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Journal of Chromatography A, 1084 (2005) 194–200
JOURNAL OF CHROMATOGRAPHY A
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On-line coupled extraction and separation using superheated water for the analysis of triazine herbicides in spiked compost samples

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Available online 5 November 2004

Abstract

An on-line method, with a purely aqueous mobile phase, has employed linked superheated water extraction and superheated water separation for the analysis of triazine herbicides in spiked compost samples. After the superheated water extraction, a X-Terra solid-phase trap was used to collect and focus the extracted analytes. The trapped analytes were then released by thermal desorption and passed directly to a superheated water chromatographic separation using a PGC column. Two clean-up steps (prior to extraction and separation) were included to remove most of the interfering matrix components. The effects of the sample matrix and the extraction temperatures on the recovery of the triazines were investigated. Despite some thermal degradation of the chloro-triazines during the SWE, the on-line SWE–SWC method was sensitive and rapid. The coupled method could potentially reduce costs and labour and by using only water in every stage is compatible with the concepts of green chemistry.

Keywords: Superheated water extraction; Superheated water chromatography; Chloro-triazines; Thiomethyl-triazines; Compost; Thermal desorption; Thermal degradation

1. Introduction

In the last few years, the changes that occur in the physicochemical properties of water at high temperatures under pressure have been exploited in extraction and separation processes. As superheated water has a similar elution strength to a mixture of organic solvent and water, it has been employed as a mobile phase in the reversed-phase liquid chromatography (RP-HPLC) of moderately polar and non-polar analytes [1–5]. In addition to improving the separation process and reducing analysis time, temperature programming can be used to mimic the use of gradient elution in conventional HPLC. Because the solvent strength of water can be varied simply by changing temperature, superheated water extraction (SWE) [6] can be used for a range of applications: including the isolation of organic pollutants, pesticides, natural products, inorganic compounds and the extraction of plant materials and foodstuffs.

The rapid development of SWE has led to the direct combination of this technique with chromatographic methods, usually by using an intermediate solid-phase trap. On-line coupling of SWE with conventional LC [7–10] is straightforward as the extract from the solid-phase trap can be directly eluted to the LC column with a suitable solvent. In the on-line coupling of SWE with gas chromatography [11,12], the trap must be dried with a gas flow, after which the analytes are eluted with a suitable organic solvent. However, on-line SWE–GC using a membrane unit as the interface [13] enabled the extract to be directly transferred to the chromatograph.

Even though the results obtained by all these on-line coupled systems showed that they worked well, they still required a significant volume of organic solvent in the preconcentration and/or assay stages. As an alternative, Bone and Smith [14] demonstrated that a superheated water extract could be trapped from a water carrier flow onto a cooled solid-phase extraction (SPE) cartridge, and then released as a concentrated solution, by using the same water flow, simply by rapidly raising the temperature of the trap. A solvent-free direct coupling of SWE–SWC should thus be possible.

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doi:10.1016/j.chroma.2004.10.034

Young et al. [15] first reported the use of only water in a coupled method by interfacing SWE with WRP-LC (water-only reversed liquid chromatography) to separate a series of aromatic analytes. The separations were carried out using a mobile phase of 100% water at room temperature with a very low retentive stationary phase. Unfortunately, the eluent was only sampled at intervals, therefore, most of the extract was not passed to the LC system. In a previous study from this laboratory, superheated water extraction (SWE) directly linked to superheated water chromatography (SWC) [16] was demonstrated to be a feasible analytical technique for the rapid and reliable qualitative analysis of pharmaceutical compounds from spiked sand samples. Subsequently, Lamm and Yang [17] reported a related off-line coupling system using superheated water for extraction and chromatography, in which the sorbent trap was removed from the extraction apparatus after analyte collection, and then placed in a separate SWC system for desorption and the analysis.

In the present work, the on-line method in this laboratory [16] was further developed for the analysis of five triazine herbicides from a spiked complex compost matrix with the inclusion of clean-up steps. The aim of the study was to demonstrate the feasibility of linking superheated water extraction and trapping directly on-line with superheated water chromatography, so that the complete sample preparation, sample concentration and separation stages of a pesticide extraction from a complex matrix can be carried out in a single sequence using only water as the solvent. The trapping and release and chromatography would be modulated by temperature changes and not as in a conventional system by using different strengths of organic eluents. This would mean that no organic solvents were used in the analysis. All the extract would be carried through to the assay stage in an aqueous mobile phase. This potentially offers considerable potential for easy automation. Two compost samples representing high organic content (100% peat) and lower organic content (up to 60% peat + sand) were compared using the on-line method and conventional solvent extraction.

