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# Green determination of the presence of volatile organic compounds in vehicle repair shops through passive sampling

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#### article info

**ABSTRACT** 

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# 1. Introduction

Emission sources of dangerous compounds for the environment and the human health are present in our daily life, as traffic, industrial processes, solvents, pesticides, paints, building materials, cleaning supplies or office equipment. Volatile organic compounds (VOCs) are commonly emitted by the aforementioned sources and constitute a wide group of chemicals with different physico-chemical properties (see [Table 1\)](#page-1-0). The determination of indoor air quality in working areas implies also the quantitative determination of VOCs as a very important parameter in order to ensure the workers health due to the high volatility of VOCs at normal atmospheric conditions of temperature and pressure [\[1\]](#page-8-0).

Monitoring campaigns of air quality are usually expensive and involve the use of high amounts of reagents and solvents. In recent years, methodologies based on passive sampling have been developed in order to reduce the costs in front of the use of active sampling methods. Low price, simplicity, ease of use, the lack of a required power supply and the fact that they provide timeweighted average (TWA) concentrations makes passive sampling a suitable tool for air monitoring. Solid-phase microextraction (SPME), polyurethane foam disks, Radiello samplers and semipermeable membrane devices (SPMDs) have been widely employed in the last years as passive samplers [\[2\].](#page-8-0)

The basic configuration of a SPMD consists of a low-density polyethylene layflat tube (LDPE) filled with triolein [\[3\].](#page-8-0) Modifications in the standard configuration of SPMDs were proposed in the

A simple, fast and green direct analytical methodology has been developed to evaluate the concentration level of volatile organic compounds (VOCs) in indoor areas of vehicle repair shops using membrane devices as passive samplers. VOCs retained in the samplers were directly determined without any sample pre-treatment and avoiding the use of solvents by head space (HS) coupled to gas chromatography–mass spectrometry (GC–MS) in only 20 min. Benzene, toluene, tetrachloroethene,  $m$ , p-xylene and o-xylene were found at concentration levels from 0.1 to 11.2 mg m<sup>-3</sup>.

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literature, changing the polymer material and filling solvent [\[4\].](#page-8-0) Recently, a versatile, easy and rapid atmospheric monitor (VERAM) passive sampler device was developed by our group [\[5\]](#page-8-0). This sampler was based on the use of a LDPE layflat tube filled with a solid-phase instead of triolein, which reduces the costs and allows the sampling of a wide range of compounds with different physicochemical properties.

The aim of this study was to develop an easy and low cost methodology to determine the contamination scenarios established by the new registration, evaluation, authorization and restriction of chemical substances (REACH) European norm [\[6\]](#page-8-0) through the use of VERAM devices as passive samplers. Head–space–gas chromatography–mass spectrometry (HS–GC–MS) was employed to evaluate the presence of a wide group of VOCs by direct measurement of samplers deployed in different sites of two vehicle repair shops as a practical application. The method employed not involved the need of using any solvent nor additional reagents, thus providing a green alternative to do this kind of determinations [\[7–8\]](#page-8-0).

# 2. Material and methods

# 2.1. Apparatus and reagents

A Finningan Trace Gas Chromatography (Waltham, MS, USA) equipped with a Phenomenex (Torrance, CA, USA) Zebron ZB-5MS  $(30 \text{ m} \times 0.32 \text{ mm}, 0.25 \text{ \mu m})$  capillary column and a Finnigan HS2000 head-space (HS) injector was used for VOCs determination. A Finnigan Polaris Q ion trap mass spectrometer detector was coupled to the chromatographic system. Glass vials, with an



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<span id="page-1-0"></span>





<span id="page-2-0"></span>Table 1 (continued )

<sup>a</sup> Octanol–air partition coefficient ( $K_{oa}$ ). b  $K_{oa}$  values were estimated with KOAWIN v1.10 software.

internal volume of 10 mL, capped with PTFE-butyl rubber seals were employed for HS measurements.

