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Short communication

Supercritical fluid extraction of chlorpyrifos and 3,5,6-trichloro-2-pyridinol from garden compost

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Abstract

A method was developed for the simultaneous supercritical carbon dioxide extraction of chlorpyrifos and its primary degradate, 3,5,6-trichloro-2-pyridinol (TCP), from garden compost. In situ derivatization with *N,O*-bis(trimethylsilyl)trifluoracetamide was necessary for extraction of TCP. Recoveries for TCP and chlorpyrifos were quantitative for spiked compost samples. Sodium chloride was used as the packing material in extractions with in situ derivatization. Optimum results were obtained for air-dried samples containing 4–7% moisture. No sample cleanup was required prior to analysis by GC–flame ionization detection. The effects of compost moisture content and ageing were investigated for chlorpyrifos recovery. No significantly negative effect on recovery for up to 20% (w/w) moisture for chlorpyrifos was observed. Effects of ageing showed a decrease in extraction efficiency over time with 52% recovery after 10 days.

Keywords: Extraction methods; Compost; Chlorpyrifos; Trichloropyridinol; Pesticides

1. Introduction

Composting of garden wastes as an alternative to landfilling will not become economically feasible until the cost of processing compost can be offset by revenues gained from selling the finished compost [1]. Garden waste, including grass clippings from lawns treated with pesticides, usually contains pesticide residues [2–4]. Whereas much work has been done on the fate and toxicity of heavy metals during composting [5–10], little is known about the fate of organic contaminants such as pesticides and their metabolites [4,5,11,12]. In addition, composting results in a reduction in volume of wastes by approximately 50% [13]. The use of composted waste products as soil conditioners without testing for hazardous residues, especially in food production, is of concern [14,15]. Until the fates of xenobiotics and their degradates in composting processes are better understood, these limitations will exist, with or without scientific evidence to support them.

Typical methods for preparation of compost samples involve solid–liquid extraction with organic solvents such as Soxhlet extraction [12,13]. The high organic matter content and moisture, which can be as high as 60% in compost, complicate the extraction

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process as most organic solvents are nonselective. These methods require clean-up and preconcentration steps prior to analysis making them tedious, time-consuming, and costly [2,16]. Extraction with supercritical carbon dioxide provides a promising alternative for the analysis of organic contaminants in compost. The potential to greatly reduce the time of extraction, cost, and sample clean-up make it a desirable alternative as long as a reliable extraction method can be established for the analytes of interest [17].

Degradates of xenobiotics tend to be less amenable to supercritical-CO_2 extraction than the parent compound due to their increased polarity and reduced solubility. Often, they require a separate extraction and analysis procedure. The addition of organic modifiers, such as methanol, has often improved recoveries to a limited extent for some analytes by increasing their solubility in the supercritical fluid [18,19]. Supercritical fluid extraction (SFE) with methanol as a modifier was applied with mixed results to the extraction of soil contaminated with explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and its metabolites [20] that had been composted with cow manure, sawdust, alfalfa, potato waste, and chicken manure. Irreproducible recoveries were thought to be the result of inconsistent packing of the extraction vessel between samples. Increasing the extraction temperature can also increase recoveries of thermally stable analytes [21,22]. More polar analytes can also be difficult to recover from solid trapping materials [23]. In situ derivatization [24,25] of a polar analyte can increase its solubility in CO_2 and may allow it to be extracted simultaneously with the parent chemical and quantitatively recovered from solid trapping materials.

Water can act as a modifier to increase recovery of more polar analytes yet the effect of water, especially at high concentrations in some environmental samples, has not been clarified [26]. Snyder et al. [27] reported optimum recoveries from soil of organophosphorus pesticides at a moisture level of 5% and significant decreases in recovery above a moisture level of 10%. Water was also reported to act as an effective modifier for the extraction of organophosphorus compounds from various soils that had ''aged'' 1–3 days after spiking [28].

Analytical methods developed using spiked samples do not necessarily produce quantitative recoveries for native samples [29]. Over time analytes are more strongly bound to the matrix and require more exhaustive treatment for their complete removal. Studies with aged samples can more closely replicate this phenomenon [28,30], however, samples are seldom aged for more than a few hours and analyte can be lost through evaporation during the ageing period [29]. Samples with higher organic matter content may also suffer from increased analyte-matrix interactions [28,31].