2. Experimental

2.1. Chemicals and samples

Acetone, acetonitrile and methylene chloride were HPLC grade and were supplied by Fisher Scientific (Loughborough, UK). Deionised water used throughout this work as a mobile phase and extraction solvent was purified via an Elga Maxima HPLC purification unit (Elga Ltd. Wycombe, Bucks, UK). Daytona sand with 40–100 mesh was obtained from Fisher Scientific (Loughborough, UK) and was cleaned using methylene chloride followed by acetone, then was dried in an oven at 100 °C for about an hour.

Atrazine, simazine, propazine, ametryn and terbutryn were analytical grade from Supelco, Bellefonte, USA. Stock solutions (1 mg/mL) of individual standards and standard mixtures were prepared by dissolving pure standards in acetone. Working standard solutions to be used as calibration standards and spiking solutions were made up each week by further dilution of the stock solutions with deionised water. All the solutions were stored at 4 °C. The compost samples used in this study were commercial ericaceous and seed compost mixtures from B&Q (Loughborough, UK).

2.2. Preparation of spiked compost samples

Compost was ground and sieved to a size smaller than 1 mm. Ten grams of the compost was then spiked with the sample mixture (containing 1 mg/mL of each atrazine, simazine, propazine, ametryn and terbutryn) and was thoroughly wet with approximately 30 mL of acetone. The slurries were mixed and shaken carefully for a few minutes to homogenise them and air-dried overnight at room temperature to allow evaporation of the solvent.

2.3. Instrumentation

The on-line coupling system of SWE–SWC (Fig. 1) consisted of three parts: extraction, trapping and separation. A Shimadzu LC-10AD HPLC pump (1) (Shimadzu Corporation, Kyoto, Japan) was employed to pump the water. The water was sonicated for 15 min and de-oxygenated by purging with nitrogen. Samples were injected using a Rheodyne 7125 injection valve (2) with a 20 μL loop.

The first part of the system consisted of a pre-heating coil (P1) (1 m × 0.17 mm i.d. stainless steel tubing) and an extraction cell (EC) (5 cm × 4.6 mm i.d. stainless steel cell fitted with stainless steel frits, 2 μm pore size), placed in a GC oven (oven-1) (series 104, Pye Unicam, Cambridge, UK) controlled by an oven programmer. A stainless steel cooling coil (C1) (1 m × 0.17 mm i.d.) was connected at the outlet of the extraction cell and ran to a second oven (oven-2) (PU 4500 gas chromatograph, Pye Unicam, Cambridge) containing a pre-heating coil (P2) and an unbonded X-Terra (3.5 μm) trapping column (TC) (50 mm × 4.6 mm i.d.) (Waters Corporation, Massachusetts, USA). This exit of the trapping column lead through a second cooling coil (C2) to a third

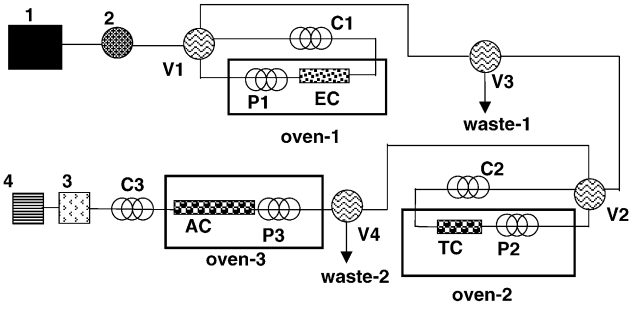

Fig. 1. On-line coupled SWE–SWC system. 1, Water pump; 2, injector; 3, UV detector; 4, back-pressure regulator; EC, extraction cell; TC, X-Terra trap column; AC, PGC analytical column; V1–V4, switching valves; P1–P3, pre-heating coils; C1–C3, cooling coils.

pre-heating coil (P3) and the analytical separation column (AC) (Hypercarb, 100 mm × 2.1 mm i.d.) packed with 5 μm porous graphitic carbon, PGC (Thermo Hypersil-Keystone, Cheshire, UK) mounted in a third GC oven (oven 3) (series 104, Pye Unicam, Cambridge, UK). The final cooling coil (C3) (1 m × 0.17 mm i.d.) was wrapped with a set of copper fins to cool the mobile phase before the Jasco model 875-UV spectrophotometric detector (3) (Jasco, Japan). Two Rheodyne six-port switching valves (V1 and V2) (model 7010) were employed to change flow routes (through or by-pass) for the extraction cell and the trap column, respectively. Another two switching valves l (V3 and V4), were used to switch the flow to waste as required. The system was completed by a Jasco model 880/81 backpressure regulator (4) (Jasco, Tokyo, Japan) maintained at 35 kg cm^{-2}, and a Viglen computer Pentium II with Varian Star software (Viglen Ltd., Middlesex, UK) for data analysis.