LDPE layflat tubing with 2.9 cm wide, obtained from Garciplast (Barcelona, Spain), activated carbon from Panreac (Barcelona, Spain) and florisil from Across (Geel, Belgium) were employed for homemade preparation of VERAMs. A Roblevoc sealer (Barcelona, Spain) was used to heat-seal the membranes after to be filled with the packaging materials.

VOC standards were obtanined from Fluka Chemie (Buchs, Switzerland), Scharlau (Barcelona, Spain), Sigma-Aldrich (St. Louis, USA) and Merck (Steinheim, Germany). VOC standard mixtures at different concentration levels were prepared in n-hexadecane from Scharlau. Toluene-d<sub>8</sub> (99.96%) from Sigma-Aldrich (St. Louis, USA) was used as internal standard (IS) at a final concentration of  $1.5 \mu g$  in *n*hexadecane.

# 2.2. Samplers preparation

Preparation of VERAM samplers was carried out according to previously described methods [\[7\]](#page-8-0). LDPE layflat tubing was cut in 10 cm length segments which were soaked overnight in hexane in order to remove any possible additives and interfering compounds. After the cleaning step, LDPE segments were placed under nitrogen flow to dry the devices. Then, the VERAM was heat-sealed at one end and 5 mg activated carbon and 50 mg of florisil were introduced into the device, shaking the membrane to homogenize the solid phase. The other end of the tubing was also heat-sealed, with a final effective length of 9 cm (See [Fig. 1](#page-3-0)).

VERAMs were wrapped in separate aluminum foils and stored individually in closed vessels at  $-20^{\circ}$  C to avoid contaminations before the field deployment. After the sampling time, the same procedure was employed for the transport and to store the devices. Furthermore, blank samplers were prepared in the same way than those deployed to confirm the absence of contaminations during samplers manufacturing and transport.

# 2.3. Field studies

Threshold limit values-time weighted average (TLV-TWA) is the level exposure values to chemical substances that a worker can be exposed daily, without adverse health effects. Thus, VERAM devices were deployed for 8 h in vehicle repair shops to compare results obtained with TLV-TWA legislated levels. Samplers were placed 3 m above the ground of two vehicle repair shops located in Valencia (Spain), a motorbike (A) and a car (B) shop respectively. Additionally, VERAM devices were also deployed at different deployment times of 24, 48, 72 and 96 h in order to evaluate the influence of the indoor activity during the week. Moreover, one sampler was placed in the motorbike repair shop during 15 days to compare the short exposition time data with a long exposition time one. [Table 2](#page-3-0) shows a description of the sampling sites selected in each place.

**SCHEME OF THE PROPOSED METHODOLOGY**

<span id="page-3-0"></span>

Fig. 1. Sampler preparation and HS-GC-MS analytical method employed for the determination of VOCs in vehicle repair shops. Inset 1: Green analytical parameters of the employed method. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Description of sampling sites selected of vehicle						
repair shops evaluated in this study.						



#### 2.4. VOCs determination by HS–GC–MS

The determination of VOCs retained in VERAM samplers was evaluated based on studies made on previous VOCs spiked samplers loaded also with 5 µL of IS, which were analyzed by HS–GC–MS. Each device was heated in the HS oven at  $150^{\circ}$  C for 10 min. A volume of 100 µL from the vapor phase generated inside the HS vial was injected in the GC–MS system with a syringe temperature of  $150^{\circ}$  C and a constant air flow purge. The injection was done in split mode  $(1:10)$  at 200 $^{\circ}$  C, employing 1 mL min<sup>-1</sup> constant flow of helium as carrier gas. The GC oven program temperature was  $40^{\circ}$  C, held for

9 min, increased at a rate of 20 $^{\circ}$  C min<sup>-1</sup> up to 200 $^{\circ}$  C, and finally held for 2 min. The transfer line and source temperatures were 300 and 250  $°C$ , respectively. Electron impact ionization at 70 eV was employed and a mass scanning range from 40 to  $180 \, m/z$  was used for full scan acquisitions. [Table 3](#page-4-0) shows the measured  $m/z$  ions employed for each studied compound, together with their chromatographic retention times.

