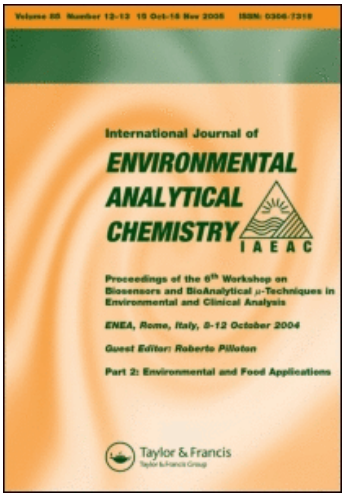


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Application of Supercritical fluid Extraction For Analysis of Organophosphates in Cereals

J. Poustka[a]; K. Holadová[a]; J. HajšLová[a]
[a] Department of Food Chemistry and Analysis, Institute of Chemical Technology, Prague, Czech Republic

To cite this Article Poustka, J. , Holadová, K. and HajšLová, J.(1995) 'Application of Supercritical fluid Extraction For Analysis of Organophosphates in Cereals', International Journal of Environmental Analytical Chemistry, 60: 2, 139 — 144
To link to this Article: DOI: 10.1080/03067319508042871
URL: http://dx.doi.org/10.1080/03067319508042871

Intern. J. Environ. Anal. Chem., Vol. 60, pp. 139–144
Reprints available directly from the publisher
Photocopying permitted by license only

APPLICATION OF SUPERCRITICAL FLUID EXTRACTION FOR ANALYSIS OF ORGANOPHOSPHATES IN CEREALS

J. POUSTKA*, K. HOLADOVÁ and J. HAJŠLOVÁ

Institute of Chemical Technology, Department of Food Chemistry and Analysis, Technická 3, 16628 Prague, Czech Republic

(Received, 3 August 1994; in final form, 26 September 1994)

Application of supercritical fluid extraction (SFE) utilizing pure carbon dioxide for selective isolation of organophosphates from contaminated cereals has been tested.

At the beginning of the experiments the extractability of added standards from an empty extraction vessel (thimble) and from various materials such as filter paper, sand, Celite and anhydrous sodium sulfate was tested to estimate the behavior of organophosphates. Further method development was carried out using a spiked sample of flour, which was analyzed within the proficiency testing for organophosphorus pesticides analysis (round 7) organized by Food Analysis Performance Assessment Scheme (FAPAS, MAFF-UK).

Comparison of the SFE method with a classical method currently employed for sample preparation (i.e. extraction with acetone/methanol mixture followed by gel permeation chromatographic clean up) showed advantages of the SFE technique such as simplification of the sample preparation step and thereby significant speeding up of the determination of organophosphates in cereals.

KEY WORDS: Supercritical fluid extraction, SFE, organophosphates, cereals.

INTRODUCTION

Supercritical fluid extraction (SFE) has been used in many ways for analysis of pesticides and other environmental pollutants in various matrices. An analysis of organophosphorus insecticides in cereals is one of its applications. Recent studies in this field have been focused on the development of suitable methods. King *et al.*[1] achieved good recoveries in the range from 77 to 115% with pure carbon dioxide under different conditions using the combinations of three temperatures (40, 60 and 80°C) and two pressures (5000 and 10000 psi). Resulting extracts were cleaned up by gel permeation chromatography (GPC) and GC with flame photometric detection (FPD) was used for quantitation. Skopec *et al.*[2] used carbon dioxide modified with 5% (v/v) of methanol for the isolation of organophosphates from rice. Recoveries ranging from 70 to 105% were recorded. Extracts were analyzed without further clean up or concentration by GC with atomic emission detection.

The objective of our experiments was to develop a method based on a simple and rapid sample preparation step, which can be used in routine practice.

* To whom correspondence should be addressed.

EXPERIMENTAL

Chemicals

Methanol, acetone, chloroform and toluene p.a. (Lachema Brno, CR) were redistilled before the use. Anhydrous sodium sulfare (Lachema Brno, CR) – heated 4 h at 500°C, sodium chloride (Lachema Brno, CR). Standards of organophosphates: dichlorvos, mevinphos, methacrifos, diazinon, monocrotophos, etrimfos, chlorpyrifos methyl, phosphamidon, parathion methyl, formothion, pirimiphos methyl, chlorpyrifos, fenitrothion, malathion, methidathion, phosalone were supplied by Dr. Ehrenstorfer, FRG. Both stock and working solutions were prepared in toluene.

Materials

Filter paper, sand and Celite were supplied by Lachema Brno (CR). Sample of spiked flour was obtained within the proficiency testing for organophosphorus pesticides analysis organized by Food Analysis Performance Assessment Scheme (FAPAS, MAFF - UK).