2.4. Analytical procedure

The analytical procedure was divided into four steps:

2.4.1. Cold extraction (cold wash)

A 0.5 g of ground, sieved ericaceous compost or 1.0 g of sieved seed compost sample spiked with 20 μg/g of a triazine mixture, was placed in an extraction cell. Firstly, the sample was extracted at ambient temperature by flowing water through the extraction cell at a flow rate of 2 mL/min for about 10 min. Valve-V1 (extraction valve) and valve-V3 were set so that the extracted polar compounds were sent to waste.

2.4.2. Superheated water extraction

The water flow was stopped by switching valve-V1, and the extraction oven was heated to 170 °C. The water was then passed through the extraction cell at 1 mL/min. Valve-V3 was now closed and valve-V2 (trapping valve) was switched to pass the water through the X-Terra trapping column at ambient temperature. Valve-4 was set so that any untrapped components were sent to waste. After 5 min, valve-V1 was set so that the extraction cell was switched out of the water flow and could be cooled to ambient.

2.4.3. Clean-up

The trap oven was then heated up to 60 °C as the water flow continued and was held for 10 min with valve-V4 open so that any highly polar compounds were released to waste.

2.4.4. Superheated water chromatographic separation

Valve-V4 was closed so that the flow from the trap passed to the Hypercarb PGC analytical column. The temperature of the trap column was then increased up to 200 °C to fully release the trapped extract to the analytical column. After 3 min, valve-V2 was closed so that the water flow by-passed the trap and passed directly to the analytical column as the eluent. The released extract was focussed on the analytical column and was immediately assayed using a temperature gradient from 170 to 250 °C, at 10 °C/min (for the seed compost sample) or from 130 to 160 °C at 2 °C/min and up to 220 °C at 5 °C/min (for the ericaceous compost sample) and the components were detected at 222 nm.

2.5. Solvent extraction

Approximately, 5.0 g of spiked compost was placed inside a centrifuge tube and 15 mL of acetone was added. The mixture was shaken vigorously for 5 min and sonicated for 30 min. The suspension was then centrifuged at 3000 rpm for 10 min. The clear supernatant solvent was separated by filtration and evaporated in a water bath at 50 °C. Finally, the dry residue was reconstituted in 0.5 mL of acetonitrile. Ten microliters of the solution was assayed by direct injection onto the PGC analytical column and the triazines were separated using the same temperature gradient as in 2.4.4.

3. Results and discussion

The aim was to develop an overall system, which would use a single pump and a water only eluent for superheated water extraction/chromatography. The water would extract the analytes from the sample matrix, and would pass the extract to a trapping column, which would focus the extract before it was released thermally onto the analytical separation column. The release of the extract at each stage would be controlled by changing the temperature and thus the elution strength of the water. The first part of the study was to develop superheated water separation conditions, which would then be used to assess the operation of the components of the coupled system.

3.1. Superheated water chromatography of triazines

Polymer, silica and porous graphitic carbon (PGC)-based columns were investigated to separate the five structurally related triazines (atrazine, simazine, propazine, ametryn, and terbutryn) (Fig. 2) with superheated water as the mobile phase. Although thermally stable, the polystyrene divinylbenzene (PS-DVB) column failed to fully resolve the triazines. An Amide C_{16} bonded silica and unbonded X-Terra columns could also not resolve the ametryn and propazine peaks. The Amide C_{16} column also degraded at high temperatures. The Hypercarb PGC column was the most suitable as it was stable up to 220 °C and gave good selectivity for the structurally-related triazines. A temperature gradient, from 170 to 250 °C at 10 °C/min, enabled all five compounds to be resolved (Fig. 3A), whereas in an isothermal separation at 245 °C the first three compounds coeluted. However, the PGC column was susceptible to contamination from matrix components, which resulted in changes in the retention of the peaks. As a result in some separations the initial temperature and the temperature gradient had to be altered to maintain the resolution.

