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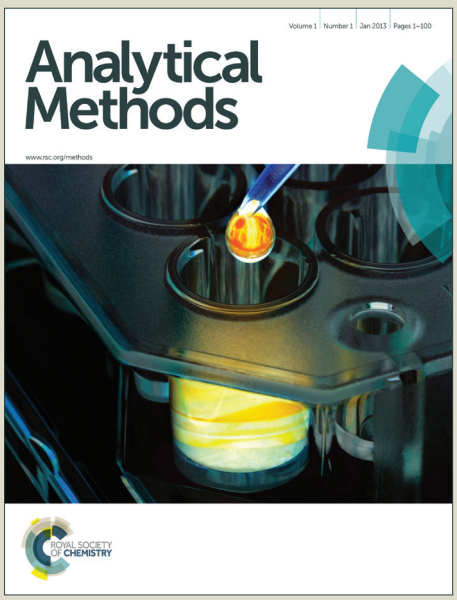

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SAMPLING AND ANALYSIS OF PESTICIDES IN THE GAS PHASE OF AIR: METHOD VALIDATION USING A VOLATILIZATION CHAMBER

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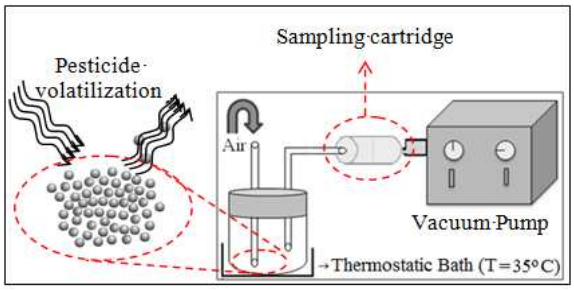
This study aimed to develop and validate an analytical method for the determination of pesticides in the gas phase of air employing a simple and cheap apparatus to simulate atmospheric contamination.



ABSTRACT

This study evaluated the efficiency of Tenax® resin to sample the pesticides atrazine, chlorpyrifos, α, β-endosulfan, metolachlor and trifluralin from contaminated air in a volatilization chamber. The air contamination was performed by adding pesticide masses in the range of 100-750 ng in a chamber at air flow rate of 2.60 L min^{-1} at 35° C for 12 h. After volatilization, pesticides followed the airflow toward the cartridges packed with two sequential sections of Tenax® resin, separated by glass wool. In this apparatus, the sampling efficiency remained between 83-119%, with RSD% lower than 14%. The method quantitation limit (LQM) was 53.4 ng m^{-3} for all studied analytes. Comparative trials with the resin XAD®-2 showed sampling efficiency between 78 and 135%, with CV less than 17%. The volatilization chamber also allowed the evaluation of the volatilization profile of each analyte and helped in the sampling cartridges setting, in order to prevent the breakthrough effect.

Keywords: Air pollution, active sampling, Tenax®, volatilization chamber, herbicide.

1. INTRODUCTION

The massive use of pesticides in modern agriculture has been causing great concern mainly regarding environmental contamination. Some studies show that 80 to 90% of the applied pesticide dose may miss their target, reaching other environmental compartments such as soil, water bodies and atmosphere.[1-4] It has been estimated that during pesticides application, around 20 to 30% of the applied dose, in some cases more than 50% is lost to the atmosphere by drift.[3] Thus, the determination of pesticides in this compartment is of great importance since the atmospheric transport is one of the major sources of environmental pollution by these substances which, once in the air, may reach areas distant from the application site.[5]

The determination of pesticides in the gaseous phase of air is preceded by two phases; the first and more critical one, the sampling, where usually a solid adsorbent associated or not to a filter is used and the second that corresponds to the extraction of the pesticides retained in the adsorbent. It is important to point out, that the efficiency assessment of the sampling procedures involving atmospheric matrix is very complex, with no normalized methods available.[6] The validation of the sampling step has been addressed in the literature using different approaches. In some cases, its efficiency is evaluated using only the recovery results obtained from the extraction of the pesticides applied directly to the adsorbent from a standard solution.[7-12] In other studies, the evaluation involves passing air through the adsorbent previously contaminated with pesticides, verifying subsequently the eventual loss of these analytes.[13,14] The validation of the sampling process has also been done using multiple sections of the adsorbent prearranged in series in a cartridge, determining the eventual transference of the pesticides to these sections.[4,15,16] Studies that assessed the efficiency of the sampling step using air previously contaminated with pesticides, a procedure that better simulate the interaction analyte/adsorbent, are still scarce.

