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Extraction of triallate from soil with supercritical carbon dioxide and determination by gas chromatography–atomic emission detection
Comparison with a solvent extraction procedure

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Abstract

The potential of supercritical CO_2 for the extraction of triallate from soil as an alternative to a conventional acetonitrile extraction procedure is investigated. Triallate is extracted at a density of 0.65 g/ml, an equilibrium time of 8 min, an extraction time of 25 min and a flow-rate of 1 ml/min. The extract is collected on an octadecylsilane trap at 5°C and eluted with 1 ml of acetonitrile. The analyte is determined by capillary gas chromatography with atomic emission detection. The validity of the supercritical fluid extraction method is tested on spiked and real soils. The triallate concentrations obtained on aged soils are lower applying supercritical fluid extraction with pure CO_2 than applying solvent extraction, making necessary the use of CO_2 modified with methanol to achieve similar results.

Keywords: Soil; Environmental analysis; Extraction methods; Triallate; Pesticides

1. Introduction

Triallate, S-(2,3,3-trichloroallyl) diisopropylthiocarbamate, is a herbicide recommended for chemical weed control in cereal, legume and beet crops [1], to which it is applied in fairly high doses. Its octanol–water partition coefficient is high and its water solubility is low, it being strongly adsorbed by soils [2,3].

The strong binding of triallate by soils entails using time-consuming solid–liquid extraction procedures for its determination, these usually involve many steps and use large organic solvent volumes, raising the analytical costs and producing solvent wastes that are cumbersome and expensive to dispose of. In addition, the potentially adverse effect of the organic solvents on the environment and human health must be considered. Thus, conventional extraction procedures for triallate in soil essentially involve Soxhlet extraction of the soil sample mixed with silica gel in *n*-hexane–acetone [2], extraction with methanol and subsequent clean-up by passage through an alumina column [4] or extraction with 2,2,4-trimethylpentane [5]. Triallate in vegetables has been extracted by shaking with an acetonitrile–water mixture, followed by clean-up on a Florisil column [6]. In most cases, the herbicide is determined by gas chromatography with electron-capture detection.

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At present, extraction with supercritical CO_2 is a valid alternative to solvent extraction methods. So far, this supercritical solvent has been used for the analysis of herbicides of various families including imidazolines [7,8], triazines [9–13], phenylureas [11,14,15], anilides [12], phenoxyacids [16–18] and sulfophenylureas [19,20], in soils, vegetables and water. Some reviews about environmental analysis with supercritical fluid extractions (SFE) have also been published [21,22].

A procedure for the extraction of triallate from soil using supercritical CO_2 has been developed in this work, and the influence of several experimental variables such as extraction density and temperature have also been studied. The proposed procedure has been applied to soils of different texture and organic matter content that were either laboratory spiked or field treated. The results obtained were compared to those provided by a conventional extraction procedure: shaking with acetonitrile. Once extracted, the herbicide was determined by capillary gas chromatography with atomic emission detection (GC–AED), monitoring mainly the sulphur emission line.

2. Experimental

2.1. Chemicals and general instrumentation

Chromatographically pure triallate and chlorpyrifos standards were obtained from Promochem (Wesel, Germany). The commercial formulation Avadex BW, 40% (w/v) triallate from Monsanto Agricultural Company (St. Louis, MO, USA) was used.

Residue analysis grade methanol and acetonitrile were provided by Labscan (Dublin, Ireland). Carbon dioxide, 99.999% minimum purity, was obtained from Air Products Special Gases (Sombreffe, Belgium).

For sample preparation, disposable PTFE syringe filter units, 0.45 μm pore size, were obtained from Microfiltration Systems (Dublin, CA, USA).

A Turbo-vap evaporator system with a thermoregulated water bath and nitrogen stream, provided by Zymark (Hopkinton, MA, USA), centrifuges supplied by Kokusan (Tokyo, Japan) and mechanic shakers from Selecta (Barcelona, Spain) were also used.