Compounds	Substituents		
	R1	R2	R3
Simazine	Cl	NHC_2H_5	NHC_2H_5
Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$
Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$
Ametryn	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$
Terbutryn	SCH_3	NHC_2H_5	$NHC(CH_3)_3$

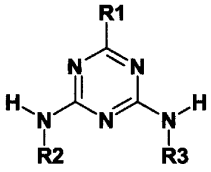

Fig. 2. Structures of triazines.

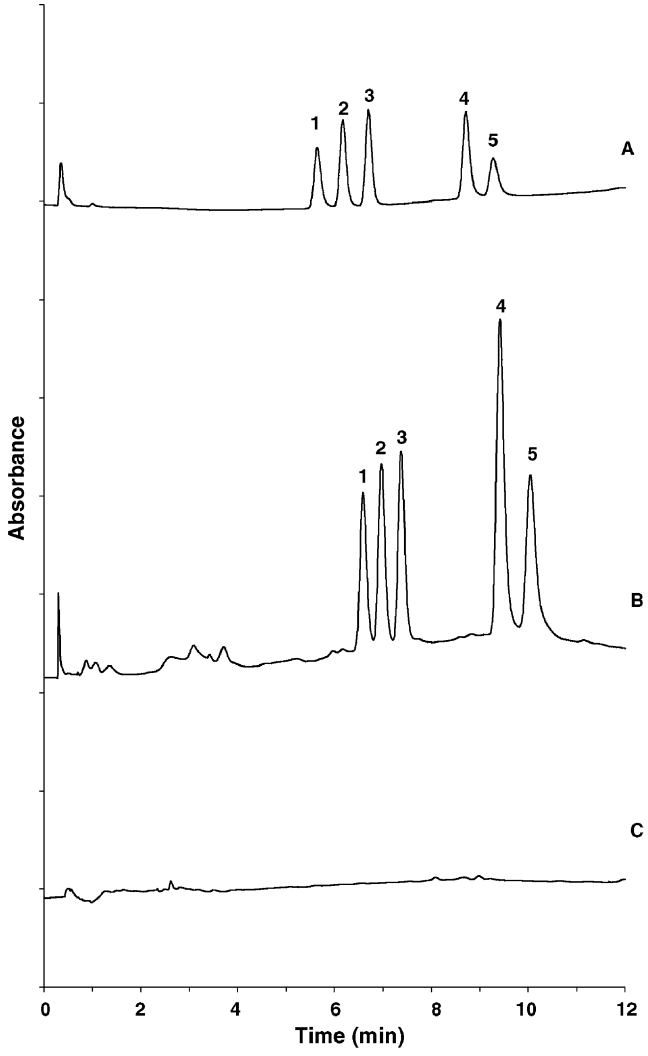

Fig. 3. Chromatograms of triazines by (A) direct injection onto the separation column, and extracted from (B) 0.1 g spiked seed compost and (C) non-spiked seed compost, at 170 °C for 5 min. Experimental conditions: analytical column: PGC (100 mm × 2.1 mm i.d.) at temperature gradient from 170 to 250 °C at 10 °C/min, mobile phase, 100% water; flow rate, 1.0 mL/min. Peaks: 1, propazine; 2, atrazine; 3, simazine; 4, ametryn; 5, terbutryn.

The order of elution, on the alkyl-bonded silica based columns, of simazine, atrazine, ametryn, propazine and terbutryn was governed mainly by their size and hydrophobicity and was very different from that on the PGC column, propazine, atrazine, simazine, ametryn and terbutryn. On this column the order was in decreasing order of steric interference and hence reflected the ability of the analyte to establish a planar configuration on the PGC surface.

3.2. Trapping and thermal desorption

The separation on the PGC column was then used to monitor the trapping and extraction conditions. To concentrate and focus the extract, the dilute aqueous solution from the extraction was cooled and passed through a solid-phase trap at ambient temperature. The intention was that by using the same flow of water, the analytes could then be released for analysis in a small volume by rapidly raising the temperature of the trap.

In trial experiments to find a suitable sorbent for the trap, 10 μL of a 25 μg/mL standard solution of the triazine mixture were directly injected onto the trap column. Initially, a PGC column was examined, however, although it efficiently trapped the triazines, its high retentivity meant that high temperatures (>200 °C) were required to release the trapped triazines and as a result, the chloro-triazines tended to decompose. A Hypersil ODS trap was examined as it should be less retentive but terbutryn was still retained at 150 °C and this temperature would cause rapid degradation of the trap silica material.