In this context, the present study aimed to develop and validate an analytical method for the determination of atrazine (Atraz.), chlorpyrifos (Chorp.), α and β-endosulfan (End.), metolachlor (Metol.) and trifluralin (Trif.) in the gas phase of air employing a simple and cheap apparatus to simulate atmospheric contamination. The resin Tenax® was used as adsorbent due to its high capability to retain organic compounds from the atmosphere.[5,6] The analytes were selected due to their relatively high volatility and large use in agricultural regions in several parts of the world.

2. MATERIAL AND METHODS

2.1 Glassware cleaning

The glassware was immersed in a 2% (v/v) aqueous solution of Extran Alkaline MA-01 (Merck®) for six hours. After this period, they were rinsed successively with tap water, distilled water and small portions of acetone p.a. grade (Cromoline). After rinsing, the non-volumetric glassware was dried at 150 ºC in a forced air circulation drying oven. The volumetric material was dried at ambient temperature (27±3 °C).

2.2 Solvents, primary standard and adsorbents

Standard solutions were prepared in acetone HPLC grade, Tedia (for spiking) and toluene HPLC grade, Tedia (for chromatographic analysis). In the extraction procedure, pesticide grade isooctane (Mallinckrodt Chemicals), ethyl acetate, n-hexane and acetone (Tedia), were used. Primary standards of atrazine, chlorpyrifos, β-endosulfan, metolachlor and trifluralin were acquired from Sigma-Aldrich and α-endosulfan from Dr. Ehrenstorfer, all with purity equal or higher than 97%. Deuterated phenanthrene-d_{10} (Phen.) 99% pure, used as internal standard, as well as, the resins Tenax® (SKC®) and XAD®-2 were from Supelco.

2.3 Equipment

In the weighing of the standards and adsorbent, an analytical balance was used (precision ± 0,0001 g) Bel Mark, model 210 A; dispensers Eppendorf of fixed volume (50 µL) and adjustable volume (100-1000 µL) were used for solutions preparation; flow calibrator and vacuum pumps SKC, model 224-PCXR8 were used for air sampling. During the experiments, the volatilization chamber was kept in a thermostatic bath Marconi, model MA 146. An ultrasound assisted extraction of pesticides was carried out in an ultrasonic bath Bransonic, model 3510RMTH, operated at 42 kHz (± 6%). The extracts containing the pesticides were pre-concentrated in a rotary evaporator Büchi R-134 (80 rpm, 40 C and 400 mBar) followed by a concentration close near dryness under nitrogen stream.

The pesticides in the extracts were quantified in a gas chromatograph Agilent model 6890 with an electron impact mass selective detector model 5973 (GC/MS), capillary column HP-5MS 30 m long, 0.25 mm id and 0.25 µm of stationary phase width. The following operating conditions were used: oven initial temperature of 90 ºC

kept for 2 min, ramped at 20 °C min^{-1} up to 175 ºC which was kept for 10 min followed by a final ramp of 40 °C min^{-1} up to 280 ºC held for 6 min. Injector operated at splitless mode (t = 1 min) at 280 °C and the interface were kept at 280 °C. Injection volume was 1 µL. Helium (99.9999% purity) at 1 mL min^{-1} was used as carrier gas. The electron impact ion source operated at 70 eV and 250 °C. Quadrupole temperature was 150 °C.

2.4 Standard solutions

Individual stock solutions were prepared from the pesticides primary standards at 100 µg mL^{-1} in toluene, except for atrazine which was prepared in acetone:toluene (1:19, v/v) due to its lower solubility in toluene. From the stock solutions, intermediate standard mixtures of pesticides were prepared at 1.00 and 10.00 µg mL^{-1}. To obtain the analytical curves, working solutions were prepared in the range of 0.10 to 0.50 µg mL^{-1} for analyte quantification in the chamber and 0.50 to 4.00 µg mL^{-1} for analyte quantification in the sample resin. Phenanthrene-d_{10} was added as internal standard at 0.15 and 0.30 µg mL^{-1}, for the lower and higher range, respectively.

In the experiments where rapid volatilization of the solvent is desirable such as determination of volatilization profile of the pesticides, evaluation of sampling efficiency and in recovery tests, the standards solutions at 0.53, 1.00, 2.50, 2.67, 3.00, 5.33, 7.50, 10.00 and 15.00 µg mL^{-1} of the analytes were prepared in acetone.