Fig. 1 shows, additionally than sampler preparation, the HS– GC–MS determination steps including also a pictogram (inset 1), describing the green parameters of the employed method.

# 3. Results and discussion

### 3.1. Analytical features

Calibration curves were obtained at seven concentration levels with VERAM samplers spiked with VOC standards from 15 ng to 15  $\mu$ g also spiked with IS (1.5  $\mu$ g). A linear response was obtained along the studied interval with correlation coefficients  $(r)$  ranging from 0.9881 to 0.9999. Limit of detection values (LOD) were established as the VOC concentration that provided a signal-tonoise ratio (S/N) higher than 3, which was calculated using Xcalibur software from Thermo-Finnigan. [Table 3](#page-4-0) shows the

#### <span id="page-4-0"></span>Table 3

GC–MS parameters and figures of merit of the direct green determination of VOCs in VERAM samplers.



<sup>a</sup> Retention time.

**b** Correlation coefficient.

 $c$  Relative standard deviation of 3 measurements made on a standard mixture at 1.5 µg concentration level.

<sup>d</sup> Reproducibility at 1.5 µg spiked level (n=5).

<sup>e</sup> Internal standard.



**Fig. 2.** HS–GC–MS chromatograms of a VOCs standard mixture of 7.5 µg VERAM $^{-1}$  concentration level measured in full scan mode (a), and extracted ion chromatograms obtained at  $m/z$  78 (b),  $m/z$  166 (c) and  $m/z$  91 (d) for a VERAM sampler deployed in a car repair shop for 48 h.

LOD and RSD values for every VOC with experimental values ranging from 15 to 75 ng VERAM<sup> $-1$ </sup> and from 2.8% to 9.2% for all compounds respectively. Precision expressed as reproducibility was also evaluated with five injections of 1.5 µg VOC standard in 5 consecutive days. Good precision was obtained for the majority of studied compounds.

Method quantitation limit (MQL) for compounds present in the air of studied places was evaluated for the whole procedure, starting from the sampling of air and ending with the transport and handling of the VERAM deployed devices in vehicle repair shops. To do it, the chromatographic signals obtained in the different places in which the target molecules were identified, were evaluated; taking into account the S/N ratio in order to fix the minimum amount of considered compounds that provide a S/N ratio of 10. In these conditions the MQL value for benzene was 40, for toluene was 30, for ethylbenzene 140, for m,p-xylene 180, for o-xylene 150 and for tetrachloroethene 50 ng VERAM<sup> $-1$ </sup>, which correspond to 0.05 till 0.15 mg m<sup>-3</sup>.

Fig. 2 shows the HS–GC–MS chromatogram obtained in full scan mode for a VERAM device spiked with 7.5  $\mu$ g VERAM<sup>-1</sup> VOC standard mixture and extracted ion chromatograms found for one VERAM deployed in a sampling site of a car repair shop for 48 h. As it can be seen the peak resolution achieved was satisfactory to analyze all considered VOCs with enough sensitivity in only 10 min.

# 3.2. Uptake behavior of pollutants in VERAM devices

The uptake of chemicals by passive samplers can be easily explained in three different stages: (i) a linear uptake, (ii) a curvilinear step, and (iii) equilibrium with the sampling media [\[4\].](#page-8-0) Thus, the same passive sampler can operate in two modes: kinetic, for short sampling times, and equilibrium, for long times, depending only on the exposure time. Laboratory calibration experiments are required to estimate the corresponding uptake parameters, by means of the use of adsorption isotherm data of VERAM samplers deployed at different times in containers with well known air concentrations of the target compounds. This calibration was performed by our group in previous studies [\[8\]](#page-8-0) for all the aforementioned VOCs under study and the equilibrium was reached in less than 24 h for all the evaluated compounds.