An unbonded X-Terra hybrid silica column was then examined, which is effectively a partially methyl bonded silica, as this should have a lower retentivity and good thermal stability. Although a higher temperature of 200 °C was required to thermally desorb all the triazines, the elution was complete in 3 min and this short exposure did not appear to damage the trapping material. On injection of the triazine mixture in a water stream passing through the trap all the compounds were retained at ambient temperature. Desorption into the flowing mobile phase at 180 °C (Fig. 4A) released only atrazine and simazine and a temperature of 200 °C was need to release propazine, ametryn and terbutryn (Fig. 4B). The high temperature required to release propazine, confirmed that the interaction of the analytes with the X-Terra column was primarily according to their hydrophobicity, but the lower retention of this compound than the other two chloro-triazines on the PGC column reflected its lack of planarity. A direct comparison of the separation after a direct injection onto the PGC column and following trapping and thermal release onto the column showed that no measurable losses were occurring.

It was thought that decomposition of the chloro-triazines was not observed because the heating was carried out ballistically over a period of about 2 min and they would have been swept out of the trap at lower temperatures before reaching their degradation temperatures. A final 3 min high temperature period was used to clean the trap. To increase its lifetime,

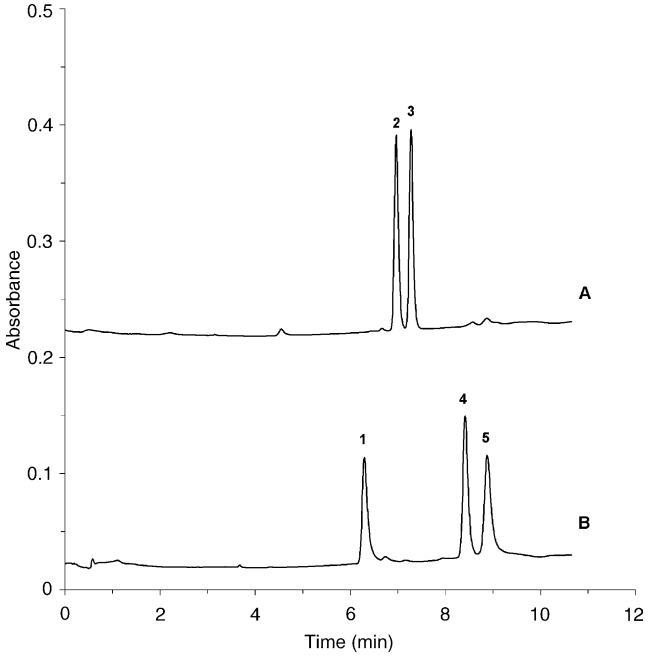

Fig. 4. Chromatograms showing the separation of the triazines released from X-Terra trap in dynamic mode at (A) 180 °C and (B) 200 °C, separated on PGC (100 mm × 2.1 mm i.d.) analytical column with gradient temperature from 160 to 260 °C, 15 °C/min. Experimental conditions: mobile phase, 100% water; flow rate, 1.0 mL/min: detection, 222 nm. Peaks: 1, propazine; 2, atrazine; 3, simazine; 4, ametryn; 5, terbutryn.

it was then switched out of the water flow and cooled to ambient temperature, while the chromatographic separation was taking place.

3.3. Superheated water extraction

The study then examined the extraction of the triazines from spiked composts, as model soils, to determine the effect of potential interferences from organic components in the sample matrix. Two sample matrices were examined, the first was a seed compost, which consisted of a mixture of 60% peat and ground limestone with sand, representing a matrix with a moderate lower organic content. The second matrix material was an ericaceous compost comprising 100% peat, representing an acidic matrix with a high organic level. Previous work by Curren and King [18] has shown that the triazines were readily soluble in superheated water and that the solubility increased three-fold for each 25 °C rise in temperature. They found that the triazines were stable over the temperature range (up to 125 °C) examined.

