and to determine some analytical features.

2. Materials and methods

2.1. Apparatus and reagents

Membranes employed for passive sampling consist of 2.9 cm wide and 87 μm thick LDPE layflat tube, obtained from Garciplast (Barcelona, Spain) and filled with kaolin. A Rovebloc sealer (Barcelona, Spain) was used to heat-seal the membranes.

Kaolin was obtained from an inorganic chemistry working group of the University of Valencia and the granulation of these particles was smaller than 2.5 μm.

The identification of kaolin was performed by X-ray powder diffraction using a Philips PW2400 (Einhoven, Neederlands) and ATR-FTIR-spectroscopy (attenuated total reflection-Fourier transformation infrared spectroscopy) using a Bruker Tensor 27 (Bremen, Germany). To measure the sample with the IR-spectrometer, the device was flushed with nitrogen and a small amount of kaolin was laid onto the total reflection crystal of the spectrometer. The measurements were run in triplicate.

The characterization of kaolin by its elemental composition was done by SEM-energy dispersive X-ray spectroscopy (EDAX). The scanning electron microscopy (SEM) and EDAX measurements were performed with the Philips XL30 ESEM (Einhoven, Neederlands) system. Therefore, kaolin was strewn on the sampler plate, prepared with an adhesive foil, and put into the measuring chamber. The EDAX measurements were performed for 50 seconds and were carried out by triplicate. The adsorbed VOCs were vaporized with a HS2000 headspace injector from Finnigan (Waltham, MS, USA). The separation and determination was done with a Finnigan Trace gas chromatograpgh equipped with a low bleed Zebron (Newport Beach, CA, USA) ZB-5MS column (30m × 0.32 mm, 0.25 μm), coupled to a Finnigan Polaris Q ion trap mass spectrometer. The 10 mL glass vials, employed for HS measurements, were capped with PTFE- butyl rubber seals.

Standard solution of different VOCs were obtained from Fluka Chemie (Buchs, Switzerland), Scharlau (Barcelona, Spain), Sigma-Aldrich (St. Louis, USA) and Merck (Steinheim, Germany). Stock solutions at different concentration levels were prepared by dissolving known amounts of each compound standard in *n*-hexadecane from Scharlau (Barcelona, Spain). As an internal standard a solution of toluene-d_8 from Sigma-Aldrich (St. Louis, USA) dissolved *n*-hexadecane was prepared at a concentration level of 1,5 μg L^{-1}.

Brown glass bottles were employed to evaluate the sampling capability of the passive samplers assayed. They were decontaminated with a flow of nitrogen for 5 min before using in this study and blank samplers were employed in cleaned bottles in order to assure the complete release of VOCs from the containers before to do the adsorption studies.

2.2. Preparation of samplers

The SPMDs were prepared with a LDPE layflat tube cut into segments of 10 cm, followed up by a cleaning step in hexane for 24 hours to remove lubricants and additives, like antioxidants and photochemical stabilizers, out of the polymer network. After drying, one end was heat-sealed and a known amount of kaolin was filled into the membrane. Then the adsorption medium in the membrane was homogenized and the other end of the membrane was sealed (10, 23).

The prepared samplers were wrapped separately into aluminium foils and stored in closed vessels at –20°C until the deployment. The deployed samplers were placed into 10 mL HS vials with an internal standard, capped hermetically and stored at –5°C until the HS-GC-MS measurement.

The absence of contaminants in samplers, being capable of interfering with our investigated analytes, was verified through the measurement of blank samplers. The low manipulation of samplers reduces the risks of contamination, nevertheless possible sources of contamination are raw fabricates, such as membranes and reagents as well as storage, transport and retrieval of the manufactured samplers.

2.3. Preparation of spiked samplers

The preparation of spiked samplers was made by addition of VOCs standard mixtures to the filled layflat tubes using a 10 μL glass syringe. The prepared membranes were placed immediately inside, hermetically capped HS vials and stored in a freezer at –5°C until the measurement.

Spiked samplers were used to establish calibration curves for each considered compounds over a linear range from 15 ng to 15 μg of VOCs.

