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Pressurized liquid extraction followed by gas chromatography with atomic emission detection for the determination of fenbutatin oxide in soil samples

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ABSTRACT

A novel method for the determination of the miticide bis[tris(2-methyl-2-phenylpropyl)tin] oxide, also known as fenbutatin oxide (FBTO), in agricultural soils is presented. Pressurized liquid extraction (PLE) followed by analyte derivatization and extraction into isooctane was the used sample preparation approach. Selective determination was achieved by gas chromatography with atomic emission detection (GC-AED). Influence of different parameters on the performance of the extraction process is thoroughly discussed; moreover, some relevant aspects related to derivatization, determination and quantification steps are also presented. As regards PLE, the type of solvent and the temperature were the most relevant variables. Under optimized conditions, acetone, without any acidic modifier, was employed as extractant at 80 °C. Cells were pressurized at 1500 psi, and 2 static cycles of 1 min each were applied. Acetone extracts (ca. 25 mL) were concentrated to 1 mL, derivatized with sodium tetraethyl borate ($NaBEt_4$) and the FBTO derivative, resulting from cleavage of the Sn–O–Sn bond followed by ethylation of the hydroxyl fragments, extracted into isooctane and determined by GC-AED. Under final working conditions, the proposed method provided recoveries from 76 to 99% for spiked soil samples, a limit of quantification of 2 ng g^{-1} and an acceptable precision. Analysis of samples from vineyards sprayed with FBTO, confirmed the persistence of the miticide in soil for more than 1 year after being applied.

1. Introduction

Fenbutatin oxide (bis[tris(2-methyl-2-phenylpropyl)tin] oxide, FBTO), also known as bis(trineophyltin) oxide, is a non-systemic, selective insecticide used for the protection of crops, particularly fruits, against mites [1,2]. Its large molecular weight (1053 amu), extremely high octanol–water partition coefficient ($\log K_{ow}$ 12.8), negligible vapour pressure and chemical stability convert FBTO into a persistent compound in plants and soil. The European Union has set maximum allowable residues of FBTO up to 5 μg g^{-1} in some fruits [3], which can be considered a relatively high level, taking into account that this compound remains on the surface of vegetables [4] and thus, it could be removed during raining or through photochemical degradation reactions. Although, in presence of water traces, FBTO breaks down rendering two molecules of tris(2-methyl-2-phenylpropyl)tin hydroxide [5], this reaction is reversible and the resulting tri-substituted organotin species is still relatively lipophilic ($\log K_{ow}$ 7.9); thus, its mobility in the environment it is expected to be low. FBTO is highly toxic to some aquatic organisms with lethal concentration doses (LC_{50}) in the low ng mL^{-1} range for several fish species [6].

Conversely to other organotin compounds, particularly tributyl and triphenyltin, whose analytical determination and environmental fate have been exhaustively investigated during last 20 years, little attention has been paid to FBTO. In the middle of the 1990s, FBTO was included in generic sample preparation methodologies for the determination of organotin species in environmental samples using gas chromatography (GC) based techniques [7,8]. In these early works, time and solvent-consuming sample preparation approaches such as Soxhlet and liquid–solid extraction, using manual shaking, followed by concentration of the extracts and analyte alkylation with Grignard reagents were employed [7–9]. Although FBTO was found in sediments and agricultural soils [7–9], further works dealing with improvements in the analytical methodology for the determination of FBTO in these solid matrices were not found. In fact, the applicability of sodium tetraethyl borate ($NaBEt_4$) to the derivatization of FBTO in aqueous solutions was not demonstrated until 2005 by Devos et al. [10], who developed a method for the sensitive determination of this compound in water samples using in situ derivatization followed by headspace extraction of the ethyl derivative with solid-phase microextraction (SPME). On the other hand, $NaBEt_4$ has been employed in GC analysis of butyl

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and phenyl tin species since long time ago [11]. In the same way, the usefulness of modern extraction techniques requiring moderate consumption of organic solvents, e.g. microwave assisted extraction (MAE), sonication or pressurized-liquid extraction (PLE), and systematically evaluated for the extraction of other organotin compounds from solid matrices [12–17], has not been demonstrated for FBTO. Among the above techniques, PLE does not only achieve high recoveries in the extraction of organotin compounds from environmental samples [14–17]; in addition, it provides filtrated extracts, avoiding the risk of analytes re-adsorption on the particles of the solid residue after finishing the extraction step and before phases separation.

The aim of this work was to develop a fast and sensitive procedure for the determination of FBTO in agricultural soils and to investigate the levels and persistence of this compound in vineyards treated with commercial formulations containing this miticide as active ingredient. After extraction, using an aqueous miscible solvent, FBTO was derivatized with $NaBEt_4$ and selectively determined by GC with atomic emission detection (AED). Effects of different factors on the performance of the extraction process and influence of the quantification method on the accuracy of measured concentrations are thoroughly discussed.