To determine the optimum extraction temperature, atrazine, simazine, propazine, ametryn, and terbutryn were spiked onto samples of a seed compost mixture at a rate of 20 μg/g. On extraction with superheated water, the recovery of the triazines was poor at temperatures lower than 100 °C, especially for the thiomethyl-triazines (ametryn and terbutryn). The extraction of the chloro-triazines improved as the temperature was increased up to 60–63% at 170 °C but the recoveries decreased to 15–18% at 210 °C. The recovery of the thiomethyl-triazines over this temperature range was higher (102–108%), except for an anomalous result of 144% for terbutryn at 210 °C. This was subsequently attributed to a co-eluting peak originating from the compost. A solvent extraction of the triazines from spiked seed compost with acetone followed by analysis using superheated water chromatography gave recoveries of 81–93%. The superheated water extractions were carried out for 5 min as longer periods led to an increase in the amount of background material being extracted. Therefore, an extraction temperature of 170 °C for 5 min was selected for future work as this gave a clean chromatogram (Fig. 3B) very similar to a direct injection of the standards (Fig. 3A). A blank extraction of the seed compost (Fig. 3C) suggested that there was little problem with interferences.

The study then examined the extraction of ericaceous compost spiked at the same level. However, it was found that the performance of the PGC analytical column rapidly deteriorated and it needed frequent cleaning to maintain the resolution and retention of the separation on the PGC column. This suggested that polar components were being carried from the extraction though the trap column and were contaminating the surface of the stationary phase. The chromatograms from these extracts were complex and the triazine peaks were largely obscured. The high level of co-extractives was confirmed in direct extraction studies, when the extracts from the ericaceous compost were dark brown in colour and dirtier in contrast with the light yellow extracts from seed compost. An initial ambient temperature wash of the compost matrix with water at 2 mL/min for 10 min was then included in the procedure. The wash water was passed directly to waste through valve V3 to avoid contaminating the trap or the analytical column. After the wash period, the flow was switched back to the trap column and the temperature increased to carry out the extraction. During this period of extraction, the effluent from the trap column was passed to waste through V4 so that any polar analytes, that were not retained on the X-Terra trap, were also discarded and were not transferred to the analytical column. These wash steps considerably reduced the level of interferences but the chromatogram was still complex (Fig. 5) although interferences at the start of the chromatogram had been reduced. However, many less polar peaks were still present, representing compounds, which had been retained on the trap column. As the triazines were not released at trap temperature below 100 °C, a fractional release of the polar components from the trap was examined. The trap was first raised to 60 °C and 1 mL/min of warm water was washed through for 10 min and passed to waste through switching valve V4. Without this non-polar wash, the extract of the spiked ericaceous compost had a pH of 3.8 compared to pH 4.8 after washing, indicating that the mild conditions were removing humic acids, which had remained in the sample extract. The waste valve V4 was then closed and the eluent was passed directly to the analytical column. The trap temperature raised to 200 °C and the eluate was assayed using a slower

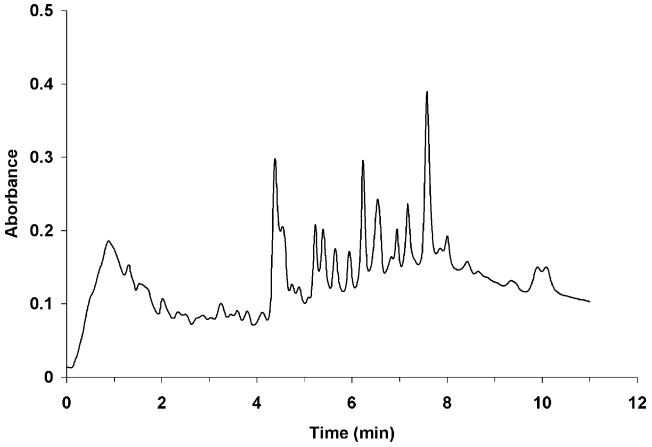

Fig. 5. On-line SWE–SWC chromatograms of the extract from spiked ericaceous compost, after the polar wash. Experimental conditions: analytical column, PGC (100 mm × 2.1 mm i.d.) with gradient temperature from 160 to 260 °C at 15 °C/min; mobile phase, 100% water; flow rate, 1.3 mL/min; detection, 222 nm.

temperature gradient to increase the resolution (Fig. 6B). It gave a similar triazine profile to a standard sample (Fig. 6A). However, there was a significant rising background during the chromatogram, which was also found in an extract from an unspiked ericaceous compost sample (Fig. 6C).