2.4. Adsorption of VOCs

The uptake behaviour of VOCs was investigated by exposing prepared membranes to known air concentrations of VOCs. Therefore the amount of 10, 15 or 20 μg of VOCs was added to a 2 m^2 piece of paper filter, which was put inside a closed 2.85 ± 0.01 L topaz glass bottles. The use of a filter paper increases the volatilization area and ensures the whole evaporation of the VOCs. Supposing that the entire quantity of VOC will be located in the gas phase, the concentration in the bottles will be 3.51 mg m^{-3}, 5.2 mg m^{-3} and 7.02 mg m^{-3}, respectively. Membranes were pierced above the sealed end and deployed with a thread inside the bottles for 24 hours.

2.5. HS-GC-MS direct determination of VOCs

The adsorbed VOCs were vaporized at a temperature of 150°C for 10 minutes. The temperature of the syringe was set at 150°C with a constant air flow purge. An amount of one hundred microliters were injected onto the column. The injection was performed in split mode with a relation of 1:10 at 200°C and employing 1 mL min^{-1} helium as carrier gas. The GC oven was run with a temperature program with a starting temperature of 40°C, held for 10 minutes and a final temperature of 200°C, held for 2 minutes. The heating rate was 20°Cmin^{-1}. The transfer line and the source were held at 300 and 250°C. The potential of the electron impact ion source was 70 eV and a mass scanning range from 40 to 180 m/z was employed to detect all studied VOCs. Signals obtained for deployed membranes were interpolated in those found for spiked membranes with the target analytes treated in the same way then the samples.

The retention times and the ions used for quantification for every VOC are shown in table 1. The peak areas of m-Xylene and p-Xylene were evaluated together, due to their overlapped peaks

2.6. Field studies

Field studies were performed *in lab* sampling the analytes in a fume hood containing VOCs/BTEX and organic solvents, and the capability of our samplers to hold the analytes form waste containers. The exposure time was 24 hours for both experiments. After sampling, deployed membranes were wrapped in aluminium foils and then the membranes were placed inside a 10 mL HS vials, added the internal standard, and capped hermetically before their analysis.

3. Results and discussion

3.1. Characterization of kaolin

Kaolin, which is a clay material combination of different minerals, consists mainly of Kaolinite. The exact mineral composition of kaolin was examined by X-ray powder diffraction. The obtained diffractogram was assigned to Kaolinite and quartz. Feldspars are solid solutions that exist in numerous different compositions, see figure 1.

The elemental composition of the used kaolin was performed by EDAX spectrometry, revealing that the principal elements are silicon, aluminium and in minor part potassium. The measured amount of potassium was assigned to the presence of feldspar, and the structural formula of Kaolinite was derived from the weight percentages of the atoms. In this sense, EDAX analysis reveals a composition for Kaolin of O: 59±, Al: 14±2, Si: 27.5±0.5 and K: 1.75±0.2% in weight, see insert in figure 1.

The ATR-FTIR spectrum, which can be seen in figure 2, shows typical absorption bands, confirming the presence of Kaolinite.

The absorption bands in the range between 3600 cm^{-1} and 3800 cm^{-1} arise from O-H-stretching vibrations. The appearance of four bands can be explained through the four different locations of hydroxyl groups in the unit cell. The three highest bands derive

