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Determination of quaternary ammonium herbicides in soils Comparison of digestion, shaking and microwave-assisted extractions

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ABSTRACT

Very challenging analytical problems arise from the continuous introduction in agriculture of chemical pesticides. Particularly, diquat (DQ), paraquat (PQ) and difenzoquat (DF) are a difficult group of quaternary ammonium herbicides to analyze. This article reviews and addresses the most relevant analytical methods for determining the selected herbicides in soil. We discuss and critically evaluate procedures, such as digestion-based methods, shaking extraction and microwave-assisted extraction (MAE). Clean-up of extracts was performed by solid-phase extraction (SPE) using silica cartridges. Detection of these herbicides was carried out by liquid chromatography (LC) coupled to UV detection and mass spectrometry (MS) as confirmatory technique. Recoveries ranged from 98% to 100% by digestion, from no recovered to 61% by shaking, and from 102% to 109% by MAE with estimated quantification limits between 1.0 μg/kg and 2.0 μg/kg by digestion and 5.0 μg/kg and 7.5 μg/kg by MAE using LC/MS–MS as detection technique. The recoveries obtained under the optimum conditions are compared and discussed with those obtained from digestion extraction and MAE.

1. Introduction

The increasing concern about environmental pollution and food contamination produced by the widespread use of pesticides has led to the establishment of strict regulations and has driven the efforts to develop highly sensitive analytical methods, which do not demand time and sophisticated equipment [1]. Herbicides are essential components of modern agriculture in developed countries and their use is increasing in the third world countries [2].

The bipyridinium herbicides, diquat (DQ) and paraquat (PQ), were introduced by Imperial Chemical Industries in 1958 [3]. They are very quick-acting herbicides for both terrestrial and aquatic plants that are absorbed by plants and translocated, thus causing desiccation of foliage. The pyrazolium monocation difenzoquat (DF) is also used throughout the world as a selective herbicide for post-emergence control of wild oats in barley and fall-seeded wheat. It is the active ingredient in Avenge and Finaven (registered trademarks of American Cyanamide Co.).

Their physical properties, such as easiness of handling (crystalline salts), low vapor pressure (minimal fumes), high water solubility (easy to make up spraying solutions), high binding potential (soil binding causes deactivation and immobilization), and first working make them suitable for many agricultural uses.

Once the selected herbicides enter the soil environment, they are rapidly and strongly bound to soil components. The adsorption and desorption of these compounds in heterogeneous soils govern their fate. Tests have revealed that both are strongly adsorbed by soils and soil clays [4–6]. Also, according to Calderbank [5], some clay in soil dramatically reduces the herbicidal power of both compounds. More recent studies have shown that these herbicides have a high affinity for clay surfaces in relation to soil organic matter, especially as compared with inorganic cations [7,8]. Their interactions with clay particles depend on the particular type of clay, but even so, there have been many authenticated cases of the detection of their residuals in water sources [9,10].

The development and the application of methodology for determining the DF, DQ and PQ in soils are challenging task, as a result of some of the inherent general properties of such type of samples. First of all, the concentration of the selected analytes in soil samples could be extremely low. As a result, the corresponding analytical methods must provide extremely high sensitivities, which

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are adequate for detection and quantification of these species at such levels.

Other disadvantage consists of their strong affinity for components in plants and soils, and even though they are water soluble, they cannot be easily extracted once they have been sprayed onto and incorporated into the plant or retained in soil [3]. Therefore, drastic extraction conditions involving refluxing in acid conditions have been reported [11–15]. Microwave-assisted extraction (MAE) is a recent extraction method that was successfully used during last years in the determination of a wide range of chemicals in many matrices. Therefore, a comparison between recent extraction methods with traditional extraction methods could be very useful to put forward new alternatives, which minimize work, time and expense.

Several methods have been reported for detecting the selected herbicides with gas chromatography (GC) [16], GC/MS [17], LC/UV [11,13,18–23], LC/MS [26–29], LC/MS–MS [30–33], capillary electrophoresis (CE) [34,35], CE/MS and CE/MS–MS [3] in various matrices. Although numerous papers have been published on drastic extraction conditions involving refluxing in acids conditions for determining DF, DQ and PQ in soil samples, to our knowledge only few of them are related to MAE [35]. However, different results were found depending on soil properties.

The aim of this study was to propose and compare new analytical procedures, such as digestion-based methods, shaking extraction and MAE for determining quaternary ammonium herbicides using LC with UV and electrospray ionization (ESI) tandem mass spectrometry (MS–MS) detection as confirmatory technique. The optimized methods have been tested in different soils in order to establish global optimal conditions for soil samples, independent of their matrix components.