The kinetic sampling was governed by linear first-order kinetics, far from the equilibrium between sampler and air, thus the VOC amount accumulated in the sampler was determined by the analyte TWA concentration in air, the exposure time, and the sampling rate  $(R<sub>S</sub>)$  of accumulation of the studied compound in the sampler. While the sampler operates in the equilibrium mode, the thermodynamic equilibrium was reached and therefore the VOC amount accumulated in the sampler was directly related to the sampler-air partition coefficient  $(K_{SA})$ . The sampling was governed thus by  $R_S$  and by  $K_{SA}$ , as a function of the deployment time, as indicated in the following equations, respectively [\[9\]](#page-8-0):

$$
C_{\text{Kinetic}} = R_{\text{S}}t/N_{\text{VERAM}} \tag{1}
$$

$$
C_{Equilibrium} = N_{VERAM}/K_{SA}V_S = N_{VERAM}/K'_{SA}
$$
 (2)

where  $N_{VERAM}$  (ng) is the VOC amount determined in the sampler; t (h) is the sampling time; and  $C_{Air}$  (ng m<sup>-3</sup>) is the VOC concentration in air;  $V_S(m^3)$  is the volume of the sampling area;  $K_{SA}$  is the sampler–air partition coefficient; and  $K_{SA}$   $(m^3)$  is the pseudo-sampler–air partition coefficient. (See Fig. 3 as an indication of the isotherm obtained for toluene using VERAM samplers.)

#### 3.3. Air quality of vehicle repair shops

The air quality of two vehicle repair shops located in Valencia (Spain) was evaluated using VERAM passive samplers to determine the presence of VOCs in the working air. Devices were placed in two different sampling sites of each vehicle repair shop. Different exposure times from 8 to 96 h were employed in order to evaluate the influence of the different inter-day activity in the places under study being also studied the deployment time of 15 days in the case of the motorbike repair shop (A). [Table 4](#page-6-0) summarizes the results obtained for all sampling sites. Benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene were detected at concentration levels ranging from 40 to 8400 ng VERAM $^{-1}$ . These results



Fig. 3. Adsorption isotherm obtained for toluene using VERAM devices at  $25^{\circ}$  C and 1.75 mg m $^{-3}$  air concentration.

are coherent with the fact that all the aforementioned VOCs are present in many products that were found in a car repair shop as fuels, oils and cleaning engine products.

[Fig. 4](#page-7-0) shows the amount of VOCs accumulated by VERAM samplers at two different sampling sites of a motorbike repair shop in four consecutive days. In some cases, the amount of VOCs increases on increasing the sampling time. However, in other cases, increases and decreases of the amounts detected as a function of time were found. These variations can be explained by the different inter-day activity in the motorbike repair shop and shows that samplers are, in all cases in equilibrium with the air, except for 8 h sampling time, for which deployment time the equilibrium was not reached (see Fig. 3). So, it can be seen that VERAM samplers are able to catch and release pollutants as a function of increases or decreases of the pollutant concentrations in the indoor air, reflecting thus the average concentration of VOCs in the air during the sampling period. Samplers deployed during 15 days confirm the aforementioned situation and evidenced that results obtained for this sampling time were comparable with those found after 72 and 96 h. On the other hand, samplers deployed during 8 h workday show concentration values below TLV-TWA legislated levels. [Fig. 5](#page-7-0) also shows that the VOCs present in a car repair shop are practically the same than those measured in the motorbike repair shop except for tetrachloroethene in the warehouse for which concentrations from 1000 to 3000 ng VERAM $^{-1}$  were found for long deployment times and 75 ng VERAM $^{-1}$  for a sampling period of 8 h. This compound is commonly used to clean the motor engines and motor pieces and thus it is not surprising that the concentrations found in the working area could be three orders of magnitude lower than those found in the warehouse.

