Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1000 (2003) 299–309
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Multi-residue screening of pesticides in vegetables, fruits and baby food by stir bar sorptive extraction–thermal desorption–capillary gas chromatography–mass spectrometry

Pat Sandra[a,b,c,*], Bart Tienpont[b], Frank David[a]

[a]*Research Institute for Chromatography, Kennedypark 20, B-8500 Kortrijk, Belgium*
[b]*Laboratory of Organic Chemistry, University of Ghent, Krijgslaan 281 S4, B-9000 Ghent, Belgium*
[c]*Department of Chemistry, CENSSUS, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa*

Abstract

The performance of stir bar sorptive extraction (SBSE) for the enrichment of pesticides from vegetables, fruits and baby food samples is discussed. After extraction with methanol, an aliquot is diluted with water and SBSE is performed for 60 min. By applying a new thermal desorption unit (TDU), fully automated and unattended desorption of 98 stir bars is feasible, making SBSE very cost-effective. The presence of pesticide residues is elucidated with the retention time locked gas chromatography–mass spectroscopy method (RTL-capillary GC–MS). With SBSE–RTL-capillary GC–MS operated in the scan mode, more than 300 pesticides can be monitored in vegetables, fruits and baby food. The multi-residue method (MRM) described provides detectabilities from the mg/kg (ppm) to the sub-μg/kg (ppb) level, thereby complying with the maximum residue levels (MRLs) set by regulatory organizations for pesticides in different matrices. Several examples, i.e. pesticide residues in lettuce, pears, grapes and baby food, illustrate the potential of SBSE–RTL-capillary GC–MS.

Keywords: Stir bar sorptive extraction; Retention time locking; Vegetables; Fruit; Baby food; Multi-residue analysis; Pesticides

1. Introduction

In recent years, regulatory agencies have emphasized more and more the need for the development and use of analytical methods able to determine, in food products, as many residues as possible from the many insecticides, fungicides and other compounds applied in agricultural practice. At present, single residue methods (SRMs), i.e. the determination of one pesticide, e.g. chlormequat, or selective residue methods (sMRMs), i.e. the determination of a relatively small number of chemically related compounds, e.g. *N*-methylcarbamate insecticides, are intensively applied for pesticide residue determinations in a large number of samples, the pesticide treatment history of which is known. The use of SRM and sMRM methods will continue, but the development and use of multi-residue methods (MRMs), i.e. the determination of as many pesticides as possible with only one sample preparation method and one chromatographic technique, is needed to analyze samples with an unknown or doubtful pesticide treatment history.

*Corresponding author. Research Institute for Chromatography, Kennedypark 20, B-8500 Kortrijk, Belgium. Tel.: +32-56-204-031; fax: +32-56-204-859.
E-mail address: pat.sandra@richrom.com (P. Sandra).

0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00508-9

A single chromatographic technique cannot monitor the currently used 800 and almost 600 superceded pesticides (herbicides, fungicides, insecticides, araricides, nematicides, growth regulators, synergists, etc.) as listed in *The Pesticide Manual* [1], and the application of both GC and HPLC is mandatory. Half of the currently used pesticides are, however, amenable to capillary GC analysis and by replacing the classical selective detection methods by the universal and specific mass spectrometer, many classes of pesticides can be analyzed in a single run. Moreover, the need for confirmation of positive samples by a secondary technique becomes obsolete and the MS has the sensitivity required for residue analysis.

A variety of capillary GC–MS-based multi-residue methods have been developed. For example, working group 4 of the Technical Committee (TC 275) of the European Committee for Standardization (CEN) provides information on five multi-residue methods for non-fatty foods (EN 1528:1996) [2]. All methods require extraction with organic solvents such as acetone [3–5] acetonitrile [6] and ethylacetate [7]; with the exception of Ref. [7], they all require partitioning into a solvent mixture, and further clean-up by column chromatography or gel permeation chromatography (GPC) is advised. The multi-residue capillary GC–MS method that was applied in our laboratory until the application of the Twister described in this contribution is a method used by the laboratories of the Dutch Inspectorate for Health Protection [7]. This method is similar to the Luke method [3], but the extraction procedures have been miniaturized to reduce solvent consumption. Recently, Fillion described the analysis of 191 GC-amenable pesticides in fruit and vegetables by capillary GC–MS. The sample preparation comprises extraction with 150 mL acetonitrile, a salting-out step, clean-up by solid-phase extraction on octadecyl and on aminopropyl silica and a concentration step [8].

In the present era of ‘‘green chemistry’’, extraction with large quantities of toxic solvents is difficult to justify for multi-residue determinations of pesticides in foodstuffs and solventless sample preparation techniques should be favored.