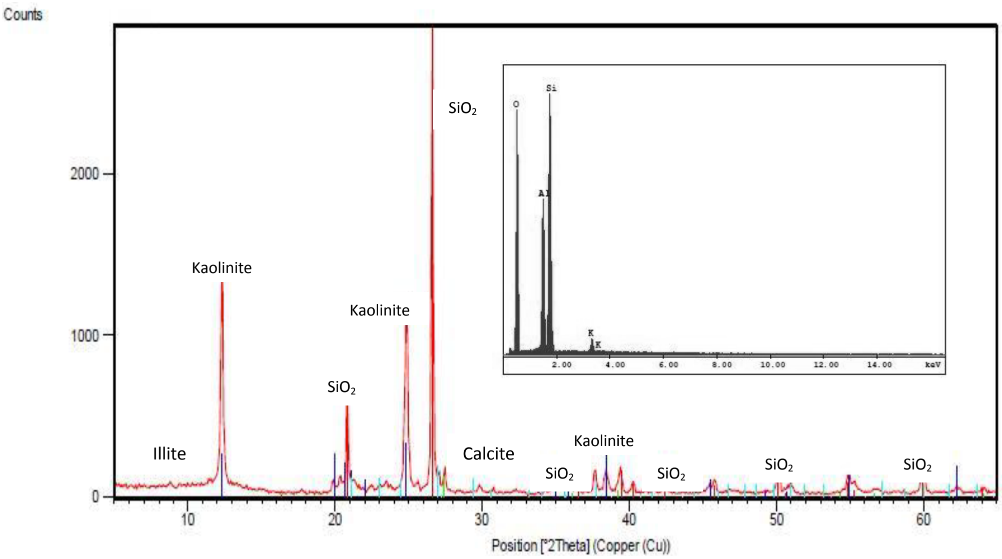


Figure 1. X-ray diffraction pattern of kaolin showing the presence of Kaolinite, quartz (SiO_2) and traces of feldspar. On this figure, as an insert, chemical composition of kaolin performed by EDAX.

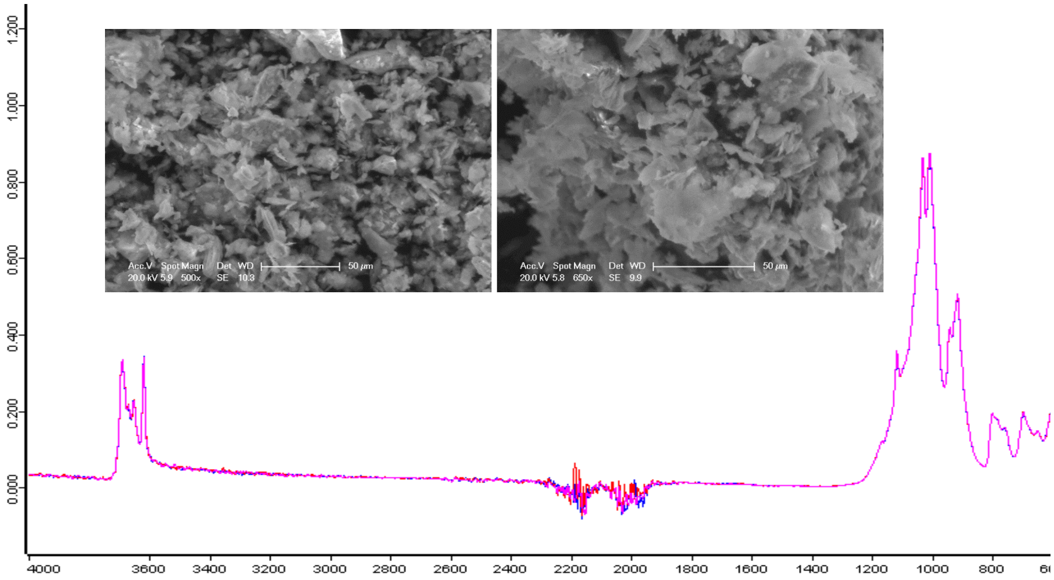


Figure 2. ATR-FTIR-spectrum of kaolin powder. The x-axis shows the wave number within a range of 600 to 4000 cm^{-1} and the y-axis absorbance. SEM images for different positions of kaolin sample in inserted images.

from the hydroxyls located on the surface of the octahedral layer and the lowest band derives from inner hydroxyls lying between the tetrahedral and octahedral sheets. The strong bands between 1000 cm^{-1} and 1200 cm^{-1} come from Si-O and Al-O vibrations, whereas the bands in the range between 900 cm^{-1} and 1000 cm^{-1} arise from O-H-stretching vibrations. The sharp pattern of the bands reveals the presence of highly crystalline Kaolinite.

The filler mapping, made by SEM, shows the clay's homogenous, porous texture which derives from the Kaolinite crystals forming plates and aggregating to clusters. The adsorption capacity strongly depends on the physical properties of the material like surface area to volume ratio, as well as on the chemical composition (25).

3.2. Determination of VOC's in presence of kaolin filled samplers

Preliminary studies on the thermal desorption of spiked samplers was performed by using four membranes spiked with a constant mass of 15 μg of VOCs and different amounts of 50, 100, 150 and 200 mg kaolin. The thermal desorption of these spiked samplers in the headspace vials showed differences regarding the vaporization of the compounds and the sensitivity of the measurements. The vaporization program for VOCs of 150°C for 10 minutes was employed in former studies providing an adequate sensitivity (26). The equilibration time for desorption of the captured molecules depends on the diffusion of the compounds from the samplers to the gaseous phase account the partition coefficient between the gas phase and the LDPE tube and kaolin.