Liquid extraction followed by GPC clean up (LE-GPC)

Flour sample (approximately 1.5 g) was extracted with two 40 ml portions of acetone/methanol (1/1, v/v) mixture, combined extracts were filtered and after the addition of 60 ml of water and of 20 ml of saturated solution of sodium chloride were re extracted with two 40 ml portions of chloroform. Extracts were filtered through a layer of anhydrous sodium sulfate and after concentration to 1.5 ml cleaned up by GPC (on Bio Beads S-X3 column eluted by chloroform).

Gel permeation system

The gel permeation system consisted of a stainless steel column 50 × 0.8 cm I.D. (Tessek, CR) filled with 200–400 mesh Bio Beads S-X3 gel (Bio Rad, USA), which was swollen in chloroform (mobile phase). A linear solvent delivery system (pump HPP 5001-Laboratorní přístroje Praha, CR) and Rheodyne 7125 valve with 1 ml injection loop (Rheodyne, USA) was used. The flow rate was 0.6 ml/min at the column head pressure 0.4 MPa. The fraction from 10 to 22 ml was collected for the organophosphate determination.

Arrangement of supercritical fluid extraction

Hewlett Packard HP 7680 T extractor was used to perform all SFE extractions. Compounds extracted by supercritical carbon dioxide were trapped on a trap filled by stainless steel balls and then eluted with 1 ml of toluene to a vial. To this eluate 5 µl of solution of internal standard in toluene (monocrotophos—concentration 96 µg/ml) were added and the obtained sample was analyzed by GC-FPD.

The conditions of supercritical fluid extraction were the following: density of extraction fluid 0.6 g/ml, pressure 1786 psi, temperature 50°C, flow rate 3.0 ml/min, extraction time 30 min, extract trapping conditions: nozzle temperature 45°C, trap temperature 10°C.

The testing of recoveries was carried out in several modes. We extracted spiked an empty thimble (200 µl of stock solution of organophosphates in toluene were spread on its internal wall and toluene was evaporated) and spiked sand, Celite, filter paper and anhydrous sodium sulfare (200 µl of stock solution of organophosphates were added into each material and toluene was evaporated). Concentrations of organophosphates in the stock solution ranged from 4.35 µg/ml to 8.75 µg/ml.

GC-FPD determination

For the purpose of quantitation the internal standard (monocrotophos in toluene) was added to each sample. Samples were then analyzed by means of a gas chromatograph (Hewlett Packard 5890 Series II) equipped with a flame photometric detector (phosphorus mode) on a capillary column DB–17 (50% phenyl methyl silicone, 30 m × 0.25 mm × 0.15 µm) under following conditions: carrier gas—nitrogen at a pressure program: 246 kPa (0.9 min), decrease 600 kPa.min^{-1} to 52 kPa, increase 1.5 kPa.min^{-1} to 102 kPa, increase 200 kPa.min^{-1} to 236 kPa, make up gas—nitrogen at a flow rate of 30 ml/min, injector temperature – 200°C, detector temperature – 250°C and oven temperature profile—initial temperature 50°C (1 min), increase 10°C.min^{-1} to 165°C, increase 1.6°C.min^{-1} to 195°C, increase 20°C.min^{-1} to 270°C, hold 5 min. Injection technique was splitless (splitless period – 1 min). Injection volume was 1 µl.

RESULTS AND DISCUSSION

Figure 1 illustrates results of the recovery testing when organophosphates were extracted by SFE from different materials. As can be seen, the influence of the material in relation to the yield of individual compounds is variable. Thus, for example, recoveries of mevinphos, diazinon and pirimiphos methyl are relatively low for sand, but for sodium sulfate these exceeded 70%. Generally low recoveries were achieved for phosphamidon. On the other hand, methacrifos, etrimfos, chlorpyrifos methyl, parathion methyl, fenitrothion, malathion, chlorpyrifos and phosalone were well recovered from all materials. Evidently in the case of a such diverse group of compounds like organophosphates is necessary to verify recoveries on a referent material or by a comparison with another method of isolation.

Figure 2 and Table 1 demonstrate results of the determination of organophosphates in flour provided within the proficiency testing for organophosphorus pesticides analysis organized by Food Analysis Performance Assessment Scheme (FAPAS, MAFF—UK). Two methods for the organophosphates isolation from this matrix were compared (*a*- SFE method and *b*- LE-GPC method, for description see experimental). Both procedures gave similar results, but from the comparison of results with the FAPAS assigned values it is notable that the reliability of the SFE method needs more testing. Chromatograms of samples isolated by both LE-GPC and SFE methods are shown in Figure 2. Although the injected volume of the SFE extract corresponds to a higher amount of original flour, less interfering compounds were recorded in chromatogram. As can be seen from Table 2 comparing LE-GPC and SFE methods also most of parameters important from the practical point of view are more favourable for the later method.