Solventless sample preparation techniques based on sorptive extraction have been demonstrated to be good and environmentally friendly alternatives to liquid extraction. The principles and applications of sorptive extraction have recently been reviewed [9]. Solid-phase microextraction (SPME) [10] and stir bar sorptive extraction [11] on polydimethylsiloxane (PDMS) as extraction medium have been applied for the determination of pesticides in aqueous food samples such as drinking water, fruit juices, beverages, etc. Yang et al. [12] applied SPME for the determination of pesticide residues in fruit juice and Boyd-Boland et al. [13] used SPME for the analysis of pesticide residues in water samples. In both cases, PDMS was selected as being the best sorbent. SBSE followed by thermal desorption or liquid desorption was used by Sandra et al. [14] for the analysis of dicarboximide fungicides in wines. The main difference between SPME and SBSE is the much larger quantity of PDMS used in the latter, resulting in very high recoveries.

For multi-residue analysis by capillary GC–MS, important improvements have been made in recent years. Through the features of electronic pneumatic control (EPC), retention time locked libraries (RTLs) for GC-amenable pesticides and endocrine disrupters can be constructed, and by linking the locked retention times to the mass spectral data, hardly any pesticide that is in the library can escape detection and elucidation [15,16]. The Agilent RTL-MS library presently comprises 567 substances. We recently evaluated SBSE as a sample preparation technique for the enrichment of pesticides from aqueous matrices (water and beverages) and came to the conclusion that more than 400 pesticides in the RTL-MS library can be enriched with recoveries complying with the required limits of quantification (LOQs) set by regulatory organizations, e.g. the 0.1 μg/l (ppb) norm for drinking water. The list of pesticides amenable to SBSE enrichment and RTL-capillary GC–MS analysis for solid food samples is somewhat smaller (i.e. ca. 350 pesticides) because of matrix effects in solid samples. The complete pesticide lists for both aqueous (Tables 1–4) and food samples (Tables 3 and 4) can be found on the website www.richrom.com/html/ric_appnotes.html. The lists contain the locked retention times, four qualifier ions for MS confirmation, the $\log P$ values and the theoretical SBSE recoveries on Twisters of 24 and 116 μL. The maximum residue levels (MRLs) set by the European Community (Directives 645/2000 and

466/2001) strongly depend on the nature of the pesticide and the matrix, e.g. 5 mg/kg (ppm) procymidone in grapes and 3 μg/kg (ppb) heptachlor in baby food (SANCO/2075/2002-rev. 2 amending directive 96/5/EC). Applications were selected to illustrate that these MRLs can readily be obtained with the described method. Moreover, the recent introduction of a new desorption unit enabling fully automated analysis of 98 or 196 PDMS-coated stir bars makes the application of this new MRM for pesticide residue screening very cost-effective.

2. Experimental

2.1. Sample preparation

Approximately 15 g of a vegetable, fruit or baby food sample was accurately weighed into a 100 mL flask and 30 mL of methanol (ChromaSolv, Merck, VWR, Leuven, Belgium) was added. The mixture was homogenized using an Ultra Turrax mixer for 5 min and the flask was then placed in an ultrasonic bath for 15 min. A fraction (approx. 10 mL) of the blend was placed in a closed 20 mL vial and centrifuged for 5 min at 5000 rpm. One milliliter of the supernatant methanol phase was placed in a 20 mL headspace vial and 10 mL of HPLC-grade water (ChromaSolv, Merck) was added. A SBSE stir bar (Twister, Gerstel, Müllheim a/d Ruhr, Germany), 10 mm long coated with a 0.5 mm PDMS layer (24 μL), was added and the mixture stirred for 60 min at 1000 rpm. After sampling, the stir bar was removed with tweezers, dipped briefly in bi-distilled water, placed on lint-free tissue to remove residual droplets and finally placed in the liner of a TDU thermal desorption system (Gerstel). For quantification, 5 μL of the appropriate pesticide standard solutions in methanol were added to the sample before Ultra Turrax mixing and ultrasonic treatment. The standard pesticides were obtained from Dr. Ehrenstorfer, Augsburg, Germany.