2.5 Apparatus for volatilization of the pesticides

The apparatus used to simulate the atmosphere contaminated by pesticides consisted of a glass volatilization chamber, a sampling cartridge and a vacuum pump (Figure 1). The volatilization chamber was 9 cm high with a diameter of 7 cm, covered with threaded plastic top containing two small holes for the introduction of 4 mm glass tubes. The cartridges were prepared in the laboratory using polypropylene tubes, 5.50 cm long with an internal diameter of 0.8 cm with the adsorbent packed in two sections separated by glass wool plugs. Different masses of adsorbent were tested to optimize the sampling efficiency.

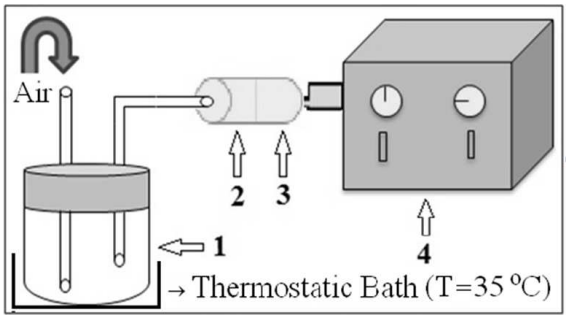


Figure 1 – Schematic representation of the apparatus used for air contamination and sampling: (1) volatilization chamber, (2) first section of the cartridge, (3) second section of the cartridge and (4) vacuum pump.

Initially, a predetermined amount of a standard solution in acetone was added to the volatilization chamber. After two minutes, the solvent was volatilized and the vacuum pump was turned on to force the air through the chamber in the direction of the cartridge. The air movement inside the chamber, associated to the vapor pressure of the pesticides, supported their volatilization.

2.6 Extraction of the pesticides from the volatilization chamber

To evaluate the efficiency of pesticides extraction from the chamber, 0.10, 0.30, 0.75, 1.00 and 1.50 μg of each pesticide was added to separate chambers by the addition of 100 μL of mixed standard solution of pesticides in acetone in the respective concentrations: 1.00; 3.00; 7.50; 10.00 e 15.00 μg mL^{-1}. After two minutes the solvent was volatilized and the pesticides extracted by three sequential extractions, each with 2.0 mL of acetone.

Each extract was transferred to a conical round glass flask and pre-concentrated in a rotary evaporator (40º C, 400 mbar) until an approximate volume of 300 μL. Subsequently, this volume was transferred to a 400 μL insert and concentrated to dryness under nitrogen stream. The residue was re-dissolved using 300 μL of phenanthrene-d_{10} solution in toluene (0.15 or 0.30 μg mL^{-1}, depending on the pesticides concentration in the extract) and injected in the GC/MS. These experiments were done in six replicates with an analytical blank.

2.7 Recovery experiments with pesticides applied directly in the adsorbents

In these assays, 80 mg of the adsorbent, Tenax® or XAD®-2, were transferred to a glass tube (100 mm long, 18 mm id). Aliquots of 100 μL from different standard

solutions in acetone were added to the adsorbent in order to achieve spiking levels of 0.67, 1.67, 3.33, 5.00 and 6.67 ng mg^{-1} for Tenax® and 0.67, 3.33 and 6.67 ng mg^{-1} for XAD®-2. The mixture was homogenized in an orbital agitator for 10 minutes at 300 rpm and kept for 24 hours at 4 °C in the dark. After this period, the tubes were kept for 10 minutes at ambient temperature (27 ± 3 °C) to achieve thermal equilibrium. The pesticides extraction from the resin was performed by sonication with 3 cycles of 15 min employing a 2 mL of the acetone per cycle. The extracts were transferred and combined in a 50 mL round-bottom flask and concentrated as described above.

Stability of the pesticides in the Tenax® resin at the spiking level of 0.67 ng mg^{-1}, the lower level used in this study, was checked using the same procedure described above but extracting the pesticides 1, 7 and 14 days after spiking. During these periods the tubes were kept at 4 °C. All these experiments were carried out in three replicates together with an analytical blank.