Chlorpyrifos is an organophosphorous pesticide (OPP) commonly used for the eradication of termites and has a half-life in soil of about two weeks, although its degradation rate decreases with increasing concentration [32]. The fate of chlorpyrifos in compost is similar to that in soil [4], however, most reports on the fate of chlorpyrifos in soil and compost fail to examine the fate of its primary degradate by hydrolysis, 3,5,6-trichloro-2-pyridinol (TCP). While chlorpyrifos has been determined to be immobile in soil [33], TCP is moderately mobile due to its greater water solubility. The use of chlorpyrifos in water and as a cattle dip has been discontinued [33]. The moderate mobility of TCP in the environment is cause for concern due to the widespread consumer use of chlorpyrifos.

Supercritical fluid extraction of trace-level chlorpyrifos from grass [34] yielded a mean recovery of 97.5% with methanol-modified CO_2. Recoveries ranging from 55 to 87% were reported for the extraction of chlorpyrifos from spiked sand with and without various modifiers [35]. The addition of methanol has been demonstrated to increase recovery of chlorpyrifos from soil [36] and food [37] matrices. Supercritical fluid extraction of TCP from soil using methanol modifier and ion-pair reagent preceding immunoassay analysis was recently reported to yield 95% recovery [38].

For environmental fate studies, there is a great advantage in developing methods which allow for analysis of a xenobiotic and its primary degradate simultaneously. The following procedure utilizes in situ derivatization of TCP for the extraction of chlorpyrifos and TCP simultaneously from garden waste compost resulting in a sample that can be analyzed directly by gas chromatography–flame ionization detection (GC–FID). The effects of moisture content and ageing of spiked samples on chlorpyrifos recovery were also investigated.

2. Experimental

2.1. Materials

Chlorpyrifos, [*O,O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate], [2921-88-2] 99.0%, and its major metabolite, 3,5,6-trichloro-2-pyridinol (TCP) 98.7%, and tributyl phosphate (TBP) [126-73-8] 98.0%, were obtained from ChemService (West Chester, PA, USA).

N,O-bis(trimethylsilyl)trifluoracetamide (BSTFA, 98%) was obtained from Acros Organics (NJ, USA). All solvents were GC resolv or optima quality from Fisher Scientific. Water was provided by a Labconco WaterPro PS water system (Labconco, Kansas City, MO, USA). All reagents, stock, and standard solutions were stored in a freezer at −5°C unless in use. SFE-grade carbon dioxide with helium head pressure and a dip tube was obtained from Air Products and Chemical, (Allentown, PA, USA). Pesticide-grade silanized glass wool, used as extraction cell packing material, was obtained from Supelco (Bellefonte, PA, USA). Certified ACS, sodium chloride (Fisher) as used as an alternative packing material.

Garden compost was obtained from a local organic farmer. The compost was produced from grass clippings with some garden and kitchen wastes that were composted over a two-year period. Two-year-old compost is ''mature'', that is, the composition changes would be negligible over the course of the study. This provided a more stable matrix than ''fresh'' compost so the various extraction parameters could be evaluated individually. The compost was chopped in a blender, air-dried, and ground with a mortar and pestle. It was air-dried again until the moisture content reached a constant level and sieved through a 2-mm screen. Storage was in a polypropylene bottle in the refrigerator.

2.2. Instruments

2.2.1. SFE

All extractions were performed using a Prepmaster EL Supercritical Fluid Extractor (Suprex, Pittsburgh, PA, USA) equipped with a pressure transducer and a heated, stainless steel restrictor. Two extraction vessels were used, both stainless steel, with either a 10-ml or 5-ml internal volume with 0.2 μm frits at each end. Packing material was placed in the bottom (inlet) end of the extraction vessel followed by fortified compost and another layer of packing material on top (outlet).