2.2. Instrumentation

A newly designed TDU thermo-desorption unit from Gerstel (Fig. 1A) was installed on an MPS-2 xyz robot (Gerstel) placed on top of an Agilent 6890 GC (Agilent Technologies, Little Falls, DE, USA) equipped with a CIS-4 programmed temperature vaporization (PTV) injector (Gerstel). The MPS-2

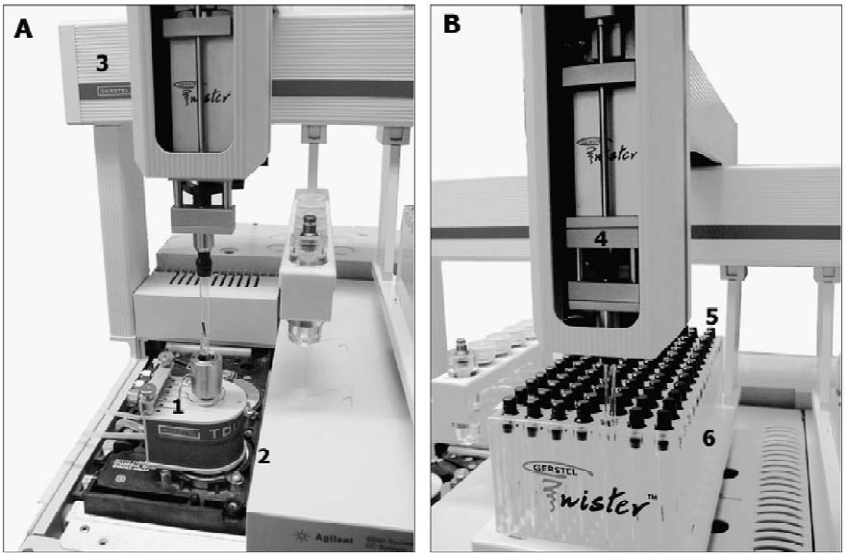

Fig. 1. (A) TDU thermo-desorption unit (1) installed on an Agilent 6890 equipped with a CIS-4 programmed temperature vaporization (PTV) injector (2). Twister tubes are loaded with an MPS-2 xyz robot (3). (B) The MPS-2 is equipped with a Twister holder (4) and a Twister tray (5) containing the liners with Twisters (6).

was equipped with a Twister tray (Fig. 1B) allowing automated and unattended desorption of 98 Twisters.

Splitless thermal desorption was performed by programming the TDU from 40 to 280 °C (5 min) at a rate of 60 °C/min. The analytes were cryo-focused in the PTV at −150 °C with liquid nitrogen prior to injection. An empty baffled liner was used in the PTV injector. For splitless injection (2 min) the PTV was ramped from −150 to 280 °C (2 min) at a rate of 600 °C/min. Capillary GC analysis was performed on a 30 m×250 μm I.D., 0.25 μm d_f HP-5MS column (Agilent Technologies). The oven was programmed from 70 °C (2 min) at 25 °C/min to 150 °C, at 3 °C/min to 200 °C and finally at 8 °C/min to 300 °C. This is the temperature program required for the RTL screener option (Agilent Technologies). Helium was used as carrier gas. The head pressure was calculated using the retention time locking (RTL) software so that *p,p′*-DDT was eluting at a constant retention time of 26.98 min. An Agilent 5973 mass spectrometric detector (MSD) was used in the scan mode (*m/z* 40–500) for all samples. Screening of pesticides was performed using the automatic RTL screener software in combination with the Agilent RTL pesticide library. For the baby food sample, quantitation of piperonyl butoxide was performed using the MSD in the selected-ion monitoring (SIM) mode at *m/z* 176 (quantitation ion) and *m/z* 177, 144 and 178 (confirmation ions). The dwell time was set to 100 ms.

3. Results and discussion

3.1. SBSE–TD-capillary GC–MS analysis of pesticides

Solid samples cannot be extracted directly using stir bar sorptive extraction and a pre-extraction of pesticides in vegetables, fruits or baby food is therefore performed. Acetonitrile, methanol and acetone were evaluated as extraction media and extraction efficiencies for acetonitrile and methanol were very similar, both being more efficient than acetone. Methanol was preferred because it is environmentally more friendly than acetonitrile. Vegetables and fruit samples were homogenized in an Ultra Turrax and 30 mL methanol was added to 15 g of the homogenized sample. Baby food samples were generally pastes and were extracted as such. One milliliter of the methanol extract was then diluted with water to obtain an aqueous matrix before extraction. To the best of our knowledge this is the first enrichment technique described in which dilution is involved. Recoveries of pesticides from aqueous samples by SBSE can be estimated from the octanol–water distribution coefficient ($K_{o/w}$) and the sample–PDMS phase ratio, β [11]. The lists at www.richrom.com/html/ric_appnotes.html contain the $K_{o/w}$ or log *P* values, calculated with a dedicated SRC-KOWWIN software package (Syracuse Research, Syracuse, NY, USA) according to a fragment constant estimation methodology [17] for a wide variety of pesticides. The theoretical SBSE recoveries were calculated for a 10 mL water sample using Twisters containing 24 μL (10 mm L×0.5 mm d_f) and 116 μL PDMS (20 mm L×1.0 mm d_f). A larger PDMS phase volume affects the sorptive enrichment and recoveries are higher for the larger Twister. For variations in PDMS and/or water volume the Twister calculator present on the same website may be applied. For the pesticides listed in Tables 3 and 4 on the website, the stir bar with 24 μL PDMS performs very well and this Twister was applied throughout this work.