2.8 Volatilization profile of pesticides

The volatilization profile of each pesticide was evaluated in order to determine the time necessary to carry out the sampling in the laboratory. For this purpose, 1.500 ng of each analyte was added to the volatilization chamber. After two minutes, the chamber was closed and placed in a thermostatic bath at 35 °C, connected to a cartridge containing 100 mg of Tenax®, as shown in Figure 1. The sampling pump flow rate was adjusted to 2.60 L min^{-1}. The pump was kept running and the amount of pesticides remaining in the chamber was determined after the following time intervals: 15, 30, 60, 120, 240, 480 and 720 minutes. The experiments were carried out in triplicate together with an analytical blank.

2.9 Sampling efficiency of pesticides

2.9.1 Breakthrough

The eventual occurrence of breakthrough, i.e., the loss of pesticides retained on the adsorbent as a consequence of the air passage through it, was evaluated by two different procedures. The first one was consisted on spiking the adsorbent packed in the cartridge first section with 100 µL of standard solutions 10.00 µg mL^{-1} prepared in acetone. Different masses of Tenax® in the cartridge first section were tested (80, 120 and 150 mg), providing the spiking levels of 12.50, 8.33 and 6.67 ng mg^{-1}, respectively.

The mass of adsorbent in the second section was kept the same (40 mg) at all experiments. The fortified cartridges were then connected to the volatilization apparatus (Figure 1) pulling air through the cartridge for 12 hours at flow rate of 2.60 L min^{-1}. After this period, the adsorbent from each section of the cartridges was submitted to extraction and the pesticides were quantified.

The second procedure for breakthrough evaluation was similar to the first one except for the adsorbent spiking that occurred in the volatilization chamber instead of directly on the resin. When using XAD®-2, breakthrough was evaluated at only one spiking level 6.67 ng mg^{-1}, by adding to the volatilization chamber 534 ng of each pesticide. The cartridges were packed with 80 mg and 40 mg of XAD®-2 in the first and second sections, respectively. The criteria used to characterize the occurrence of breakthrough was the one reported by Tsiropoulos,[17] i.e., when the amount of pesticide present in the second section of the cartridge was greater than 1% of that found in the first section. These assays were carried out in triplicate together with an analytical blank.

2.9.2 Sampling efficiency

In the experiments using Tenax® cartridges, 0.10, 0.25, 0.50, 0.75 and 1.00 µg of the each pesticide, were added to five distinct volatilization chambers by the addition of an appropriate volume of analytical standards in acetone. With XAD®-2 cartridges, three distinct volatilization chambers with 0.053, 0.267 and 0.533 µg of each pesticide were used.

The sampling time, temperature of thermostatic bath and flow rate were the same as that used in the breakthrough experiments. All cartridges were packed in the laboratory with 150 mg and 40 mg of the resin in the first and second sections, respectively when packed with Tenax® and 80 mg and 40 mg in the first and second sections when packed with XAD®-2. Between each section of the cartridges as well as at the extremities, small plugs of glass wool were used to avoid the entry of particulate in the cartridge, delimitate the two sections and avoid the entry of adsorbent in the sampling pump.

The efficiency of the sampling step was assessed by calculating the mass balance for each pesticide, expressed as percent recovery. For this purpose, the mass extracted from the resin was divided by that volatilized in the chamber. This last one,

consider the mass of pesticide applied in the chamber (m_i) and the remaining in this compartment after the sampling.

The method detection (MDL) and quantification (MQL) limits were estimated according to Thier and Zeumer.[18] The linearity of the detector response at the working intervals was evaluated using criteria such as the correlation coefficient (r) and the visual evaluation of the curve.[19] The instrumental limits of detection (LOD) and quantification (LOQ) were obtained from the signal-noise ratio of chromatograms of standard solutions.[20] The instrumental precision, expressed as relative standard deviation RSD%, was determined from ten successive injections of each of the standard solution mixture of pesticides prepared in toluene at 0.10, 1.0 and 5.0 μg mL^{-1}.

3. RESULTS AND DISCUSSION

3.1 Instrumental parameters

The chromatographic operating conditions provided resolutions (Rs) greater than 3.5 except for the metolachlor/chlorpyrifos pair with resolution of 1.24 (Figure 2). In chromatographic separations, values of resolution equal to or greater than 1.5 are desirable, but values above 1.0 are acceptable.[19] The retention factor (k) varied from 4.00 to 8.68 and selectivity (α) from 1.01 to 3.82, with the lower value also for the metolachlor/chlorpyrifos pair.

