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# Simultaneous analysis of pesticides from different chemical classes by using a derivatisation step and gas chromatography–mass spectrometry

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ABSTRACT

This work presents a new method to analyse simultaneously by GC–MS 31 pesticides from different chemical classes (2,4 D, 2,4 MCPA, alphacypermethrin, bifenthrin, bromoxynil, buprofezin, carbaryl, carbofuran, clopyralid, cyprodinil, deltamethrin dicamba, dichlobenil, dichlorprop, diflufenican, diuron, fenoxaprop, flazasulfuron, fluroxypyr, ioxynil, isoxaben, mecoprop-P, myclobutanil, oryzalin, oxadiazon, picloram, tau-fluvalinate tebuconazole, triclopyr, trifluralin and trinexapac-p-ethyl). This GC–MS method will be applied to the analysis of passive samplers (Tenax® tubes and SPME fiber) used for the evaluation of the indoor and outdoor atmospheric contamination by non-agricultural pesticides. The method involves a derivatisation step for thermo-labile or polar pesticides. Different agents were tested and M*t*BSTFA (N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide), a sylilation agent producing very specific fragments [M−57], was retained. However, diuron could not be derivatised and the isocyanate product was used for identification and quantification. Pesticides which did not need a derivatisation step were not affected by the presence of the derivatisation agent and they could easily be analysed in mixture with derivatised pesticides. The method can be coupled to a thermal-desorption unit or to SPME extraction for a multiresidue analysis of various pesticides in atmospheric samples.



## 1. Introduction

The atmosphere is known to be a good pathway for the world dissemination of pollutants. Among the great variety of organic contaminants, current-used pesticides are a class of compounds with growing interest for airborne human exposure in particular due to the suspicion, for some of them, to be endocrine disruptors or carcinogens. Pesticides can enter into the atmosphere through "spray drift" followed by volatilisation during application, post-application volatilisation from treated crops and leaves and wind erosion of fine soil particles where pesticides are adsorbed. Once in the atmosphere, pesticides can be transported, sometimes far from their application site, depending on their potentiality of persistence and atmospheric degradation [1,2].

If the atmospheric behaviour of pesticides used in agriculture is relatively well documented [1,3–9], few studies are available on pesticides applied in non agricultural areas like public private gardens, railways,... Recently Scheyer et al. [2,8] have observed in rainwater that diuron, an herbicide intensively used in non agricultural areas, presents more important concentrations in urban areas than in rural areas and a non seasonal frequency of detection. In air samples, aryloxyacids have been also detected more frequently in urban areas in relation to their uses in public gardens and residential areas.

Pesticides can also contaminate indoor air as a result of direct indoor applications but also through transfer processes from outdoor applications (residential and occupational uses). It has been demonstrated that pesticide residues may moved from their original points of application as vapors, or bound to particles. The principal factors that influence their movement are the compounds physicochemical properties, the type of substrates in contact with the substance, and the physical activities of humans and their pet animals [10]. Bouvier et al. [11] states that domestic pesticide uses include pet treatments, extermination of household pests, removal of lice, and garden and lawn treatments while professional uses include crop, greenhouse, cattle and pet treatments, but also pest control operations in buildings. In addition to the direct use of pesticides in closed areas, indoor contamination by pesticides can also

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result from transfers of outdoor pesticides by shoes, clothes and air drift [12–15].

The evaluation of the airborne exposure to pesticides in outdoor as well as indoor air needs the collection of representative air samples. Actually, systems usually used are active samplers and consist of high or low volume of air pumping on filters followed by a solid adsorbent for the simultaneous sampling of the particle and gas phase [2,9–11,16]. These systems are well efficient but are heavy, time consumers and expensive especially when spatial and temporal variations of atmospheric contamination by pesticides are undertaken in a large scale. In addition, when they are used in indoor environment, the noise and their dimensions have to be considered. An alternative to these techniques is commonly called "passive sampling", as opposed to "active sampling". Using this approach, analytes migrate from the sampled medium to the sampler (collecting medium) through molecular diffusion. No pump and power are needed, limiting inconvenience at the sampling point (important for indoor use), and costs for samplers deployment. The equipment used for passive sampling is generally very simple and does not require any skilled workers. After sampling, extraction techniques and analysis methods are similar to those used for active sampling and consist generally to a solvent extraction (i.e. Soxhlet), a purification step and an injection on GC.

Some other extraction techniques using thermal desorption followed by direct injection into GC can be used for passive sampling. These techniques used Tenax® tubes or SPME. Thermal desorption can present a novel approach since it substantially simplifies analyses (no concentration step is needed) and increases sensitivity (a large part of the pre-concentrated material may be recovered for determination). Detection limits and background noise are lower because of the disappearance of solvent components. Moreover, these techniques are easily automatable. Because of these aspects, it seems to be an interesting alternative to solvent extraction to assess atmospheric exposure to pesticides in indoor and outdoor atmosphere through passive sampling. However, thermal desorption requires one unique injection per sample and consequently needs a multi-class analytical method.