2. Experimental

2.1. Chemicals

The quaternary ammonium herbicides were obtained from the following sources: diquat (1,1′-diethylene-2,2′-bipyridinium ion), difenzoquat (1,2-dimethyl-3,5-diphenylpyrazolium ion) and paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) from Sigma (Madrid, Spain). Heptafluorobutyric acid (HFBA) was obtained from Scharlau (Santiago de Compostela, Spain). Ethylenediaminetetraacetic acid (EDTA), formic and acetic acids, ammonium formate and acetate were supplied from Panreac (Vigo, Spain), silica Sep-Pak cartridges were obtained from Waters (Santiago de Compostela, Spain). Stock standard solutions of the selected herbicides, 1 mg/mL, were prepared in water. Working solutions were prepared by diluting the stock solutions in mobile phase. All solutions were stored in plastic vials to prevent adsorption.

2.2. Chromatography and detection technique

The liquid chromatographic system used was a Finnigan Surveyor HPLC system Thermo Fisher Scientific (Madrid, Spain), which contains a quaternary pump, auto sampler, degasser and column department. Separations were performed with 150 mm × 4.60 mm i.d. (LC/UV) and 150 mm × 2 mm i.d. (LC/MS–MS), 5 μm particle, Luna C18 analytical columns obtained from Phenomenex (Madrid, Spain) and a 4 mm × 2 mm i.d., 5 μm particle, guard column containing the same packing material. The temperature of the HPLC column was kept constant at 40 °C.

The used mobile phases were water containing 100 mM NH_4COOH/HCOOH to bring the solution to pH 3.0/15 mM HFBA (A), MeOH (B) and isopropanol (C). The gradient was as follows: 90% A and 10% B for 3 min, change to 90% B and 10% A in 2 min and hold for 5 min, change to 40% B and 50% C in 2.0 min and hold for 4 min, and finally, change to 90% A and 10% B in 0.1 min giving an analysis time of 26 min. The injection volume was set to 50 μL and LC flow rate of 0.70 mL/min, when the analyses were performed by LC/UV. Twenty microliters and 0.25 mL/min flow rate were used by LC/MS–MS.

A UV 2000 (Thermo Fisher Scientific) detector was used as UV detector. In order to confirm the obtained results, a TSQ Quantum Discovery triple stage quadrupole mass spectrometer equipped to an electrospray interface from Thermo Fisher Scientific was employed. MS/MS analysis was performed using argon as the collision gas and nitrogen as the nebulizer gas. Quantification was performed using selected reaction monitoring (SRM) in positive mode of precursor > product ion transitions at m/z 183 > 157 (collision energy, −25 eV) for diquat, m/z 185 > 169 (collision energy, −20 eV) for paraquat and m/z 249 > 193 (collision energy, −33 eV) for difenzoquat. Capillary voltage was set to 4.0 kV. Capillary temperature of 270 °C, sheath gas and auxiliary gas pressure of 35 and 5 units, were selected.

2.3. Soil samples

Two samples of soil were obtained from the 0 cm to 5 cm deep layer of two vineyard soils developed on granite materials in Galicia (NW Spain). The soils differed in the length of time they had been used for vine growing (more than 100 years for soil 1 and only 7 years for soil 2). Five replicates of each soil were collected within 0.5 m of each other and pooled. Once in the laboratory, the soils were dried at room temperature, passed through a 2 mm mesh sieve, homogenized, and stored until analysis. Properties of the selected soils are shown in Table 1.

2.4. Solid–liquid extraction procedures

2.4.1. Digestion

A sample of 5 g of soil was extracted for 3 h with 30 mL of a 70/30 mixture of methanol/5% EDTA, which was previously acidified with the addition of 2% (v/v) HCOOH. The resulting extract was concentrated by nitrogen using a TurboVap LV concentration workstation (Caliper Life Sciences, Barcelona, Spain) to 4 mL following pH adjustment to 9–10 with 3 M NaOH and cleaned up by passage through silica cartridges.

2.4.2. Shaking extraction

An analytical procedure similar to a chelating extraction procedure for the determination of micronutrients in soil, such as zinc and cupper, was carried out [36]. For the consecutive analysis 1 g soil sample was extracted with 10 mL 0.02 M EDTA/0.5 M NH_4CH_3COOH after acidification to a pH 4.7 by shaking extraction. The pH of resulting extract was adjusted to 9–10 with 3 M NaOH and cleaned up by passage through silica cartridges.

2.4.3. Microwave-assisted extraction

A CEM MarsXpress Microwave Accelerated Reaction System (CEM, Barcelona, Spain) was used. A 1 g amount of soil and 200 μL Marlon A375 (10 mg/mL in acetone) or 200 μL benzalkonium chloride (BAC) were loaded into extraction cylinders and 8 mL of HNO_3 65% was added together with 2 mL HCl (37%) and 2 mL HF (48%) using the following microwave program: a 30 min ramp time was used to reach the desired temperature of 200 °C and the power did not exceed 80% (800 W) and then the system was hold at 200 °C for 20 min. The reaction temperature was controlled via a reference vessel. After this extraction, 20 mL 4% boric acid aqueous solution was added into the extraction vessels and extracted again using the following program: a 15 min ramp time was used to reach 180 °C at 80% (800 W) and then the system was hold at 180 °C for 15 min.