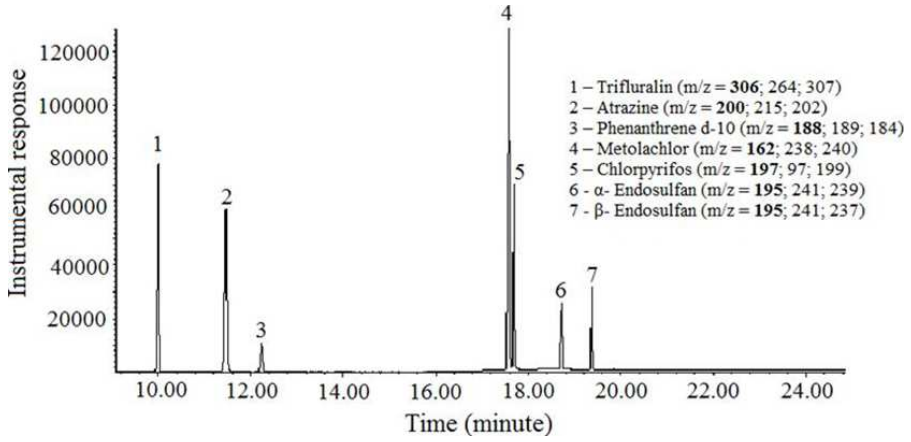


Figure 2 – Chromatogram of a mixed standard solution at 3.0 μg mL^{-1} injected in the splitless mode with selective ion monitoring (SIM). Above right, description and identification of the peaks and monitored ions, with the main ions in bold.

The chromatographic response for each analyte presented high linear correlation ($r > 0.99$) at both working intervals (0.10 to 0.50 μg mL^{-1} and 0.50 a 4.00 μg mL^{-1}). The

LOD and LOQ ranged from 20.0 to 100.0 ng mL^{-1} and 70.0 to 150.0 ng mL^{-1}, for metolachlor and chlorpyrifos, respectively. The LOQ were sufficiently low to allow the quantification of the analytes at all spiking levels used, considering recoveries higher than 80% as accepted by the validation protocols. The RSD% of the detector response was lower than 10% for all analytes.

3.2 Pesticides recovery from the adsorbents and the volatilization chamber

The sampling efficiency was evaluated by the mass balance between the amount of pesticide volatilized in the chamber and recovered from the resin. To guarantee the accuracy of this process, the experiments to determine the pesticides recovery from the chamber and resins were carried out.

The average recoveries from Tenax® at different spiking levels varied from 83 to 119%, with RSD% lower than 14% (Table 1). These values are in accordance with the ones accepted by,[19] i.e., 75 to 120% with RSD% lower than 20%, indicating good precision and accuracy of the extraction method. Similar assays were carried out with the XAD®-2 in three spiking levels, obtaining recoveries from 78 to 137% with RSD% lower than 18% (Table 1).

Table 1 – Average recovery and RSD% of the adsorbed pesticides from the Tenax® and XAD®-2 resins at different spiking levels.

Resin	Spiking level (ng mg^{-1})	Recovery (n = 3) ± CV					
		Trif.	Atraz.	Metol.	Chlorp.	End.	
						α-	β-
Tenax®	0.67	105 ± 9	108 ± 6	118 ± 6	119 ± 5	92 ± 6	104 ± 6
	1.67	91 ± 5	105 ± 3	114 ± 4	119 ± 4	92 ± 3	108 ± 2
	3.33	85 ± 6	100 ± 6	104 ± 7	108 ± 6	83 ± 6	105 ± 8
	5.00	88 ± 13	96 ± 10	101 ± 10	107 ± 11	93 ± 8	100 ± 9
	6.67	93 ± 2	100 ± 1	97 ± 1	100 ± 2	93 ± 2	109 ± 2
XAD®-2	0.67	87 ± 12	102 ± 15	132 ± 15	137 ± 17	80 ± 16	107 ± 17
	3.33	85 ± 6	88 ± 7	107 ± 7	114 ± 6	78 ± 6	91 ± 8
	6.67	82 ± 4	90 ± 6	105 ± 6	114 ± 6	80 ± 6	92 ± 6

The stability study of the pesticides applied on the Tenax® resin kept at 4° C for 1, 7 and 14 days showed average recoveries from 84 to 123%, with RSD% lower than 9%. The storage of samples collected in the field at low temperature is a procedure highly used aiming to minimize eventual losses of the analytes by degradation and/or volatilization between sampling and extraction in the laboratory.[12,14]

Regarding recovery of pesticides applied to the volatilization chamber, values varied from 73 to 117% with CV lower than 12%.