The theoretical recoveries represent only indicative values because (i) equilibrium of the solutes between the PDMS coating and the sample is not yet attained after 60 min sampling, (ii) methanol constitutes 10% of the sample and (iii) matrix effects are not taken into consideration. Reaching equilibrium conditions is impractical (several hours) and not stringent as long as sampling conditions are kept constant for calibration. For solutes with log $P > 2.5$ it has been shown that 10% methanol has no influence on recovery [18]. To compensate for matrix effects, quantitation is performed by standard addition (see further). Recovery values from water–methanol (90:10) at 60 min sampling time for some pesticides were calculated by analyzing a sample by SBSE–TD-capillary GC–MS composed of 1 mL methanol spiked with a mixture of pesticides to individual concentrations of 25 μg/L (ppb) and diluted with 10 mL water (Fig. 2). The SBSE recoveries were measured by comparison of the peak areas of the SBSE experiments with those obtained

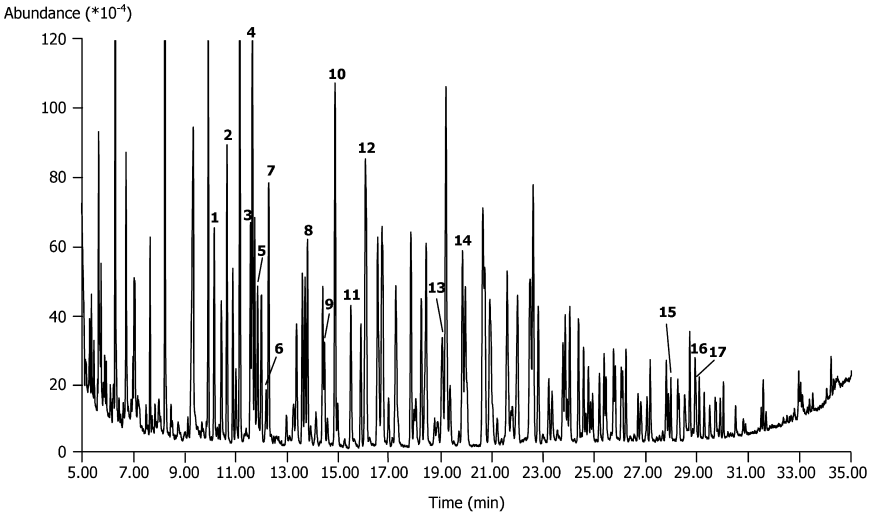

Fig. 2. Total ion chromatogram of the SBSE–TD-capillary GC–MS analysis of 1 mL methanol spiked with a mixture of pesticides at individual concentrations of 25 μg/L. For sampling and chromatographic conditions, see text. The numbers correspond to Table 1.

by analysis of 1 μL of the same pesticide mixture at the 25 mg/L level. The 1 μL sample was introduced into an empty thermal desorption liner. Table 1 lists the theoretical (REC1) and actual values (REC2) for some pesticides from Fig. 2, illustrating that REC1 and REC 2 are of the same order of magnitude. The tables at the R.I.C. website can therefore be used to obtain an estimate of the range of concentration of the pesticides present. Until now, matrix effects were not considered. During our experiments we noted that, for some pesticides, PDMS recoveries strongly depend on the sample pH [19]. For example, basic

Table 1
SBSE recoveries of some pesticides

Number	Compound name	REC 1	REC 2	R^2	REC 3
1	Tecnazene	98	72	0.997	75
2	Cycloate	94	51	0.994	48
3	Trifluralin	100	63	0.995	56
4	Benfluralin	100	63	0.992	55
5	Di-allate I	97	54	0.998	48
6	Di-allate II	97	56	0.999	45
7	Hexachlorobenzene	100	65	0.999	58
8	Fonofos	96	63	0.995	58
9	Disulfoton	95	56	0.995	55
10	Tri-allate	99	63	1.000	55
11	Pentachloroaniline	98	57	0.998	52
12	Dichlofenthion	100	61	0.996	60
13	Fenthion	97	57	0.994	53
14	Dodemorph I	100	56	0.999	49
15	Piperonyl butoxide	98	48	0.994	47
16	Bifenthrin	100	52	0.995	51
17	Methoxychlor	100	46	1.000	43