According data regarded in figure 3, generally the sensitivity decreases on increasing amount of kaolin present in HS vial. Therefore, the amount of 50 mg kaolin was selected for further studies. This trend derives from the presence of matrix effects and the fact that an increase of the kaolin provide a strong retention of VOCs in front of their thermal desorption.

3.3. Analytical features

The establishment of calibration curves for each studied compound was performed by using membranes spiked with VOCs standards at seven concentration levels and 30 μg of toluene-d_8 used as internal standard. The studied linear response ranged from 15 ng to 15 μg with determination coefficients (r^2) ranging from 0.9390 until 0.9999. The calculated slope of each calibration curve was taken as an estimation of the sensitivity. The theoretical limit of detection (LOD) was established from the lowest deployed mass of VOCs, which could be measured with a signal-to-noise ratio higher than 3, being calculated using the Xcalibur software from Thermo-Finnigan. For all compounds limit of detection values from 38 till 56.5 ng were found. The relative standard deviation (RSD) was calculated for independent measurements of membranes spiked with 10 μg of VOCs. The obtained values can be seen in table 2.

3.4. Adsorption of VOCs from air

The assessment of the adsorption behaviour of VOCs was examined with two different experiments. Previous studies were made with the uptake of VOCs through exposing membranes with different amounts kaolin to known air concentrations and additional experiments were performed with different air concentration of VOCs in air and a constant amount of kaolin.

Figure 4 shows the adsorbed amount of VOCs by exposing membranes with 50 mg of kaolin to an air concentration of 3.51 mg m^{-3} in sealed bottles for 24 hours. In general, the samplers filled shown a good compromise between the retention of VOCs from the air and afterwards release of them during the heating of the vial.

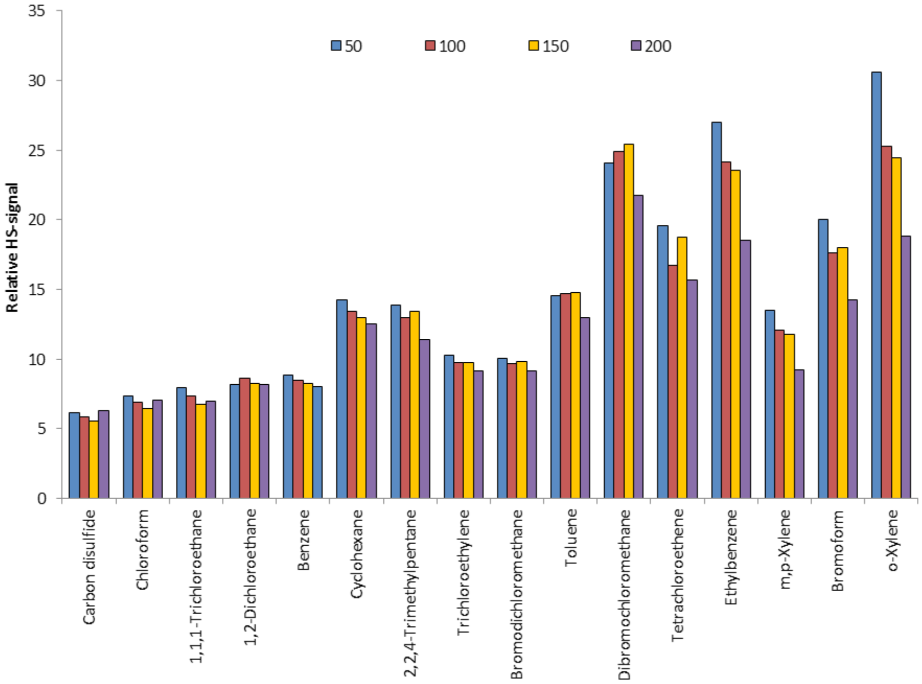


Figure 3. Relative HS signal obtained for VOCs thermal desorption in presence of kaolin filled SPMD's. The relative HS signal was calculated from the obtained peak area for each measured compound for different amounts of kaolin divided through the peak area obtained from the measurement of pure VOCs standard solution with a total amount of 15 µg of VOCs. The relative peak area was calculated by dividing the measured peak area through the area of the internal standard.