Table 1
Characterization of the soils used in the experiments

Soil	Clay (%)	pH	Organic matter (%)
A	7.2	6.4	0.6
B	8.4	7.3	0.4
C	57.3	7.5	1.1
D	36.1	7.4	1.8
E	54.5	7.6	1.5

2.2. Soil fortification

Five types of soil of different texture, pH and organic matter content were used. Table 1 shows their features. Texture, pH (Ca_2Cl procedure) and organic matter were measured according to official methods [23,24].

Fortification was done by mixing 50 g of dry and sieved soil with 5 ml of a methanol solution of Avadex BW at the desired concentration level. Spiked samples were homogenized by mechanical stirring for 24 h and stored at 4°C in the dark until analysis. Prior to extraction, samples were kept at room temperature for 2 h.

2.3. Extraction with acetonitrile

A 10 g amount of soil was weighed in a 50 ml threaded glass tube and extracted with 30 ml of acetonitrile by stirring for 1 h. Then, the liquid phase was separated by centrifugation at 4000 *g* for 10 min and collected. The residual solid-phase was extracted twice more. The three liquid portions were pooled and evaporated to dryness under a gentle nitrogen stream at 30°C. Finally, the residue was dissolved in 1 ml of acetonitrile by sonication for 30 s.

2.4. SFE

SFE experiments were carried out with an HP 7680A extractor from Hewlett-Packard (Avondale, PA, USA) equipped with an octadecylsilane (Hypersil) trap of 30–40 μm particle size for extract collection. Extractions were carried out on 5 g of sample. The following variables were kept constant: CO_2 flow-rate, 1 ml/min; dynamic extraction time, 25 min and trap temperature during extraction and

elution, 5°C and 40°C, respectively. The nozzle was kept 10°C above the extraction chamber temperature and the trap was eluted with 1 ml of acetonitrile throughout. The influence of density, extraction temperature and extraction time in the static mode (equilibrium time) were studied on the soil designated as C in Table 1, which contained 57% clay and was fortified with 0.5 mg/kg of triallate. Methanol was used as CO_2 solvent modifier; a 50 μl volume was added to the extraction thimble.

2.5. GC–AED

An HP 5890 Series II gas chromatograph equipped with an HP 7673 automatic sampler and a 30 m× 0.25 mm, 0.25 μm 5%-phenylmethylpolysiloxane capillary column (HP-5), was coupled directly through a transfer line to an HP 5921A atomic emission detector, all from Hewlett-Packard.

The conditions used in the GC–AED analysis were as follows. Temperature program: initial 57°C, held for 1 min, ramp 10 C°/min to 270°C, held for 10 min. The temperature of the transfer line and the detector cavity was 275°C. Pressure program: initially 23 p.s.i. (1 p.s.i.=6894.76 Pa), held for 0.9 min, ramp 98 psi/min to 5 psi, then ramp 0.4 psi/min to 14.6 psi, held for 7 min. Helium was the carrier gas. The injection was in splitless mode at 225°C, and the volume injected was 1 μl. In the detector, two emission lines were monitored, carbon (193 nm) and sulphur (181 nm). Scavenger gas, filter and backamount values were adjusted according to Hewlett-Packard default values.

The quantitation of triallate in the extracts was performed by measuring the peak height in the sulphur chromatograms. Linear calibration graphs were obtained for a concentration range from 0.2 to 10 mg/l (coefficient of correlation, r^2, 0.998). In order to correct for instrumental variations, the insecticide chlorpyrifos (1 mg/l) was added to the extracts as internal standard.

3. Results and discussion

3.1. Study of the extraction with supercritical CO_2

Fig. 1 shows the variation of triallate recovery with the CO_2 density at a constant extraction temperature (80°C) and equilibrium time (8 min). The recovery increased with increasing density from 0.35 g/ml (58%) to 0.85 g/ml (about 88%), above which it remained virtually constant. A density of 0.65 g/ml was adopted as optimal since higher values did not result in improvement of the extraction efficiency and co-extracted many soil compounds, some of which interfere with the determination of triallate.