REC1, calculated theoretical SBSE recoveries (%) from 10 mL water; REC2, measured SBSE recovery from a 1 mL methanol sample diluted with 10 mL water and 60 min sampling; linearity of the SBSE–TD-CGC–MS analysis of pesticides in methanol in a concentration range between 5 and 200 μg/L; REC3, SBSE recovery (%) of pesticides spiked in a salad sample. For sampling and chromatographic conditions, see text. The numbers correspond to Fig. 2.

pesticides can be protonated at low pH, giving relatively low recoveries. This was the case for triazine pesticides such as atrazine, prometon, prometryn, propyzamide, terbutylazine and terbutryne. All these pesticides are theoretically recovered by SBSE from water between 80 and 100%, with the exception of atrazine (61%). For a 1 mL methanol sample containing the triazines at 25 μg/L and dilution with water at pH 5, the recoveries dropped to 10–12%. This stresses the need for quantification by standard addition or isotope dilution (see further).

Critical in terms of accuracy and false negatives is the degradation of some ''sensitive'' pesticides that decompose during sample enrichment and/or in the injection system. The sensitive pesticides are indicated with an asterisk in the website tables. SBSE is a very gentle technique, as was illustrated with the analysis of iprodione in wine by SBSE followed by TD-capillary GC–MS analysis as well as with liquid desorption followed by LC–MS analysis [14]. This compound is known as one of the most sensitive pesticides to GC analysis and was indeed converted 90% in the injection system to (3,5-dichlorophenyl)-hydantoin, while 100% was recovered in liquid desorption LC–MS analysis. Thermodegradation in the TD-PTV GC system can be situated between PTV degradation and on-column injection, as described by Zrostikova et al. [20]. For dichlofluanid, captan and carbaryl, 98, 78 and 95%, respectively, were recovered.

3.2. Multi-residue screening of pesticides in different foodstuffs

The total ion chromatograms obtained by SBSE enrichment of food products in the first instance give the total profile of the volatiles and semi-volatiles characterizing that specific product. As an example, Fig. 3 shows the recorded total ion chromatogram of the SBSE–TD-capillary GC–MS analysis of a lettuce sample. The main peaks (1–3) correspond to C_{16}–C_{18} fatty acids. Detection and identification of trace levels of pesticides in this complex profile can be very time-consuming and laborious.

Therefore, the capillary GC analyses are in all cases performed under retention time locked (RTL) conditions, eluting the RTL calibrating solute *p,p′*-DDT at a constant retention time of 26.98 min. The presence of pesticides is then elucidated automatically via the RTL screener software in combination with the RTL-MS library for pesticides and endocrine disruptors, selecting four qualifier ions for positive identification. As an example, Fig. 4 shows

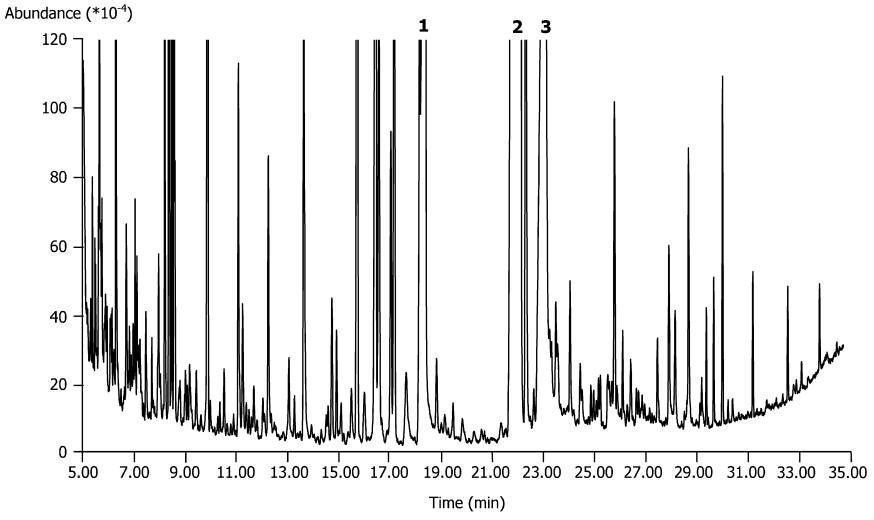

Fig. 3. Total ion chromatogram of the SBSE–TD-capillary GC–MS analysis of lettuce.