Generally, pesticides are analysed in environmental matrices by chemical classes like phenoxy acids [17,18], pyrethroids [19], ureas [20,21] or by mode of action like fungicides [22]. However, if it exists a specific method for each chemical class, the use of Tenax® passive tubes and SPME as passive samplers is a limited factor for the analysis of pesticides, because these samplers which used thermal desorption technique induce only one injection. Consequently, the evaluation of the air contamination by different class of pesticides will require the deployment of a sampler by chemical class or the development of a GC–MS method for the simultaneous determination of multi-class pesticides.

The aim of this paper is the development of a method for the simultaneous analysis of pesticides of different chemical classes. Since thermal-desorption is a method devoted to GC, a derivatisation step for thermo-labile or polar pesticides is also required. In this paper, a method for the analysis in one run of 31 pesticides including ureas, phenoxy acids, pyrethroids, carbamates,. . . mainly used in non-agricultural areas (private gardens, roads, railways,. . .) was developed in order to associate this method to thermal desorption of Tenax® passive tubes and SPME.

## 2. Materials and methods

### 2.1. Chemicals

Acetonitrile and ethyl acetate of HPLC grade were obtained from Prolabo (France). Ultrapure water was obtained from a Milli-Q water system (Millipore, St. Quentin en Yvelines, France). Standards of individual pesticides (2,4 D, 2,4 MCPA, alphacypermethrin, bifenthrin, bromoxynil, buprofezin, carbaryl, carbofuran, clopyralid, cyprodinil, deltamethrin dicamba, dichlobenil, dichlorprop, diflufenican, diuron, fenoxaprop, flazasulfuron, fluroxypyr, ioxynil, isoxaben, mecoprop-P, myclobutanil, oryzalin, oxadiazon, picloram, tau-fluvalinate tebuconazole, triclopyr, trifluralin and trinexapac-p-ethyl) of Pestanal® quality (>99% purity) were obtained from Riedel de Haën (Sigma Aldrich, St. Quentin Fallavier, France).

*Internal standards*: Tecnazen was supplied from Cluzeau Info Labo (St. Croix la Grande, France) while Nitrophénol-$D^4$ was supplied from Sigma–Aldrich (St. Quentin Fallavier, France).

M*t*BSTFA (N-(t-butyldimethylsilyl)-N-methyltrifluoroacetamide) and [BSTFA (N,O-bis(trimethylsilyl)trifluoroacétamide) + 1% TMCS (trimethylchlorosilane)] purum ≥ 97% were purchased from Sigma Aldrich (St. Quentin Fallavier, France). MBTFA (N-Methyl-N-bis(trifluoroacétamide)) and MBHFBA (N-methyl-bisheptafluorobutyramide) were obtained from Macherey-Nägel (MN Hoerth, France).

A stock solution of each pesticide was prepared in acetonitrile or ethyl acetate. A working solution at 80 mg $L^{-1}$ was prepared for each compound together with a mixture solution for full scan injection. For SIM injection and calibration, mixture solutions between 1 mg $L^{-1}$ and 5 μg $L^{-1}$ were prepared from stock solution.

### 2.2. Instrumentation and analysis

For the analysis of pesticides, a Perkin Elmer autosystem XL GC, equipped with an autosampler and a split/splitless injector, coupled to a mass detector (Turbomass gold series) have been used. Separation has been performed on a Varian Factor-Four V5-MS (equivalent to 5% phenyl, 95% polydimethylsiloxane) capillary column (60 m × 0.25 mm i.d., 250 μm film thickness) as follows: 50 °C (5 min) to 150 °C at 25 °C $min^{-1}$, to 250 °C at 3 °C $min^{-1}$ and to 300 °C (15 min) at 15 °C $min^{-1}$.

Pulsed injection (3 mL $min^{-1}$ for 1 min) of 3 μL was made in the splitless mode (270 °C for 1 min) using Helium (1 mL $min^{-1}$, regulated constant flow). The liner used is of splitless configuration without any glass wood inside (2 mm ID). The temperatures of the MS source and of the transfer line were maintained at 280 °C and 320 °C, respectively.

Spectra of pesticides were obtained by electron impact ionisation (EI) at 70 eV. Depending of pesticides, two of three ions were selected from the spectrum of each pesticide to quantify the response in the selected ion monitoring mode (SIM).

### 2.3. Derivatisation procedure

One millilitre of each pesticide solution (or mixture of pesticides) was transferred into an amber sampling vial with PTFE-lined screw caps of 4 mL and 20 μL of the derivatisation agent were added. The solution was heated at 80 °C for 1 h, under stirring with a magnetic stirrer bar. After derivatisation the vial was cooled at ambient temperature and one aliquot (3 μL) was directly injected into GC. When acylation reagents were used temperature was increased to 120 °C for 2–3 h.

## 3. Results and discussion

The originality of the analytical method is based on the possibility to analyse in one unique GC–MS run, 31 pesticides from 20 very different chemical classes (Table 1). From these 31 pesticides, most of them should require a derivatisation step since they present a labile hydrogen atom coming from different chemical functions as: secondary amine group (–NH–), primary amine group