A solid trap was used for collection of the analytes from the supercritical fluid stream exiting the restrictor. It consisted of a 10 cm×9.4 mm I.D. stainless steel chromatographic column with 2 μm frits (Keystone Scientific, Keystone, PA, USA) packed with Tenax-TA (60/80 mesh, Alltech, Deerfield, IL, USA). A liquid trap containing acetone or hexane was connected to the exit port of the solid trap to ensure that any analyte escaping the solid trap could be detected.

The SFE apparatus was modified when fitted with the solid trap. In order to recover all of the extracted analyte from the restrictor, it was washed after each extraction by connecting an HPLC pump to the restrictor and pumping solvent (acetone or hexane) through the restrictor and trap into the sample collection vials. The Tenax-TA trap was regenerated by rinsing with 20–40 ml more of acetone or hexane then drying in a stream of nitrogen and heating in an oven at 120–150°C for at least 2 h before being reused.

2.2.2. GC–FID

GC–FID analysis was performed on a Perkin-Elmer 8500 gas chromatograph with a Perkin-Elmer CP-100 graphic printer (Perkin-Elmer, Norwalk, CT, USA). A 30 m×0.328 mm, DB-1 poly(dimethylsiloxane) capillary column with a film thickness of 0.25 μm from J & W Scientific (Folsom, CA, USA) served as the analytical column with He as the carrier gas. Analyses were performed in the split/splitless mode with an injector temperature of 320°C. The carrier gas flow was 1.0 ml/min, split ratio was 1:60, and the injection volume was 1 μl. The oven temperature program began at 60°C for 3.0 min, with a ramp of 10.0°C/min to 200°C, then 20°C/min to 250°C.

2.3. Procedures

2.3.1. Supercritical CO_2 extraction of chlorpyrifos

Five 5.0 g dry mass (air-dried with 4.5% moisture) compost samples were weighed into five separate 50-ml beakers and spiked with 0.5 ml of 1008 ppm chlorpyrifos solution prepared in acetone to give a

dose rate of 100 μg chlorpyrifos per gram dry-weight compost. The solvent was allowed to evaporate for at least 10 min before each extraction was performed with the 10-ml volume extraction vessel. Table 1 shows the extraction conditions used. Acetone was used as the solvent to recover the analyte from the Tenax trap. One milliliter of a 10-ppm solution of the internal standard, TBP, was added to 1.0 ml of each sample immediately before analysis.

2.3.2. Effect of moisture on chlorpyrifos recovery

The moisture content of compost samples was adjusted with water before spiking. Duplicate samples (3.1–5.3 g) were prepared at each moisture level. Samples containing zero percent moisture were oven-dried. Air-dried samples contained 4.5% moisture. In addition, water was added to some air-dried compost samples to bring the total percent (w/w) moisture contents to 10, 20, 30, and 40%. Extractions were performed on samples spiked with 0.5 ml of 1008 ppm chlorpyrifos in acetone (100 μg/g dry mass) using the SFE conditions listed in Table 1. The 10-ml volume extraction vessel was used in these extractions. Determination of unextracted or residual chlorpyrifos was achieved by sonicating the post-extracted compost sample in 30 ml of acetone for 30 min and filtering through a 0.2-μm Whatman 13 mm ZC disposable nylon filter into a 7.4-ml vial. One milliliter of a 10-ppm solution of the internal standard, TBP, was added to 1.0 ml of each sample immediately before analysis.

2.3.3. Effect of ageing on chlorpyrifos recovery

Ten 3.13-g air-dried (4.5% moisture) compost samples were weighed into separate silanized 22.2-ml vials and 0.5 ml of 1008 ppm chlorpyrifos added to each of them to give a dose rate of 100 μg chlorpyrifos per gram dry mass compost. The solvent was allowed to evaporate before the vials were tightly closed, shaken, and stored at room temperature. They were extracted and analyzed at the rate of two per day for four consecutive days using the SFE conditions listed in Table 1. The last two samples were extracted and analyzed after ten days. Determination of residual chlorpyrifos was achieved by sonicating the post-extracted compost sample in 30 ml of acetone for 30 min and filtering through a 0.2-μm Whatman 13 mm ZC disposable nylon filter into a 7.4-ml vial. One milliliter of a 10-ppm solution of the internal standard, TBP, was added to 1.0 ml of each sample immediately before analysis.