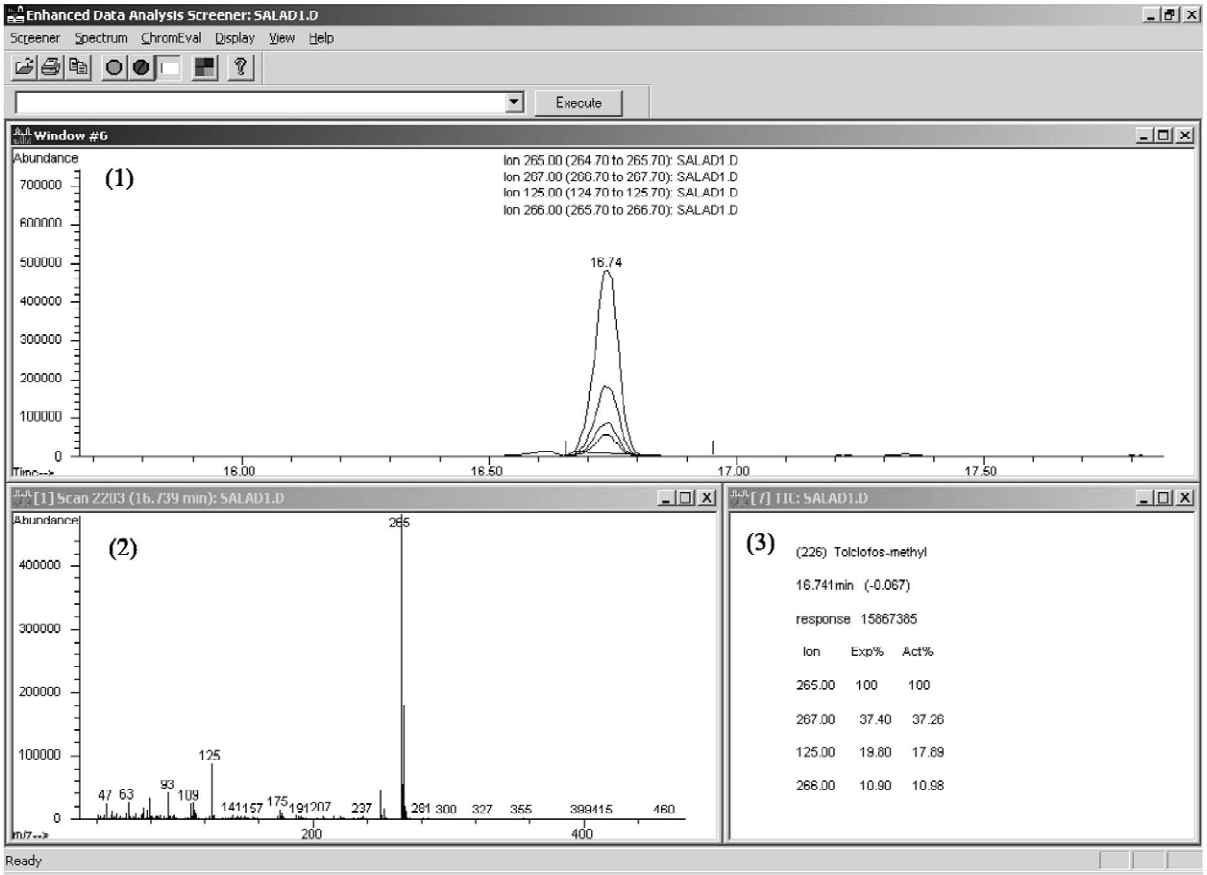

Fig. 4. Results screener windows of the positive identification of tolclofos-methyl in lettuce. (1) Extracted ion chromatograms at the qualifier ions m/z 265, 267, 125 and 266. (2) Recorded mass spectrum at the peak apex. (3) Expected and measured relative ion abundance ratios and deviation of the RTL value.

the screener software window for the positive detection and identification of tolclofos-methyl in the lettuce extract. The ratios of the four qualifier ions are measured (Fig. 4(1)) and compared with those listed in the library (Fig. 4(3)). The latter figure also presents the deviation of the measured retention time (0.067 min) with the RTL value. The recorded total spectrum is given in Fig. 4(2). Analogously, vinclozolin and procymidone were also detected by the RTL screener in the lettuce sample.

Fig. 5 shows the extracted ion chromatogram (EIC) at m/z 212, 265 and 283 for vinclozolin, tolclofos-methyl and procymidone, respectively. These pesticides have thus positively been identified in the lettuce sample and only now can MRM quantification be performed.