2. Experimental

2.1. Solvents and reagents

Acetone, ethyl acetate, dichloromethane, isooctane and n-hexane, trace analysis grade solvents, were obtained from Merck (Darmstadt, Germany). FBTO, $NaBEt_4$, glacial acetic acid, sodium acetate, potassium dihydrogen phosphate and activated alumina (0.1 mm particle size) were purchased from Aldrich (Milwaukee, WI, USA). Diatomaceous earth and acid washed quartz sand were bought from Aldrich and Riedel-de Haën (Seelze, Germany), respectively. A standard solution of triphenyl pentyltin (Ph_3SnPe) in n-hexane (10 $\mu g\,mL^{-1}$) was provided by IRMM (Geel, Belgium) with occasion of a former intercomparison exercise, further dilutions of this compound, used as internal standard (IS), were made in isooctane. The stock solution of FBTO (200 $\mu g\,mL^{-1}$) was prepared in acetone. Diluted standards and solutions used to fortify soil samples were made in the same solvent. Except otherwise is stated, concentrations of FBTO and Ph_3SnPe are referred to tin.

Sodium acetate solutions (1 M) were prepared in ultrapure water, obtained from a Milli-Q system (Millipore, Billerica, MA, USA). Their pH was adjusted at different values in the range from 4.5 to 6 units with acetic acid. Buffers at higher pHs (6.5 and 7.5 units) were obtained using potassium dihydrogen phosphate. $NaBEt_4$ was dissolved in NaOH (0.1 M in ultrapure water) to get a solution with a concentration of 1%. This reagent is stable for a maximum of 5 days when stored at 4 °C.

Derivatization, ethylation, of FBTO was carried out in 20 mL volume glass tubes furnished with PTFE layered caps. An aliquot of a FBTO standard in acetone, or a soil extract in the same solvent, was poured in the tube, 10 mL of sodium acetate/acetic acid buffer at pH 5.5 and 1 mL of $NaBEt_4$ were then added. The tube was capped and shaken vigorously for 5 min. After that, the ethylated derivative of FBTO (trineophyl ethyltin) was extracted with 2 mL of isooctane containing a known concentration of Ph_3SnPe. If necessary, this extract can be evaporated (ca. 100 μL), using a gentle stream of nitrogen, before injection in the GC-AED system. Changes in the final volume of the concentrated extract, and differences in the sensitivity of the GC-AED for standards and soil extracts, were compensated using Ph_3SnPe as IS.

Glassware and PLE cells, used during sample preparation, were washed with a common detergent followed by thorough rinsing with ultrapure water and acetone.

2.2. Samples and sample preparation

Soil from fields non-treated with FBTO was used during optimisation of extraction conditions. Samples were sieved and the fraction below 0.3 mm considered for analysis. Spiked samples were prepared adding a standard mixture of FBTO, made in acetone, to a known mass of soil. After thorough homogenization, the slurry was left in a hood, at room temperature, for 1 week. Spiked samples were then aged at 4 °C, for at least 1 month, before analysis. Soil samples from vineyards treated with plaguicides containing FBTO, as acaricide against red mites (*Tetranichus urticae*), were processed under optimised conditions. Normally, samples were sieved and extracted as received and the concentration of FBTO corrected with the humidity of the soil; however, those samples collected after intense rain episodes were previously lyophilized.

Extractions were accomplished using a pressurized liquid extractor, ASE 200 Dionex (Sunnyvale, CA, USA), equipped with 11 mL capacity stainless-steel cells. Two cellulose filters followed by 2 g of quartz sand were placed at the bottom of each cell, 0.4 g of soil, previously mixed with 2 g of diatomaceous earth, were then loaded. Finally, the remaining free volume was filled with quartz sand and another cellulose filter was placed on top. Under final working conditions, FBTO was recovered from soil samples with acetone, employing 2 static extraction cycles of 1 min each. Pressure and temperature of extraction cells were set at 1500 psi and 80 °C, respectively. The flush volume and purge time (using nitrogen) were 11 mL (equivalent to 100% of the cell's capacity) and 1 min, respectively. The acetone extract was evaporated and adjusted to 1 mL. A fraction of 0.5 mL was submitted to same derivatization conditions as FBTO standards prepared in acetone.

2.3. Determination

Levels of FBTO in spiked and non-spiked samples were determined by GC-AED using an Agilent (Wilmington, DE, USA) 6890 GC system, equipped with a split/splitless injector and connected to a G2350A atomic emission detector. Separations were carried out with an Agilent HP-5 type capillary column (30 m × 0.32 mm i.d., d_f 0.25 μm) operated at a constant helium flow of 1.4 mL min^{-1}. The GC oven was programmed as follows: 80 °C (held for 2 min), 15 °C min^{-1} to 300 °C (held for 5 min). Injections (1–2 μL volume) were made in the pulsed splitless mode (40 psi, 2 min) using an autosampler. The injection port, the transfer line between the GC and the helium microwave-induced plasma, and the plasma cavity, were set at 300 °C. Helium was used as make-up gas in the plasma at 270 mL min^{-1}. O_2 and H_2 were also added to the plasma as auxiliary gases at pressures of 30 and 20 psi, respectively. Chromatograms were recorded at 303 nm; moreover, the 301 and 271 nm wavelengths were monitored occasionally for elemental identity confirmation.

Two different quantification techniques were considered, (1) addition of known concentrations of FBTO to acetone extracts from soil samples, previously to the derivatization step, and (2) comparison with FBTO standards submitted to same derivatization conditions as soil extracts. In both cases, peak areas obtained for the ethyl derivative of FBTO were corrected with the signal of the IS.

3. Results and discussion

3.1. Ethylation of FBTO and characterization of GC-AED determination

Optimisation of GC-AED conditions was carried out with ethylated standards of FBTO in isooctane. The derivatization reaction