Table 2

Figures of merit of the HS-GC-Ms determination of VOC's in passive samplers filled with kaolin

Compounds	Kaolin filled samplers			
	Sensitivity	$r^{2\ a}$	LOD ^{b} (ng)	%RSD ^{c}
Chloroform	0,63	0,93910	47	3,0
1,1,1-Trichloroethane	0,65	0,96304	38	0,5
1,2-Dichloroethane	0,44	0,95448	38	2,7
Benzene	1,83	0,97789	41	3,3
Trichloroethylene	0,80	0,98894	44	5,0
Bromodichloromethane	0,63	0,98816	46	2,4
Toluene	2,99	0,99916	46,5	4,6
Dibromochloromethane	0,70	0,99896	47	2,0
Tetrachloroethene	1,37	0,99816	56,5	2,2
Ethylbenzene	2,39	0,99998	39	6,1
m,p-Xylene	4,90	0,99982	39	4,0
Bromoform	0,59	0,99868	48	1,6
o-Xylene	2,25	0,99947	38	4,7

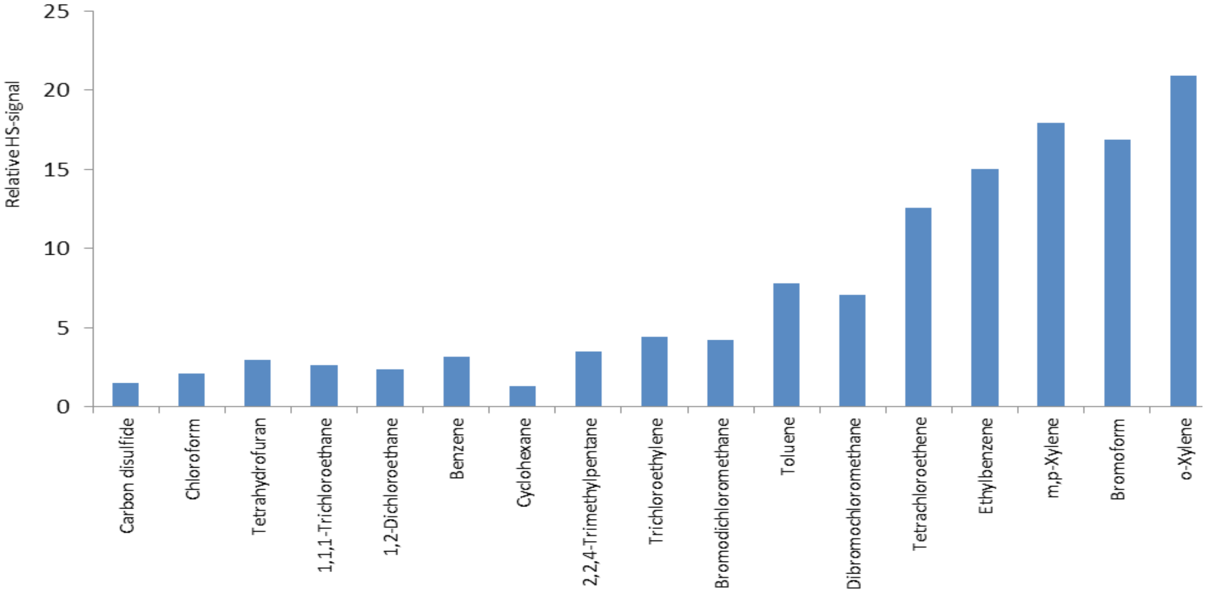


Figure 4. Relative signals obtained by HS-GC-MS for each assayed compound, using samplers deployed for 24 hours in the presence of an air concentration of 3.51 mg m^{-3} in topaz glass bottles.

Another experiment was carried out with membranes filled with 50 mg of kaolin, exposed to two different concentrations of VOCs of 7.02 mg m^{-3} and 3.51 mg m^{-3} air (obtained by vaporization of 20 and 10 μg of the VOCs standard pool) in sealed bottles. The exposition time was 24 hours in both cases. Figure 5 shows that the amounts of each compound retained in the sampler is proportional to their concentrations in the bottles for all the VOCs, indicating the capability of the samplers to provide quantitative information about the presence of VOCs in air. The high accumulation of high-boiling compounds probably is related to their high partition coefficients and therefore their high affinity to the sampler.