Table 1
Supercritical CO_2 extraction conditions for chlorpyrifos[a]

Mode of operation	Pressure (atm)	Temperature (°C)	Time (min)
Static equilibration	300	80	0.00
Dynamic extraction	300	80	5.00
Static cool down	75	30	2.00

[a] The restrictor temperature was set at 80°C with a flow-rate of 1.5 ml/min. The solid trap was washed with two 15-ml aliquots of acetone to recover the analyte. 1 atm=101 325 Pa.

2.3.4. Extraction of chlorpyrifos and TCP simultaneously from compost

Trapping efficiency investigations showed that TCP could not be recovered quantitatively from the Tenax-TA trap using various solvents, therefore, TCP was derivatized in-situ during the static phase of the extraction procedure by the addition of 500 μl BSTFA to the extraction vessel. A 5-ml volume extraction vessel and a smaller sample (1.0 g dry mass) were used in order to get greater saturation of the compost with BSTFA. Air-dried compost with a moisture content of 7.1% was used for these extractions. Spikes of 53.5 μg of chlorpyrifos and 57.3 μg of TCP were added to each sample. The type of packing material used also showed an effect on TCP derivative recovery in preliminary studies. Recoveries measured using various packing materials showed the following recoveries for the TCP derivative; NaCl (95%), silanized glass wool (74%), Ottawa sand (55%) and molecular sieves (57%), therefore NaCl was selected as the packing material for extractions with in situ derivatization. The SFE conditions used are listed in Table 2. All six extracted samples were analyzed immediately after extraction due to the instability of the TCP derivative in the solid trap rinse (hexane) although the analytical signal could be regenerated by the addition of more BSTFA to degraded samples immediately before analysis. Hexane was used to rinse the solid trap because the TCP derivative was less stable in acetone.

Table 2
Optimized supercritical CO_2 extraction conditions for chlorpyrifos and TCP derivative[a]

Mode of operation	Pressure (atm)	Temperature (°C)	Time (min)
Static equilibration	300	80	2.00
Dynamic extraction	300	80	10.00
Static cool down	75	30	2.00

[a] The restrictor temperature was set at 100°C with a flow-rate of 1.5 ml/min. The solid trap was washed with two 10-ml aliquots of hexane to recover the analytes.

3. Results and discussion

3.1. Supercritical CO_2 extraction of chlorpyrifos

The results for extraction of 100 ppm chlorpyrifos from garden compost showed percent recoveries with a range of 100–123% and a mean value of 108±9% (n=5). The method developed quantitatively and consistently produced acceptable recoveries for freshly-spiked samples with only a 5-min dynamic extraction. Greater than 100% recovery may be attributable to evaporation of the solvent, acetone, during the transfer and preparation of samples for analysis. TCP was not extractable under these conditions. This result compares well to that reported previously for chlorpyrifos extracted from grass (98% with 10% methanol modifier) [26] although no modifier was added. The residual moisture contained in the air-dried compost may have acted as an effective modifier in this case.

3.2. Effect of water on chlorpyrifos recovery

Results for the effect of moisture on extraction efficiency of chlorpyrifos are presented in Table 3. Water (up to 20%, w/w) increased the extraction efficiency over oven-dried compost with the optimum occurring in the air-dried samples containing 4.5% moisture. An increase in the average percent recovery from 83 at 0% moisture to 104 at 4.5% moisture was observed. In addition, percent recoveries of 99 and 99 were obtained at 10 and 20% moisture levels, respectively. Fig. 1A shows a GC–FID chromatogram from a compost extract spiked at 100 μg chlorpyrifos per gram dry-weight with 20% moisture. Excessive water drastically reduced recovery with the lowest value obtained at the highest moisture content (24% at 40% moisture). The high recoveries obtained for moisture levels up to 20% could be due to the fact that some amount of water serves as a modifier to the supercritical CO_2 thus increasing the solubility of the analyte or disrupting matrix–analyte interactions [26]. As the water content increased two phases were probably formed resulting in mass transfer constraints. No plugging of the heated variable restrictor was observed even at 40% moisture. The mass balance, or total recovery, which is a combination of the supercritical CO_2 extracted and residual chlorpyrifos, showed that chlorpyrifos was not hydrolyzed to TCP under the extraction conditions. Again, greater than 100% recovery may be attributable to evaporation of solvent, acetone, during preparation of samples for analysis.