3.3 Pesticides volatilization profile

The pesticides volatilization profile was determined in order to define the sampling time. After 15 minutes, 98% of the initial mass of trifluralin applied to the chamber was volatilized while for the other pesticides this quantity varied from 24 to 71% (Figure 3). After 720 minutes, the last interval was evaluated and no pesticide was detected in the chamber. Thus, this period was selected for the sampling study in the laboratory.

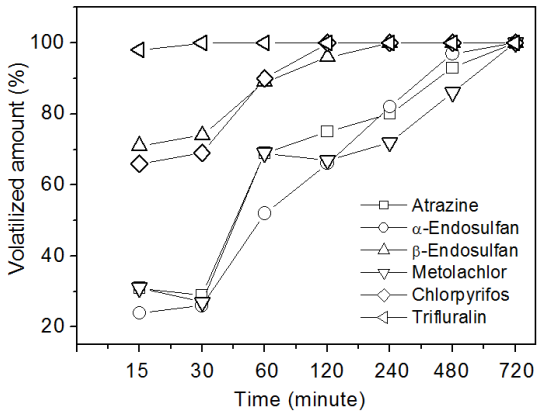


Figure 3 – Volatilization profile of the studied pesticides from the glass chamber.

Comparing the volatilization profile of the pesticides with the respective vapor pressure, whose values is expressed in mPa at 25 °C[21] in decreasing order are trifluralin (10), metolachlor (4.2), chlorpyrifos (2.7), α-endosulfan (0.4), β-endosulfan (0.08) and atrazine (0.04), it was observed that, except for metolachlor, the pesticides with higher vapor pressure volatilize more rapidly. The lower volatilization of metolachlor may be related to the experimental conditions. Since the volatilization chamber remain partially immersed in the aqueous thermostatic bath (Figure 1) to avoid temperature variations during the whole experiment, the humidity inside it may have been high. Considering that metolachlor is the most hydrosoluble amongst the studied pesticides (530 mg L^{-1} at 20° C)[21] it is likely that the water retained at the chambers inner walls might have solubilized it, increasing the time necessary for its evaporation.

Sanusi[22] evaluated the influence of air relative humidity on the partition of some pesticides between a particulate and gaseous phase. Those authors concluded that when

the air relative humidity is higher than 70%, volatile pesticides can be solubilized in the water droplets adsorbed to the solid surfaces reducing their concentration in the vapor phase. Despite the fact that those results were obtained in quite different circumstances than the present study, they support the lower volatilization of metolachlor obtained here.

3.4 Breakthrough evaluation

The occurrence of breakthrough may affect negatively the sampling efficiency. It indicates the maximum amount of pesticides than can be retained on a specific mass of adsorbent. Several studies evaluate the breakthrough by the direct addition of pesticides solutions in the adsorbent packeted in the cartridge first section. In sequence, a known volume of air is forced through it and the eventual passage of the analytes from the first to the second section is evaluated.[13,15,17,23] Using this procedure for the assays with Tenax®, no breakthrough was observed at any spiking level tested (12.50, 8.33 and 6.67 ng mg^{-1}), leading to a preliminary conclusion that any of the masses of resin (80, 120 or 150 mg) could be used for this intended application.

In contrast, in the assays where the pesticides came in contact with the resin through the contaminated atmosphere in the volatilization chamber, breakthrough was observed when the masses of 80 and 120 mg of adsorbent were used in the cartridge first section (Table 2). In the second section of these cartridges, the pesticides α-endosulfan, metolachlor and trifluralin were detected in quantities higher than 1% of the amount quantified in the first section. In the assays using cartridges packed with 80 mg of resin, besides these three pesticides all the others were also detected in the second section although in concentrations that did not characterize breakthrough. Breakthrough was not observed when the mass of Tenax® was increased to 150 mg.

For comparison, breakthrough was also evaluated using XAD®-2 cartridges employing the method of contaminated atmosphere. In these experiments, breakthrough was observed at the spiking level of 6.67 ng mg^{-1}, since more than 1% of trifluralin and metolachlor present in the first section passed to the second one (Table 2). In all experiments for breakthrough evaluation a sampling volume of 1.872 m^3 was used.

Table 2 – Average mass (n = 3) of pesticides determined in the two sections of the sampling cartridges in the experiments for breakthrough evaluation via contaminated air at the flow of 2,6 L min.$^{-1}$ for 12 hours.