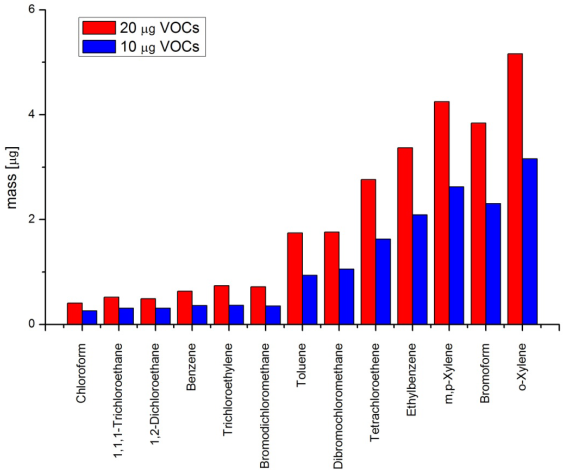


Figure 5. Adsorbed masses of each considered compound determined by HS-GC-MS using two different air concentrations of VOCs.

So, the efficiency of adsorption is mainly affected by the physical properties of the adsorbed molecules, such as molecular weight, boiling point, vapour pressure and octanol-air partition coefficient as well as the exposure conditions, like temperature and wind speed and figure 5 shows that the most volatile compounds are worse retained than the less volatile. Chloroform and 1,1,2-trichlorethane have high vapour pressures and low boiling points and are frequently found in the gas phase. These non-polar organic substances could be bound to the adsorbent through van der Waals forces. On the other hand, substances like bromoform and tetrachlorethane are adsorbed because of these weak physical interactions, as well. However, they have low vapour pressures and extend, thus tend be retained on the solid phase. Aromatic compounds, like xylenes were retained in a big, even if they have low boiling points and high vapour pressures than bromoform. This special adsorption behaviour of aromatic compounds can be explained because of the reinforcement of the bonding between the aromatic system and the clay surface by donation of π-electrons. Moreover the aromatic system can act as an acceptor for the protons located in the hydroxyl inter-layer (25).

For most of the investigated VOCs, the signals obtained for the membranes exposed to 20 μg of VOCs is not twice of those exposed to 10 μg of VOCs, indicating that maybe the sampler could be saturated at such high air concentrations of VOCs.

3.5. Field studies

The air quality in a fume hood and the gas phase composition inside a waste container were evaluated with SPMD´s filled with kaolin. Samplers were exposed for 24 hours to evaluate the concentration of VOCs.

For air quality evaluation, samplers were placed on a fume hood were VOCs standard were used and after that were capped on HS vials and analysed by HS-GC-MS. Figure 6 shows the results for this study.

In the determination of gas phase waste composition, samplers were placed into the empty part of a waste container. As in previous study, the waste consists mainly of VOCs, hexane and solvents employed for liquid chromatography and almost all investigated VOCs could be found in the chromatograms. The measurement of the samplers exposed in gas phase waste container reveals that volatile compounds like chloroform, 1,1,1-trichloroethane, 1,2 dichloroethane and benzene, were detectable (see figure 7).