3.3. Effect of ageing on chlorpyrifos recovery

Composting allows time for pollutants to become more strongly sorbed, and even become incorporated into the compost/soil matrix. Chlorpyrifos is strong-

Table 3
Effect of moisture on the extraction efficiency of chlorpyrifos from compost (spiking level was 100 ppm, n=2 except at 0.0% moisture where n=3)

Moisture content (%)	Recovery (%)		
	Supercritical fluid extracted chlorpyrifos	Residual chlorpyrifos	Mass balance
0.0	83±17	30±14	112±7
4.5	104±1	7±1	111±0
10.0	99±1	14±3	113±4
20.0	99±3	14±0	113±3
30.0	57±15	52±3	109±12
40.0	24±1	91±3	115±2

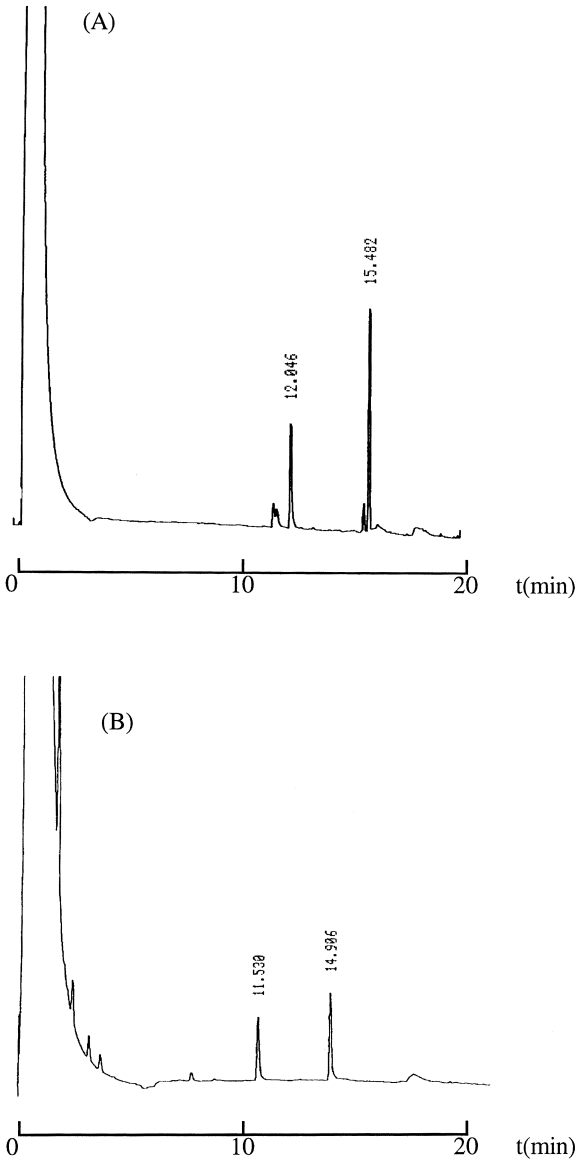

Fig. 1. GC–FID chromatograms of supercritical CO_2 extracts of compost spiked with (A) 100 ppm chlorpyrifos with TBP as the internal standard and (B) 53.5 ppm chlorpyrifos and 57.3 ppm TCP with BSTFA added. Identification by retention times: chlorpyrifos 15 min; TBP 12 min; and TCP derivative 11 min.

ly bound to the organic matter in soil [33]. Table 4 shows results for the effect that ageing has on the extraction efficiency of chlorpyrifos from residential compost. Reduction in recovery from 102% on the day of dosing to 52% on the tenth day was observed.