3.3. Quantitative analysis of pesticides identified by SBSE–RTL-capillary GC–MS

There are different ways to accurately quantify positive findings. Conventional methods in food analysis are single calibrations with a standard, the concentration of which is close to the estimated concentration and prepared in a blank matrix to compensate for matrix effects, the internal standard addition of D- or ^{13}C-labeled pesticides and standard addition at five or six concentration levels. The first

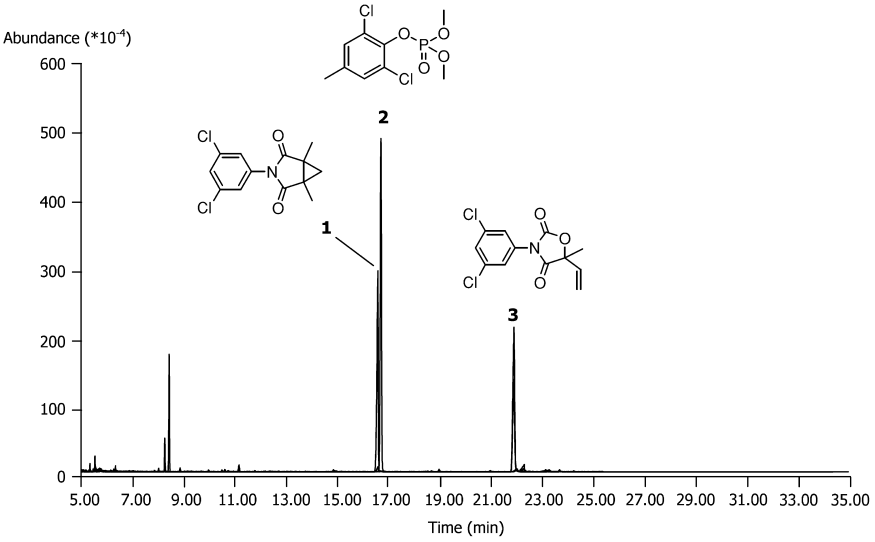

Fig. 5. Extracted ion chromatograms at m/z 212, 265 and 283 for vinclozolin (peak 1), tolclofos-methyl (peak 2) and procymidone (peak 3), respectively, in the analysis of lettuce.

method requires a blank sample to compensate for matrix effects, but as strange as this may appear, such samples are not readily available. The second approach cannot be applied in a MRM because labeled standards of only a few pesticides are commercially available. The last method is by far the easiest to use in a routine environment and has been applied for the determination of dicarboximide fungicides in wines by SBSE–capillary GC–MS [14]. However, this method is time-consuming and thus costly. Precise quantification, in fact, is only needed when the detected quantity is expected to exceed the maximum allowable level. Maximum residue levels (MRLs) in foodstuffs, with the exception of baby food, are relatively high and, with semi-quantitative methods, elucidation of negative, i.e. far below the MRL, and positive samples, i.e. concentration around the MRL values, can easily be made. Only accurate quantification is needed for positive samples.

For the lettuce sample (Fig. 5) the methanol extraction efficiency and matrix effects were measured indirectly by SBSE recovery calculation of some pesticides spiked in 15 g lettuce at the individual level of 5 μg/kg. The spiked sample was extracted with 30 mL methanol and 1 mL of the extract was analyzed as described above. The total methanol liquid extraction-SBSE recoveries (REC3) are listed in Table 1 and are very similar to those of REC2. This indicates a nearly quantitative extraction of the pesticides by methanol from the salad sample. This implies that semi-quantitation can be performed by constructing a calibration line in methanol and recalculation of the concentration to the sample amount. A pesticide mixture containing the identified pesticides was prepared and spiked in 1 mL of methanol to concentrations of 5, 10, 25, 50, 100 and 200 μg/L, corresponding to approximate levels of 10, 20, 50, 100, 200 and 400 μg/kg sample. The correlation coefficients are listed in Table 1 and are all greater than 0.99. The main qualifier ion was used to construct the calibration graphs. Vinclozolin, tolclofos-methyl and procymidone in the lettuce sample (Fig. 5) were quantified at 175, 17 and 249 μg/kg, respectively. These are mean values of six complete analyses ($n=6$) and the RSDs % were 5.4, 8.8 and 4.6, respectively. All these values are far below the MRL of the European Community, which are 5 mg/kg for vinclozolin and procymidone and 0.5 mg/kg for tolclofos-methyl in lettuce. Accurate quantitation is thus not required because the lettuce sample can be considered negative. In the same way, pear and grape samples were analyzed by the SBSE–