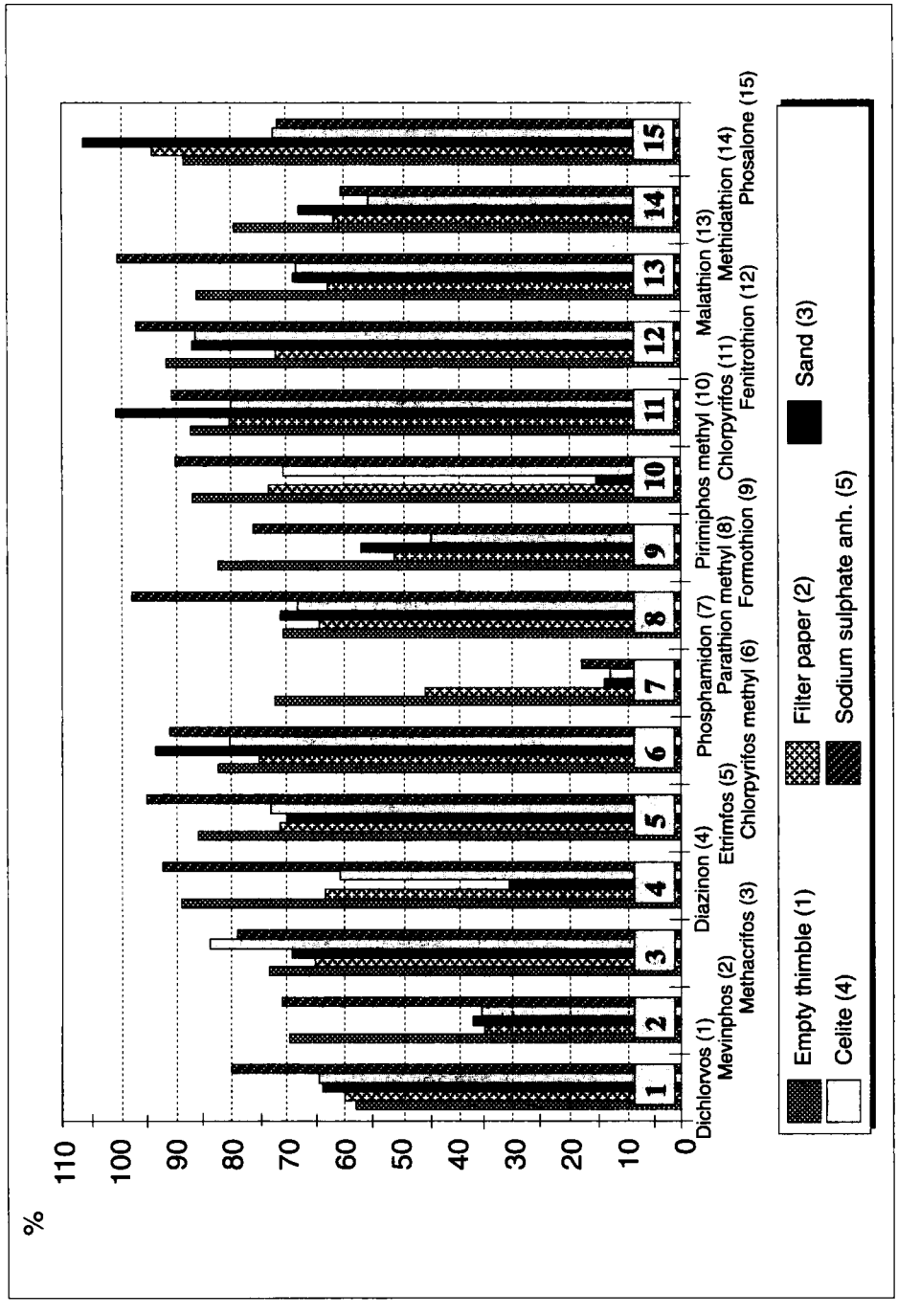
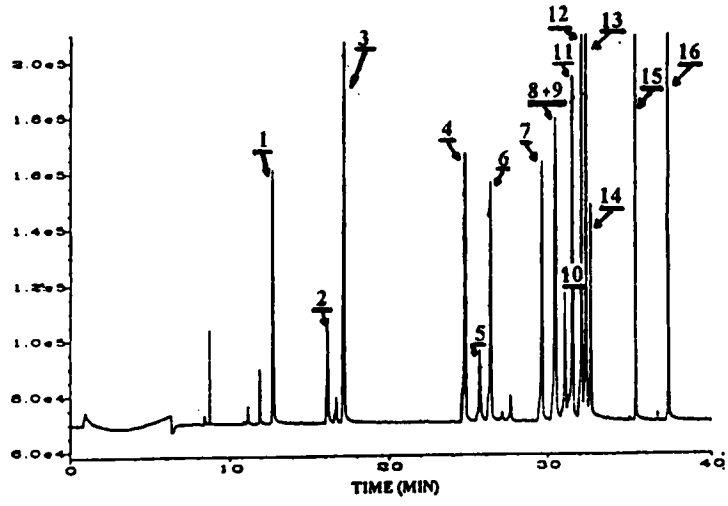
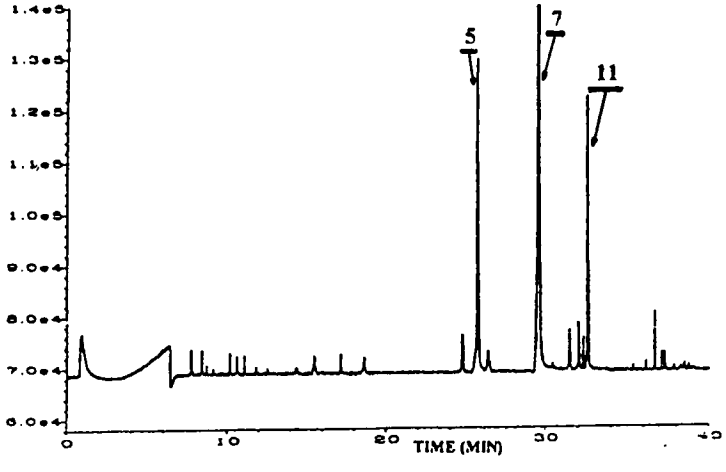