Table 4
Effect of ageing on the extraction efficiency of chlorpyrifos from compost (spiking level was 100 ppm, $n=2$)

Day	Recovery (%)		
	Supercritical fluid extracted chlorpyrifos	Residual chlorpyrifos	Mass balance
0	102±3	6.8±0.2	109±2
1	81±2	26±2	107±4
2	80±14	37±13	117±0
3	72±28	39±22	111±6
4	75±4	37±6	112±3
10	52±2	54±0	106±1

Significant evaporative losses of chlorpyrifos occur from soil [33] so the potential for this was minimized by keeping the spiked samples in tightly sealed sample vials. Similar reports for sample ageing studies in soil show significantly lower recoveries over time as compounds are degraded or more strongly bound to organic matter in the matrix [26,29]. Since compost is typically higher in organic matter than soil, the effects may be greater in compost. It is clear that more severe extraction conditions would be required to quantitatively extract native compost samples contaminated with chlorpyrifos. The addition of modifiers in addition to residual moisture in air-dried samples may also be required. The mass balance results shown in Table 4 show that chlorpyrifos did not hydrolyze or degrade significantly during the 10-day ageing period. A 30-min sonicated extraction with acetone was able to recover essentially all of the residual chlorpyrifos from the supercritical CO_2-extracted sample.

3.4. Extraction of chlorpyrifos and TCP simultaneously from compost

The results of chlorpyrifos and TCP in the simultaneous extraction procedure gave mean recoveries of 94±3% for TCP and 106±7% for chlorpyrifos ($n=6$). The samples had to be analyzed within 1 h of extraction due to the instability of the derivatized TCP in the recovery solvent. Fig. 1B shows a GC–FID chromatogram from an extract of compost spiked at 53.5 μg of chlorpyrifos and 57.3 μg of TCP per gram dry mass. Addition of excess BSTFA immediately before analysis to degraded samples restored the signal to the level obtained

immediately after extraction. Water in the samples, resulting from co-extraction of the residual moisture, may compete with TCP for derivatizing reagent in the sample. A modifier other than methanol used with a dry sample would be needed to alleviate this problem. The extraction time was increased by 7 min, 2 min static time was added at the beginning of the cycle to allow the derivatization to occur and the dynamic extraction time was increased by 5 min to allow for complete extraction of the TCP derivative. No TCP could be detected in samples extracted without the addition of BSTFA.

4. Conclusions

The amount of moisture in the sample greatly affected recovery of chlorpyrifos. A small amount of water in the compost (up to 20% w/w) acted as a modifier to improve analyte recovery. Since compost typically contains 40–60% (w/w) moisture, air-drying is necessary prior to extraction although the effectiveness of drying agents was not investigated. As the compost samples aged, extraction efficiency was reduced for chlorpyrifos. Increasing the extraction time, increasing temperature, and the use of polar organic modifiers may result in greater extraction efficiencies for aged samples. A method was developed for the simultaneous extraction of chlorpyrifos and its primary degradate, TCP, from garden waste compost. In-situ derivatization and supercritical fluid extraction were successful, along with NaCl as packing material, to quantitatively extract the analytes in a simple and rapid technique that produced a sample ready for direct injection onto GC–FID. Neither chlorpyrifos nor TCP derivative were detected in any of the liquid trap samples indicating that efficient trapping was achieved in all extractions with the solid Tenax trap. The results of this study indicate that supercritical fluid extraction has the potential to provide a promising alternative for the analysis of organic contaminants in compost.