4. Conclusions

This study shows the opportunity to determine VOCs in air by using passive sam-

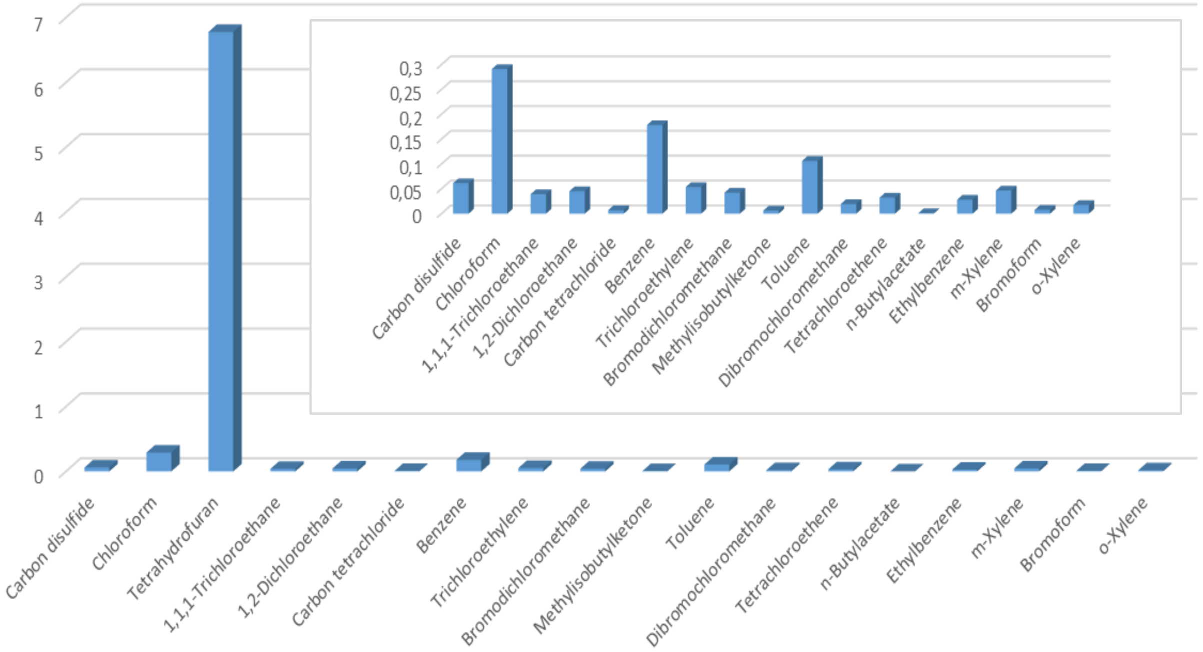


Figure 6. Relative response obtained for analytes under the study in a laboratory fume hood obtained after the deployment of kaolin filled samplers for 24 hours.

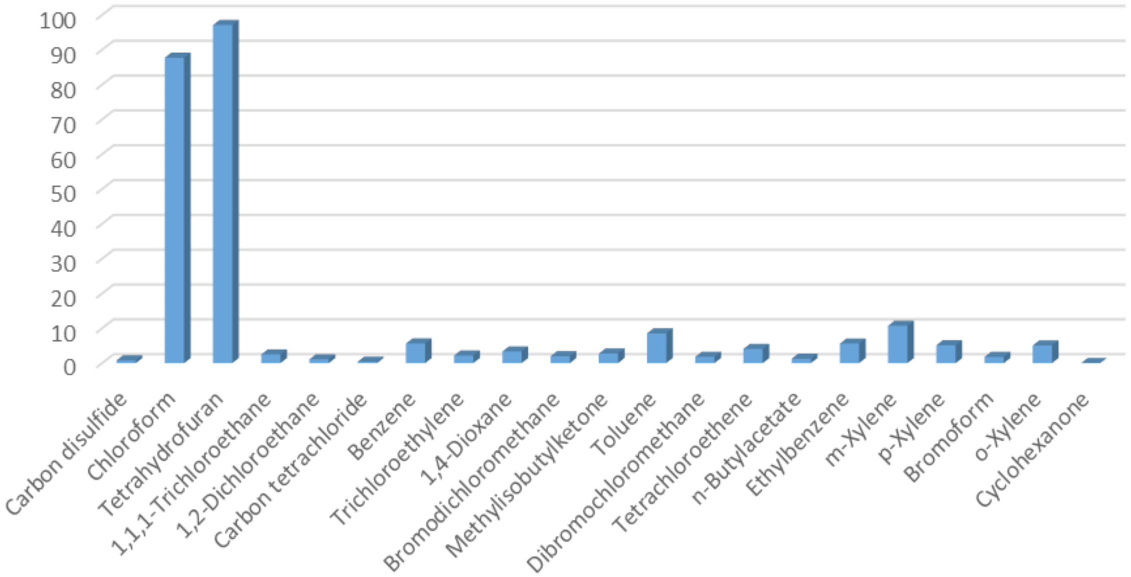


Figure 7. Gas phase composition obtained by analysis of deployed samplers.

plers filled with kaolin. The omission of organic solvents in this process reduces the risks of contamination of both, laboratory workers and the environment, providing a green methodology.

On the other hand, kaolin is a natural product and the replacement of previously used samplers filled with activated carbon and florisil improves the analytical figures and reduces the cost of the devices.