3.4. Quantitative analysis

Direct injection of each of the triazines onto a cleaned PGC column with superheated water chromatography gave linear responses (r^2 = 0.992–0.997) from 5 to 50 μg/mL. However, on repeating the calibration on a column that had been used for separating extracts the correlation coefficient for terbutryn dropped to 0.9085, the other triazines still gave good correlations. These were then used to determine the reproducibility of the extractions by the SHWE–SHWC method using spiked seed compost samples at five different concentrations from 3 to 15 μg/g. Good correlation coefficients (r^2 = 0.992–0.997) were obtained for the triazines, except for terbutryn (r^2 = 0.9373). Based on these values the limit of detection (LOD) for the triazines was 1–1.4 μg/g except for terbutryn, which was 2.4 μg/g. However, it was difficult to obtain reasonable comparable correlation curves or quantitative results from spiked ericaceous compost because the analytical column was rapidly contaminated.

Because the recovery from soil is often dependent on the nature and organic content, a study was then carried out to compare the recovery of the triazine from seed and ericaceous composts spiked at the 20 μg/g level (Table 1). The recoveries of the triazines from the ericaceous compost were lower in each case than from the seed compost and the reproducibility was poorer. These lower recoveries can be probably attributed to the higher organic content, as reported earlier [19]. The interfering background signals from this compost (Fig. 6) were probably major contributors to the poorer reproducibility.

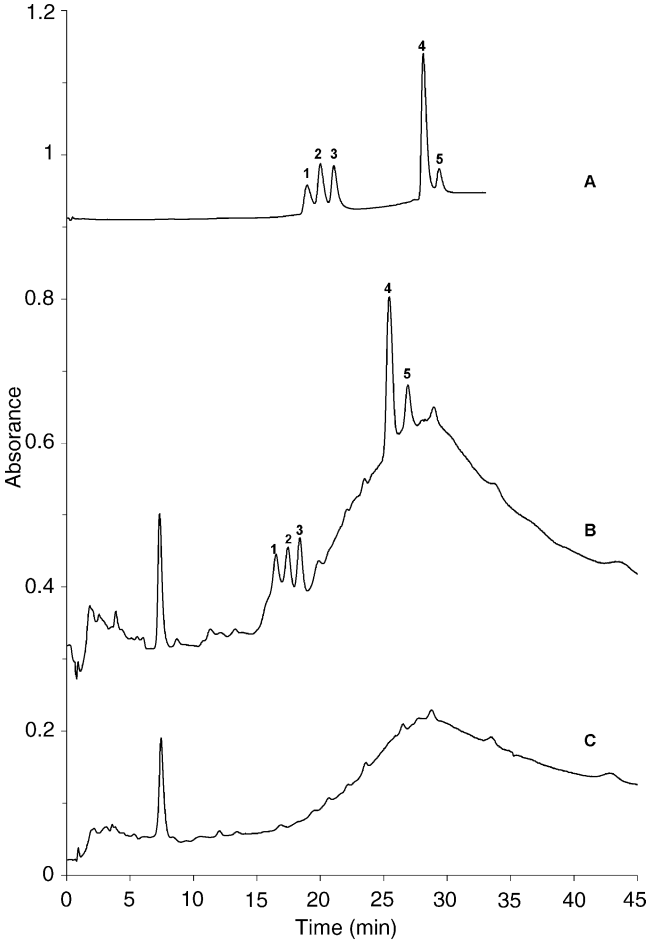

Fig. 6. Chromatograms of triazines by (A) direct injection onto the separation column, and extracted from (B) 0.5 g spiked ericaceous compost and (C) non-spiked compost, at 170 °C for 5 min. Experimental conditions: analytical column: PGC (100 mm × 2.1 mm i.d.) with gradient temperature from 130 to 160 °C at 2 °C/min and up to 220 °C at 5 °C/min; mobile phase, water; flow rate, 0.9 mL/min; detection, 222 nm. Peaks: 1, promazine; 2, atrazine; 3, simazine; 4, ametryn; 5, terbutryn.

The degradation of the chloro-triazines at elevated temperatures and hence generally poorer recoveries had been expected. In previous work McGowin et al. [20] reported that the recoveries of chlorine-containing triazines, such as atrazine and propazine, decreased significantly when the extraction temperature was raised from 110 to 250 °C, whereas the recovery of the thiomethyl-triazine, ametryn was less affected.