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References

[1] M. Renkow, A.R. Rubin, J. Environ. Mgmt. 53 (1998) 339–347.
[2] I. Déportes, J. Benoit-Guyod, D. Zmirou, Sci. Total Environ. 172 (1995) 197–222.
[3] A.M. Fogarty, O.H. Tuovinen, Microbiol. Rev. 55 (1991) 225–233.
[4] C.R. Lemmon, H.M. Pylypiw Jr., Bull. Environ. Contam. Toxicol. 48 (1992) 409–415.
[5] B.D. Eitzer, W.A. IannucciBerger, G. Mark, C. Zito, Bull. Environ. Contam. Toxicol. 58 (1997) 953–960.
[6] J. Chwastowska, K. Skalmowski, Int. J. Environ. Anal. Chem. 68 (1997) 13–24.
[7] P.B. Woodbury, V.T. Breslin, Biomass Bioenerg. 3 (1992) 213–225.
[8] J.W.A. Lustenhouwer, J.A. Hin, F.J.M.J. Maessen, G. Denboef, Int. J. Environ. Anal. Chem. 39 (1990) 209–222.
[9] G.L.F. Cater, Chemosphere 37 (1998) 1073–1077.
[10] A. Gomez, Trends Anal. Chem. 17 (1998) 310–314.
[11] D.A. Kovacic, R.A. Cahill, T.J. Bicki, Environ. Sci. Technol. 26 (1992) 38–41.
[12] T.A. Malloy, T.D. Goldfarb, M.T.J. Surico, Chemosphere 27 (1993) 325–334.
[13] J.F. Joyce, C. Sato, R. Cardenas, R.Y. Surampalli, Water Environ. Res. 70 (1998) 356–361.
[14] J.E. Rechcigl, H.C. MacKinnon (Eds.), Agricultural Uses of By-Products and Wastes (ACS Symposium Series, No. 668), American Chemical Society, Washington, DC, 1997.
[15] A.S. Jarvis, V.A. McFarland, M.E. Honeycutt, Ecotoxicol. Environ. Saf. 39 (1998) 131–135.
[16] M.D. Webber, H.R. Rogers, C.D. Watts, A.B.A. Boxall, R.D. Davis, R. Scoffin, Total Environ. 185 (1996) 27–44.
[17] D.H. Kim, G.S. Heo, D.W. Lee, J. Chromatogr. A 824 (1998) 63–70.
[18] T.M. Fahmy, M.E. Paulaitis, D.M. Johnson, M.P. McNally, Anal. Chem. 65 (1993) 1462–1469.
[19] K. Wuchner, R.T. Ghijsen, U.A.Th. Brinkman, R. Grob, J. Mathieu, Analyst 118 (1993) 11–16.
[20] G. Martinez, C.-H. Ho, W.H. Griest, Anal. Lett. 28 (1995) 1499–1511.
[21] S.B. Hawthorne, D.J. Miller, Anal. Chem. 66 (1994) 4005–4012.
[22] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, J. Pawliszyn, Anal. Chem. 67 (1995) 1727–1736.
[23] N. Alexandrou, M.J. Lawrence, J. Pawliszyn, Anal. Chem. 64 (1992) 301–311.
[24] J.W. Hills, H.H. Hill Jr., Anal. Chem. 63 (1991) 2152–2155.
[25] S.B. Hawthorne, D.J. Miller, D.E. Nivens, D.C. White, Anal. Chem. 64 (1992) 405–412.
[26] S. BØwadt, S.B. Hawthorne, J. Chromatogr. A 703 (1995) 549–571.

[27] J.L. Snyder, R.L. Grob, M.E. McNally, T.S. Oostdyk, J. Chromatogr. Sci. 31 (1993) 183–191.
[28] V. Camel, M. Caude, A. Tambute, J. Chromatogr. Sci. 33 (1995) 123–132.
[29] M.D. Burford, S.B. Hawthorne, D.J. Miller, Anal. Chem. 65 (1993) 1497–1505.
[30] V. Camel, A. Tambute, M. Caude, J. Chromatogr. A 693 (1995) 101–111.
[31] Y.-C. Ling, J.-H. Liao, J. Chromatogr. A 754 (1996) 285–294.
[32] K.D. Racke, A.R. Leslie (Eds.), Pesticides in Urban Environments (ACS Symposium Series, No. 522), American Chemical Society, Washington, DC, 1993.
[33] K.D. Racke, Rev. Environ. Contam. Toxicol. 131 (1993) 1–154.
[34] H.J. Cortes, L.S. Green, R.M. Campbell, Anal. Chem. 63 (1991) 2719–2724.
[35] V. Lopez-Avila, N.S. Dodhiwala, J. Chromatogr. Sci. 28 (1990) 468–476.
[36] Y.T. Huang, J.H. Yen, Y.S. Wang, Anal. Sci. 13 (Suppl. S) (1997) 137–140.
[37] C. Nerín, R. Batlle, J. Cacho, J. Chromatogr. A 795 (1998) 117–124.
[38] M.M. Jiménez-Carmona, J.J. Manclús, A. Montoya, M.D. Luque de Castro, J. Chromatogr. A 785 (1997) 329–336.