Resin	SFR[a] ng mg^{-1}	Section	Mass of recovered pesticides in the cartridge sections (ng) ± CV					
			Trif.	Atraz.	Metol.	Chlorp.	End.	
							α-	β-
Tenax®	12.50	1st - 80 mg	640 ± 2	830±6	720 ± 8	830 ± 18	650 ± 16	670 ± 22
		2nd - 40 mg	40 ± 7 (6%)[b]	< LQ	20 ± 6 (3%)[b]	< LQ	70 ± 3 (11%)[b]	< LQ
	8.33	1st - 120 mg	1220 ± 4	1140 ± 5	1150 ± 4	1210 ± 6	1002 ± 4	850 ± 21
		2nd - 40 mg	40 ± 21 (3%)[b]	nd[c]	30 ±0.10 (3%)[b]	nd[c]	40 ± 15 (4%)[b]	nd[c]
	6.67	1st- 150 mg	930 ± 2	910 ± 4	1000 ± 3	990 ± 4	890 ± 2	890 ± 12
		2nd- 40 mg	nd[c]	nd[c]	nd[c]	nd[c]	nd[c]	nd[c]
XAD®-2	6.67	1st - 80 mg	440 ± 2	480 ± 5	460 ± 4	510 ± 10	440 ± 1	410 ± 5
		2nd - 40 mg	30 ± 8 (7%)[b]	nd[c]	40 ± 5 (8%)[b]	nd[c]	nd[c]	nd[c]

[a] Spiking level in the resin via contaminated atmosphere.
[b] Pesticide percentage in the second section of the sampling cartridge relative to the first section.
[c] nd: not detected.

Santos et al.[23] evaluated breakthrough for the same analytes shown in Table 2 using the method of direct fortification of the cartridges first section packed with XAD®-2. The authors did not observe breakthrough at concentrations similar to the ones used here. These results support the hypothesis that the evaluation of breakthrough carried out using the direct fortification of the resin may overestimate the capacity of the resin to retain the analytes present in the atmosphere.

The addition of the analytes in the solution may contribute to the formation of zones with high concentrations at the surface of the adsorbent which may facilitate the occurrence of longitudinal diffusion inside the pores reducing the movement of the analytes with the air flow. In the evaluation of breakthrough via contaminated atmosphere, the continuous flow of the analytes in the gas phase may reduce the residence time in the adsorbent, decreasing the probability of occurrence of diffusion in the resin.

3.5 Sampling efficiency

Once the mass of Tenax® necessary to avoid breakthrough was established, the sampling efficiency was evaluated at different pesticides concentration. In all cases, Tenax® was able to retain 82 to 118% of the mass of pesticides volatilized in the chamber, with RSD% lower than 14% (Table 3), in compliance with the acceptable limits.[19]

The sampling efficiency of XAD®-2 was also evaluated showing that this resin retained 83 to 92% of the mass of pesticides volatilized in the chamber, with RSD% lower than 9% (Table 3). In these last experiments, to avoid breakthrough, the mass of pesticides applied to the chamber was 267 ng.

Table 3 – Efficiency of Tenax® and XAD®-2 to retain pesticides in the gas phase of atmosphere.

Resin	MAC[a] (ng)	NF[b] (ng m^{-3})	Recovery (n = 3) ± CV					
			Trif.	Atraz.	Metol.	Chlorp.	End.	
							α-	β-
Tenax®	100	53.42	101 ± 11	97 ± 8	100 ± 2	118 ± 1	98 ± 4	82 ± 13
	250	133.55	95 ± 4	91 ± 5	87 ± 4	102 ± 7	82 ± 3	89 ± 10
	500	267.09	83 ± 4	83 ± 3	82 ± 4	85 ± 1	88 ± 2	84 ± 2
	750	400.64	92 ± 2	89 ± 3	101 ± 3	100 ± 1	95 ± 2	91 ± 9
	1000	534.19	93 ± 2	91 ± 4	100 ± 3	99 ± 4	89 ± 2	89 ± 12
XAD®-2	267	142.63	83 ± 3	89 ± 6	88 ± 3	92 ± 9	89 ± 4	86 ± 4

[a] Mass of pesticides added to the volatilization chamber.
[b] Spiking level of the air – mass of pesticide volatilized/air volume forced through the chamber (1,872 m^3).

In all experiments, no pesticides were detected at the chambers after the sampling period, indicating complete volatilization and consequent total transfer to the resin. The analytical blanks did not indicate the presence of interferents. Also, no breakthrough was observed in any case.