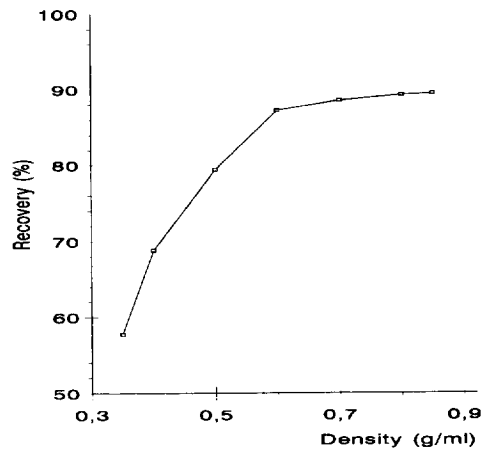

Fig. 1. Influence of the supercritical carbon dioxide density on the recovery of triallate from spiked soil.

Fig. 2 shows the influence of the extraction chamber temperature, varied from 40 to 100°C at 10°C intervals, at a density of 0.65 g/ml and an

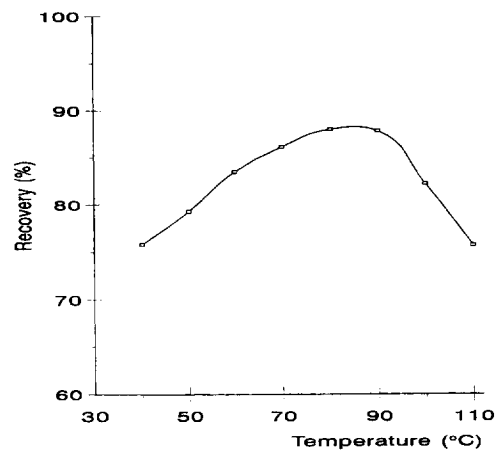

Fig. 2. Influence of the extraction chamber temperature on the recovery of triallate from spiked soil.

equilibrium time of 8 min. The recovery increased with increasing temperature up to 80–90°C, but at a lower rate than the density. Above 90°C, recoveries were much poorer. The trend observed in the low-temperature range can be ascribed to the increasing solubility and diffusivity of triallate in CO_2 with increase in the temperature [25]. On the other hand, the declining recoveries observed above 90°C could be attributed to the thermal degradation of the triallate, a thermally labile compound; evidence of this phenomenon has not been observed in the chromatograms obtained, but has been reported in the SFE of other herbicides [26]. No residual triallate was detected by back-extracting soil samples which had previously been extracted at a temperature above 90°C.

The equilibrium time was studied, keeping constant the density at 0.65 g/ml and the extraction temperature at 80°C. As can be seen from Fig. 3, it also had a marked effect on triallate recovery, reaching the highest recovery at 7–8 min and increasing gradually from 0 to 8 min. Unlike other herbicides [8], ensuring maximum desorption of triallate entailed a considerably long time of contact between the soil matrix and the CO_2.

The extracts were collected on an octadecylsilane trap that was initially eluted with methanol, but a 1 ml final volume resulted in incomplete elution (the highest recovery was about 60%). Acetonitrile (1 ml final volume) was preferred as it ensured higher recoveries.

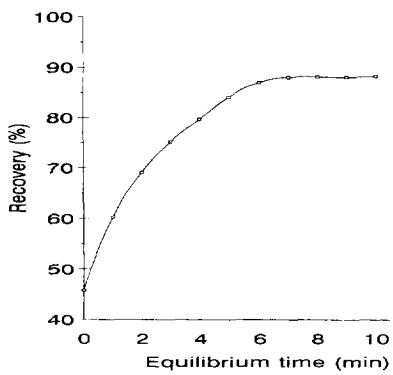

Fig. 3. Influence of the equilibrium time on the recovery of triallate from spiked soil.