The equilibrium concentration of detected VOCs in the air was calculated from the amount of VOCs found in VERAM samplers combined with uptake parameters ( $K_{SA}$  and  $R_s$ ) obtained from previous studies  $[8]$  at 25 $^{\circ}$  C. In fact the temperature in the sampling sites was  $25\pm3$ °C. So, uptake parameters obtained from isotherms studies made at  $25^{\circ}$  C could be employed for calculations. The VOCs concentration levels found ranged from 0.1 to 11.2 mg  $m^{-3}$  and are quite below the legislated levels (see [Table 4\)](#page-6-0).

#### 3.4. Evaluation of the green parameters of the method

HS–GC–MS determination of VOCs in indoor air is a totally green alternative which avoids the use of organic solvents and the addition of reagents apart from those employed for calibration and toluene-d $_8$  which was used as internal standard. The use of very small amounts of reagents and the mg amounts of florisil and activated carbon used to fill up the passive samplers provides less than 100 mg of solid residues for each analysis. On the other hand, the heating at  $150^{\circ}$  C of the samplers, made to do the determinations, put outside of the residues, the VOCs and thus we can conclude that the remaining solid wastes of the method are nontoxic. So, pictograms in the inset of [Fig. 1](#page-3-0) well show that the proposed methodology is a green alternative in all senses [\[8\]](#page-8-0) except in the case of energy consumes which corresponds to a heating time of 10 min at  $150^{\circ}$  C for each sample.

On making the evaluation of the strengths, weaknesses, opportunities, and threats (SWOT) of the proposed procedure [\[10\]](#page-8-0) it is clear that the methodology is fast, suitable for a long series of target compounds, cheap and safe. However, the need of a deep evaluation of adsorption isotherms to be able to evaluate the air concentrations, from the amount of compounds caught by the samplers, can be considered as a weakness of the methodology for its extension to additional compounds. The main opportunity of the methodology is its good analytical and green



<span id="page-6-0"></span>Concentration of VOCs found in the air of car repair shops sampled with VERAM and estimated levels in air.

<sup>a</sup> Standard deviation (n=3).<br><sup>b</sup> Threshold limit values-time weighted average obtained for reference www.insht.es.<br><sup>c</sup> Values under method quantitation limit (MQL).

<span id="page-7-0"></span>

Fig. 4. VOCs determination in a washing area (1) and working area (2) of a motorbike repair shop after different VERAM deployment times.



Fig. 5. VOCs concentration in VERAM samplers deployed in a warehouse (1) and a painting area (2) of a car repair shop, for different VERAM deployment times.

parameters and the good performance of the method to evaluate the contaminated scenarios in the frame of the REACH norm which provides an excellent tool for both, industrials and workers, to evaluate the indoor conditions in a fast way and at a cheap price.

On looking for the threats it must be assumed that for specific volatile emerging contaminants, not considered in this study, probably it will be required the use of alternative solid phases to fill the membranes but that will open new opportunities for basic research.

<span id="page-8-0"></span>Shortly, this applied methodology works better than previous ones suggested in the literature with the use of Radiello samplers, which can be directly analyzed by high temperature thermal desorption involving a big consumption of energy [11]. In other cases, the elution of the retained VOCs on Radiello samplers with carbon disulfide avoids the use of high temperatures but implies a consumption of organic solvents [12].

### 4. Conclusions

VERAM passive sampling methodology has been successfully applied to determine the indoor quality of air in vehicle repair shops. VOCs were detected at trace levels (few  $\rm ng\,m^{-3})$  and LODs obtained were clearly below legislated levels. So, it can be concluded that VERAM samplers are suitable tools to evaluate the air quality in the studied places and that the studied places are in good agreement with the mean tolerated threshold limit values of the time weighted average concentration of VOCs [13].

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