3.6 Sampling limits of detection and quantification

In the proposed method, the minimum mass of pesticide detected in the resin was calculated using the procedure described by Thier and Zeumer.[18] The ratio of this minimum mass and the sampled volume, 1.872 m^3, gave the MDL estimated for each pesticide (Table 4).

Table 4 – MDL and MQL of the sampling experiments using Tenax® as adsorbent and variables used for the limits calculation.

Pesticides	S_{comb} [a]	Linear equation [b]	r	MMD [c] (pg)	MDL_{Air} (pg m^{-3})	MQL (ng m^{-3})
Trif.	0.0075	y = 0.9034x+ 10.2439	0.9945	35.4	18.9	53.4
Atraz.	0.0039	y = 0.8838x + 2.2115	0.9977	18.8	9.96	53.4
Metol.	0.0015	y = 1.0109x – 21.493	0.9965	6.33	3.34	53.4
Chlorp.	0.0061	y = 0.9815x + 15.986	0.9992	26.5	14.1	53.4
α-End.	0.0028	y = 0.9121x – 5.9024	0.9950	13.1	7.00	53.4
β-End.	0.0216	y = 0.9906x - 13.245	0.9968	93.0	49.7	53.4

[a] Combined standard deviation calculated for 4 degrees of freedom ($t_{Student\ unilateral}$ = 2.132).
[b] Linear adjustment between pesticides masses recovered from the resin and added to the volatilization chamber (Table 3).
[c] Minimum mass of pesticide detected using the proposed method.

The procedure described by Their and Zeumer[18] for the determination of the detection limit is indicated since it considers not only the equipment capacity in detecting the injected amount but also all the analytical methods from extraction to detection. According to those same authors, MQL is the smallest concentration level for which the precision and accuracy are known and are in compliance with the acceptable criteria (recovery higher than 70% and RSD% less than 20%). Thus, 53.42 ng m^{-3} was the MQL obtained for all studied pesticides.

Borràs et al.[14] reported detection limits of 86.75 pg m^{-3} for chlorpyrifos and 88.53 pg m^{-3} for trifluralin, sampled using the resins XAD®-2 and XAD®-4. For this purpose, a sampling volume of 1.44 m^3, with a flow rate and sampling time of 1.0 L min^{-1} and 24 hours were used. The limits obtained by those authors are then comparable with the ones obtained in the present study, considering the higher sampled volume used here.

Since the method capacity to detect the pesticides in the gas phase depends on their concentration in this phase, the adsorbent retention capacity and the volume of sampled air, among other factors, make the comparison of the performance of other sampling methods difficult. Coscollà et al.[12] reported a MQL of 1.32 pg m^{-3} for trifluralin determined in the particulate phase of air, whose sampling was performed using a glass fiber filter. However the low MQL obtained by those authors is due to the use of a high volume pump with a total sampling volume of 720 to 750 m^3. Scheyer et al.[24] reported MQL between 2.5 and 625 pg m^{-3} for 27 pesticides (atrazine, α,β-endosulfan, metolachlor, trifluralin among others) in air samples retained in XAD®-2 resin. This study also sampled an air volume much higher than the one used in our study, varying from 240 to 360 m^3.

4. CONCLUSIONS

The results obtained in the different phases of the present study permitted the following conclusions:

1 – The volatilization chamber is a good alternative to overcome the difficulties in standard addition and recovery experiments using gaseous sample.

2 – The breakthrough evaluation by direct addition of pesticides standards in the cartridge first section may overestimate the resin retention capacity.

3 – In all tests to evaluate sampling efficiency, the resin Tenax® retained more than 80% of the analytes present in the atmosphere contaminated in the laboratory showing its applicability for the determination of the studied analytes in gaseous samples.

4 – Tenax® showed a retention capacity comparable to the resin XAD®-2, therefore, it is a good alternative as adsorbent for sampling pesticides in gaseous samples.

5 – The laboratory-packed cartridges provided good sampling efficiency for all the analytes and spiking levels and contributed to reduce the analysis costs.

6 – The stability of the analytes adsorbed to the Tenax® resin at low temperatures was shown, indicating that the cartridges can be stored for at least 14 days after sampling without significant alterations.

7 – The instrumental parameters as well as the analytical methods used were in compliance with the validation protocols. Moreover, the small dimensions and simplicity of the sampling apparatus suggest that it may be useful for the validation of sampling procedures for other analytes and adsorbents.

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Graphical abstract