Figure 1 Recoveries of organophosphates extracted from different materials by the SFE method.



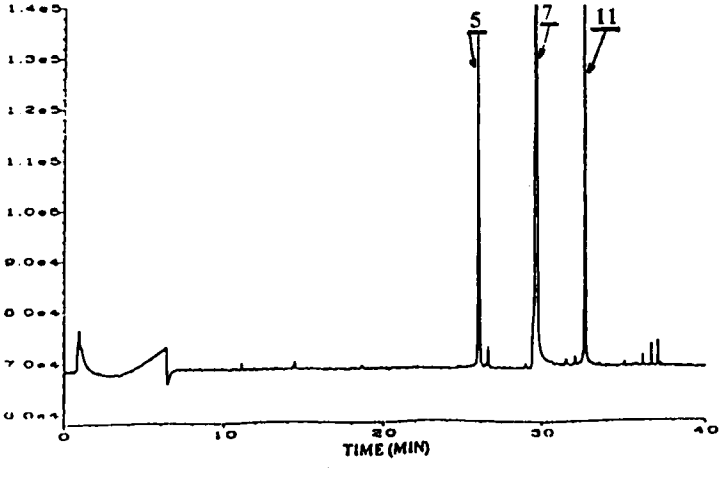
Chromatogram A.

Standard mixture of organophosphorus insecticides (concentration level is approx. 1 µg/ml)



Chromatogram B.

Extract of flour obtained by the LE-GPC method (injection represents 1.01 mg of original matrix)



Chromatogram C.

Extract of flour obtained by the SFE method (injection represents 2.68 mg of original matrix)

Figure 2 Chromatograms from the determination of organophosphates in a flour sample.

Table 1 The comparison of organophosphate levels (μg/kg) in flour obtained by two alternative methods (SFE and LE-GPC) and assigned values of FAPAS (UK).

Compound	*SFE method*	*LE-GPC method*	*FAPAS*
Chlorpyrifos methyl	1295	1306	1730
Malathion	310	300	291

Table 2 Comparison of SFE and LE-GPC methods for isolation of organophosphates from flour.

SFE method	*LE-GPC method*
40 min per sample	2 hours per sample
Lower organic solvent consumption	Higher organic solvent consumption
Good quality of final extract	Acceptable quality of final extract
More expensive equipment	Cheaper equipement

CONCLUSION

Generally poor predictability of the behavior of analytes for the SFE technique was shown during our experiments. Comparison of the classic method (LE-GPC) with the recently introduced SFE method of sample preparation demonstrate the possibility of the later use of SFE technique for routine analyses of organophosphates in cereals.

Acknowledgement

This project was supported within the framework of COST program "Pesticides—soil environment" reg. No. OC 66.30.

References

1. J. W. King, M. L. Hopper, R. G. Luchtefeld, S. L. Taylor and W. L. Orton, *J. AOAC Int.*, **76**, 857–864 (1993).
2. Z. V. Skopec, R. C. Clark, P. M. A. Harvey and R. J. Wells, *J. Chromatogr. Sci.*, **31**, 445–449 (1993).