Acknowledgement

Authors thanks for the economic support to Ministerio de Economia y Competitividad-Feder (Projects CTQ2011-25743 and CTQ 2012-38635) and Generalitat Valenciana (Project Prometeo 2010-55)

References

1. BARRO R., REGUEIRO J., LLOMPART M., GARCIA-JARES C. ***J Chromatogr A*** 1216: 540-566. 2009.
2. http://www.epa.gov/iaq/voc.html (2012).
3. Esteve-Turrillas F. A., Pastor A., de la Guardia M. ***Anal Chim Acta*** 593 (1): 108-116. 2007.
4. SANJUAN-HERRAEZ D., RODRIGUEZ-CARRASCO Y., JUAN-PEIRO L., PASTOR A., DE LA GUARDIA M. ***Anal Chim Acta*** 694 (1-2): 67-74. 2011.
5. YUSA V., COSCOLLA C., MELLOUKI W., PASTOR A., DE LA GUARDIA M. ***J Chromatogr A*** 1216 (15): 2972–2983. 2009.
6. ZHANG Z., MA Y., LI G. ***Anal Methods*** 5 (1): 20-29. 2013.
7. BAROJA O., RODRIGUEZ E., GOMEZ DE BALUGERA Z., GOICOLEA A., UNCETA N., SAMPEDRO C., ALONSO A., BARRIO R.J. ***J Environ Sci Heal A*** 40: 343-367. 2005.
8. MUEZZINOGLU A., ODABASI M., ONAT L. ***Atmos Environ*** 35 (4): 753-760. 2001.
9. SRIVASTAVA A., DEVOTTA S. ***Environ Monit Assess*** 133 (1-3): 127-138. 2007.
10. PASTOR A., DE LA GUARDIA M., ESTEVE-TURRILLAS F.A. Patent application number P200900912/6.
11. ESTEVE-TURRILLAS F.A., LY-VERDU S., PASTOR A., DE LA GUARDIA M. ***J. Chromatogr A*** 1216 (48): 2849-8553. 2009.
12. KOSIKOWSKA M., BIZIUK M. ***Trend Anal Chem*** 29 (9): 1064-1072. 2010.

13. ESTEVE-TURRILLAS F. A., LY-VERDU S., PASTOR A., DE LA GUARDIA M. ***J Chromatogr A*** 1216 (48): 2849-8553. 2009.
14. HUCKINS J. N., BOOIJ K., PETTY J. D. ***Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices***. Springer Science+Business Media, USA, 2006.
15. LY-VERDU S., ESTEVE-TURRILLAS F. A., PASTOR A., DE LA GUARDIA M***. Anal. Chim. Acta*** 677: 131-139. 2010.
16. KRÓL S., ZABIEGAŁA B., NAMIESNIK J. ***Trends Anal Chem*** 29 (9): 1101-1112. 2010.
17. TUDURI L., MILLET M., BRIAND O., MONTURY M. ***Trends Anal Chem*** 31: 38-49. 2012.
18. SNOW N.H., BULLOCK G.P. ***J Chromatogr. A*** 1217: 2726-2735. 2010.
19. TIAN J. ***J Food Compos Anal*** 23: 475-479. 2010.
20. DELLE SITE A. ***J Phys Chem-US*** Ref. Data 30: 187-438.2001.
21. AHN M.-Y., FILLEY T.R., JAFVERT C.T., NIES L., HUA I., BEZARES-CRUZ J. ***Environ Sci Technol*** 40: 215-220. 2006.
22. KIBANOVA D., TREJO M., DESTAILLATS H., CERVINI-SILVA J. ***Catal Commun*** 12: 698-702. 2011.
23. MOA J., ZHANG Y., XU Q., LAMSON J.J., ZHAO R. ***Atmosph Environ*** 43: 2229-2246. 2009.
24. CONLEY ROBERT T. ***IR Spectroscopy***. Ed. Alhambra (Spain). 1979.
25. FARMER V. C., RUSSEL J. D. ***Clay Clay Miner***. 121-142. 1966.
26. RUIZ J., BILBAO R., MURILLO M. B. ***Environ Sci Technol*** 32: 1079-1084. 1998.
27. SANJUÁN-HERRÁEZ D., LLISO I., PASTOR A., DE LA GUARDIA M. ***Talanta*** 98: 40-48. 2012.
28. LY-VERDU S., ESTEVE-TURRILLAS F. A., PASTOR A., DE LA GUARDIA M. ***Talanta*** 80: 2041-2048. 2010.