Table 2
Recovery (%) of triallate from soil for different concentration levels and two extraction procedures ($n=4$)

Concentration mg/kg	CO_2 extraction Recovery±R.S.D.	Acetonitrile extraction Recovery±R.S.D.
0.05	88.2±4.0	82.7±6.0
0.5	87.8±4.0	83.0±5.5
2.0	87.8±3.5	82.4±5.2

R.S.D.: Relative standard deviation (%).

3.2. Comparison with a conventional extraction

The proposed procedure (extraction with CO_2 at density 0.65 g/ml, temperature 80°C and equilibrium time 8 min) has been applied to laboratory spiked soils of different nature and soil samples from a field of wheat treated with triallate. Portions of both types of sample were also extracted by using a solvent procedure to make a comparison in terms of performance.

Table 2 shows the recovery and precision obtained in the analysis of soil C by the two extraction procedures at three concentration levels between 0.05 and 2.0 mg/kg. Recoveries were about 5% higher with supercritical CO_2 (ca. 88%) at the three concentration levels. In addition, the results for the SFE procedure were more repeatable ($n=4$) probably as the result of the smaller number of steps involved and its automation.

Table 3 shows the results obtained for 5 soils of different characteristics, spiked with 0.05 mg/kg

Table 3
Recovery (%) of triallate for different soils spiked with 0.05 mg/kg and extracted with acetonitrile and supercritical carbon dioxide ($n=4$)

Soil	CO_2 extraction Recovery±R.S.D.	Acetonitrile extraction Recovery±R.S.D.
A	87.9±3.7	83.6±5.2
B	88.3±4.0	83.5±5.4
C	88.2±4.0	82.7±6.0
D	88.4±3.9	82.4±5.6
E	88.2±3.7	81.8±5.4

R.S.D.: Relative standard deviation (%).

triallate. The recovery and precision provided by the two extraction procedures were consistent with the previous findings; differences between fresh spiked soils, which contained 7–57% clay and 0.4–1.8% organic matter, seem not to be significative for this compound extraction. The recovery obtained by the two extraction procedures is never in excess of 90% probably as the result of herbicide volatilization [27].

Both extraction procedures were applied to soil E samples, from a cultivated plot treated with Avadex BW and collected at different times after application of the triallate formulation. Table 4 shows the triallate concentrations found at different times. Irrespective of the decrease in the herbicide content in the soil, the concentrations obtained with the two procedures tended to diverge with time. Initially, the supercritical CO_2 procedure provided higher concentrations than the acetonitrile procedure by about 4–5%, consistent with the results for the laboratory spiked samples. However, the amounts extracted from the older samples (5, 6 and 7 months) by acetonitrile were larger, increasing the recovery difference between the two procedures with time. This could be related to an increasing fixation or adsorption of triallate by the soil with time so that supercritical CO_2 could be less efficient than the organic solvent in completely extracting the analyte from aged soil under the operating conditions used; this agrees with the observations found by other authors where CO_2 was unable to fully extract the analytes [22,28,29].

To try to reduce the triallate–soil matrix interaction, which could avoid the whole triallate extraction with supercritical CO_2 on aged soils, the addition of different volumes of methanol to the sample thimble at the beginning of the extraction was tested. A final volume of 50 μl was considered the best. The results obtained are also listed in Table 4. It can be seen that the concentrations found after the acetonitrile or CO_2–methanol extractions are comparable without great differences between them. This confirms the importance of using additives in the supercritical fluids when real samples of great adsorption capacity, such as soils, are analyzed.