Table 1
Recoveries of triazines spiked at 20 μg/g onto seed and ericaceous compost using extraction with water at 170 °C

Triazine	% Recovery (% R.S.D.)	
	Seed compost (n = 5)	Ericaceous compost (n = 3)
Propazine	60 (5.8)	52 (25)
Atrazine	60 (8.2)	32 (16)
Simazine	63 (10.9)	25 (11)
Ametryn	102 (5.1)	78 (12)
Terbutryn	103 (10.5)	75 (16)

4. Conclusions

An on-line coupled system of superheated water extraction (SWE) with superheated water chromatography (SWC) has been successfully constructed by using switching valves and a solid-phase trap as the interface between the extractor and the chromatograph. The further development of this on-line SWE–SWC with the inclusion of clean-up steps (polar and non-polar washes) enabled the quantitative analysis of triazine herbicides (atrazine, simazine, propazine, ametryn, and terbutryn) from complicated sample matrices in a closed system. This eliminated the manual sample pretreatment procedure that is often time consuming, environmentally unfriendly and liable to generate errors. With the clean-up steps, the amount of co-extracted material from sample matrix was minimised, thus, background interference was minimised in the chromatogram so that the quantitation became easier and more reliable. Because the chloro-triazines are thermally labile compounds, they tended to decompose at high temperatures. However, despite the thermal degradation of the chloro-triazines, the seed compost, with lower organic content, produced a good chromatogram with less background interference and gave better recoveries and repeatability, compared to those obtained from ericaceous compost.

The advantage of this approach is that all the herbicide in the sample is conducted to the analysis column. However, it limits the amount of sample clean up that can be carried out and as seen from the ericaceous compost, co-extractives can cause problems of interferences and degradation of the analytical column. On the whole, apart from being environmentally friendly and saving costs, this on-line SWE–SWC is a convenient method because it is fast, sensitive and the method requires less manual work and smaller samples. In addition, it is possible to automate the method for multi-analyte analysis and high sample throughput.

Acknowledgement

The authors thank University of Technology Mara, Malaysia for financial support to R. Tajuddin.

References

[1] R.M. Smith, R.J. Burgess, O. Chienthavorn, J.R. Stuttard, LC-GC Int. 12 (1999) 30.
[2] R.M. Smith, R.J. Burgess, Anal. Commun. 33 (1996) 327.
[3] R.M. Smith, R.J. Burgess, J. Chromatogr. A 785 (1997) 49.
[4] S.M. Fields, C.Q. Ye, D.D. Zhang, B.R. Branch, X.J. Zhang, N. Okafo, J. Chromatogr. A 913 (2001) 197.
[5] D.J. Miller, S.B. Hawthorne, Anal. Chem. 69 (1997) 623.
[6] R.M. Smith, J. Chromatogr. A 975 (2002) 31.
[7] C. Crescenzi, A. Di Corcia, M. Nazzari, R. Samperi, Anal. Chem. 72 (2000) 3050.
[8] B. Li, Y. Yang, Y. Gan, C.D. Eaton, P. He, A.D. Jones, J. Chromatogr. A 873 (2000) 175.
[9] J.L. Luque-Garcia, M.D. Luque de Castro, J. Chromatogr. A 959 (2002) 25.
[10] M.C. Herrera, R.C. Prados-Rosales, J.L. Luque-Garcia, M.D. Luque de Castro, Anal. Chim. Acta 463 (2002) 189.
[11] K. Kuosmanen, T. Hyötylainen, K. Hartonen, M.L. Riekkola, J. Chromatogr. A 943 (2002) 113.
[12] T. Hyötylainen, T. Anderson, K. Hartonen, K. Kuosmanen, M.L. Riekkola, Anal. Chem. 72 (2000) 3070.
[13] T. Hyötylainen, M.L. Riekkola, LC-GC Europe 15 (2002) 298.
[14] J.R. Bone, R.M. Smith, Anal. Commun. 36 (1999) 375.
[15] T.E. Young, S.T. Ecker, R.E. Synovec, N.T. Hawley, J.P. Lomber, C.M. Wai, Talanta 45 (1998) 1189.
[16] R. Tajuddin, R.M. Smith, Analyst 127 (2002) 883.
[17] L.J. Lamm, Y. Yang, Anal. Chem. 75 (2003) 2237.
[18] M.S. Curren, J.W. King, Anal. Chem. 73 (2001) 740.
[19] P.J. Donerty, G.F. Warren, Weed Res. 9 (1969) 20.
[20] A.E. McGowin, K.K. Adom, A.K. Obubuafo, Chemosphere 45 (2001) 857.