3.3. Determination by AED

The two most sensitive atomic emission lines for triallate, carbon at 193 nm and sulphur at 181 nm, have been monitored in this work. The carbon chromatograms for the extracts obtained with acetonitrile reflected co-extraction of a larger number of compounds relative to supercritical CO_2 chromatograms; however, the chromatograms obtained for the sulphur emission line were similar in both procedures having only two chromatographic peaks corresponding to triallate and chlorpyrifos, the internal standard (Fig. 4). The use of methanol-containing CO_2 increased slightly the intensity of some chromatographic peaks in the carbon chromatogram with regard to the CO_2 extracts whereas there was not modification in the sulphur one. The selectivity of this emission line enabled the correct integration and quantitation of the analyte chromatographic peak even in dirty extracts. In addition, the AED enabled a 50 nm portion of the emission spectrum to be recorded in order to confirm the presence of a sulphur-containing compound by checking the emis-

Table 4
Triallate concentration obtained by the supercritical fluid and solvent extraction procedures on field soil collected in different months after treatment ($n=3$)

Month	CO_2 extraction mg/kg	Acetonitrile extraction mg/kg	Difference CO_2–Acet (%)	CO_2+ methanol mg/kg	Difference CO_2/Met–CO_2 (%)
0	0.75	0.71	+ 5.3	-	-
1	0.69	0.66	+ 4.3	-	-
5	0.26	0.30	−15.3	0.30	+15.3
6	0.17	0.21	−23.5	0.22	+29.4
7	0.11	0.14	−27.8	0.15	+36.4

-=no data.

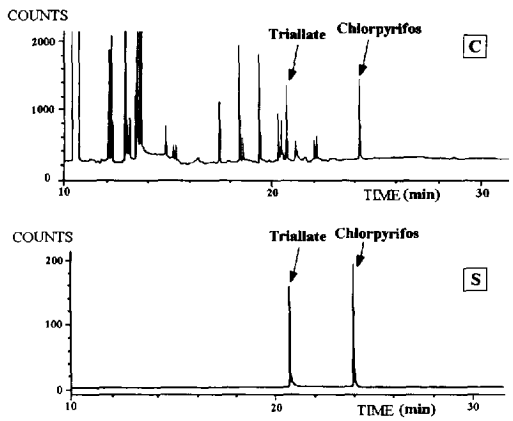

Fig. 4. Carbon and sulphur chromatograms of a soil extract obtained by supercritical fluid extraction.

sion spectrum of the atomic sulphur (lines at 181, 182 and 182.5 nm, with a given intensity distribution). Fig. 5 shows the three-dimensional emission spectrum for elemental sulphur.

As regards the detection limit, the emission line for carbon was about 50 times more sensitive than that for sulphur. The detection limit for the methanol modified supercritical CO_2 procedure was about 0.4 and 20 μg/kg for the carbon and sulphur line, respectively, considering a signal/noise ratio of about 3 and a 100% recovery on soil extract chromatograms, spiked with triallate after extraction. The detection limit in the sulphur line for the conventional extraction procedure was similar to that obtained in the SFE procedure, whereas in the carbon line the detection limit was higher in the extraction with acetonitrile (1.4 μg/kg).

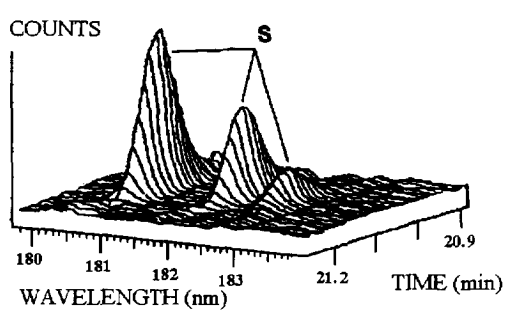

Fig. 5. Emission spectrum of elemental sulphur.

4. Conclusions

Supercritical CO_2 can be used to extract triallate from soils of different characteristics although the extraction seems not to be total on aged soils in comparison with a solvent extraction procedure. This can be ascribed to the gradual settling of triallate in soil with time. The retention of the analyte by the soil matrix is overcome by the use of methanol-modified CO_2 yielding similar concentrations from both extraction procedures. The automation, reduced operational time and smaller organic solvent consumption of the SFE procedure are the greatest advantages over the conventional extraction.

The selective extraction with supercritical methanol-modified CO_2, in combination with the selectivity of the sulphur emission line from AED, constitutes a powerful and valid tool for analyzing triallate traces in soil allowing the identity of a compound to be confirmed from its emission spectrum.

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