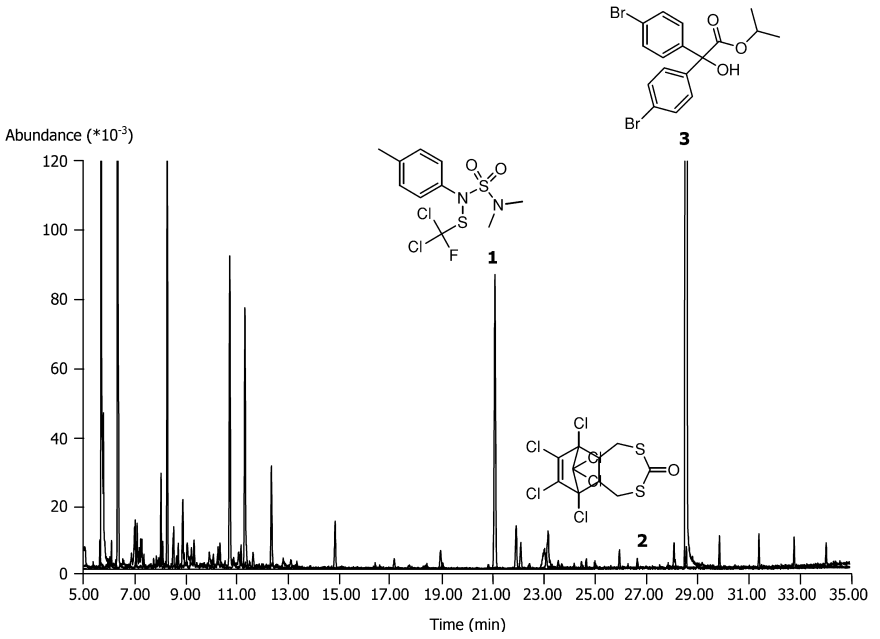

Fig. 6. Extracted ion chromatograms at m/z 137, 272 and 341 for tolylfluanid (peak 1), endosulfan-sulfate (peak 2) and bromopropylate (peak 3, out of scale), respectively, of a pear sample analysed by SBSE–TD-capillary GC–MS. For sampling and chromatographic conditions, see text.

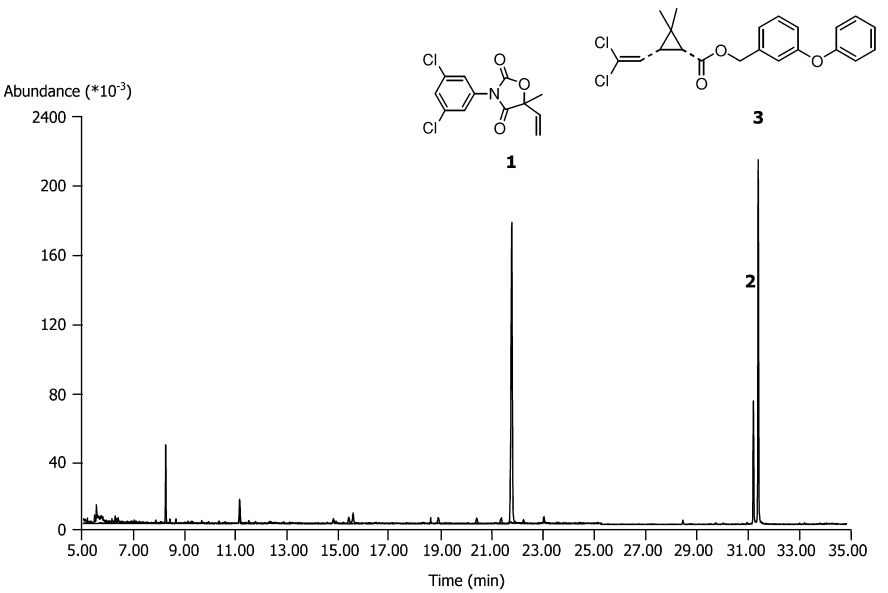

Fig. 7. Extracted ion chromatograms at m/z 283 for procymidone (peak 1) and m/z 183 for permethrin I (peak 2) and II (peak 3) of a grape sample analyzed by SBSE–TD-capillary GC–MS. For sampling and chromatographic conditions, see text.

capillary GC–MS procedure. Fig. 6 shows the extracted ion chromatograms at m/z 137, 272 and 341 of the pear sample, indicating the presence of tolylfluamid at 59 μg/kg (peak 1), endosulfan-sulfate at 3 μg/kg (peak 2) and bromopropylate at 190 μg/kg (peak 3), respectively. The EC MRL values for pears are 2, 0.3 and 2 mg/kg, respectively.

Fig. 7 shows the EICs at m/z 283 and 183 for procymidone (peak 1) and permethrin I and II (peaks 2 and 3) elucidated by the RTL screener in a grape sample. The concentration levels were measured at 172 μg/kg (EC norm 5 mg/kg), 20 μg/kg and 83 μg/kg (EC norm for the sum 1 mg/kg), respectively.

MRLs in baby food are becoming more and more stringent and ultra-trace level analysis (μg/kg and sub-μg/kg) is required. Baby food is a more complex matrix because, besides vegetables or fruits, small quantities of fat are also present. This also affects the efficiency of the pre-extraction in methanol as well as the SBSE recovery. Standard addition calibration is the only valid alternative for baby food.

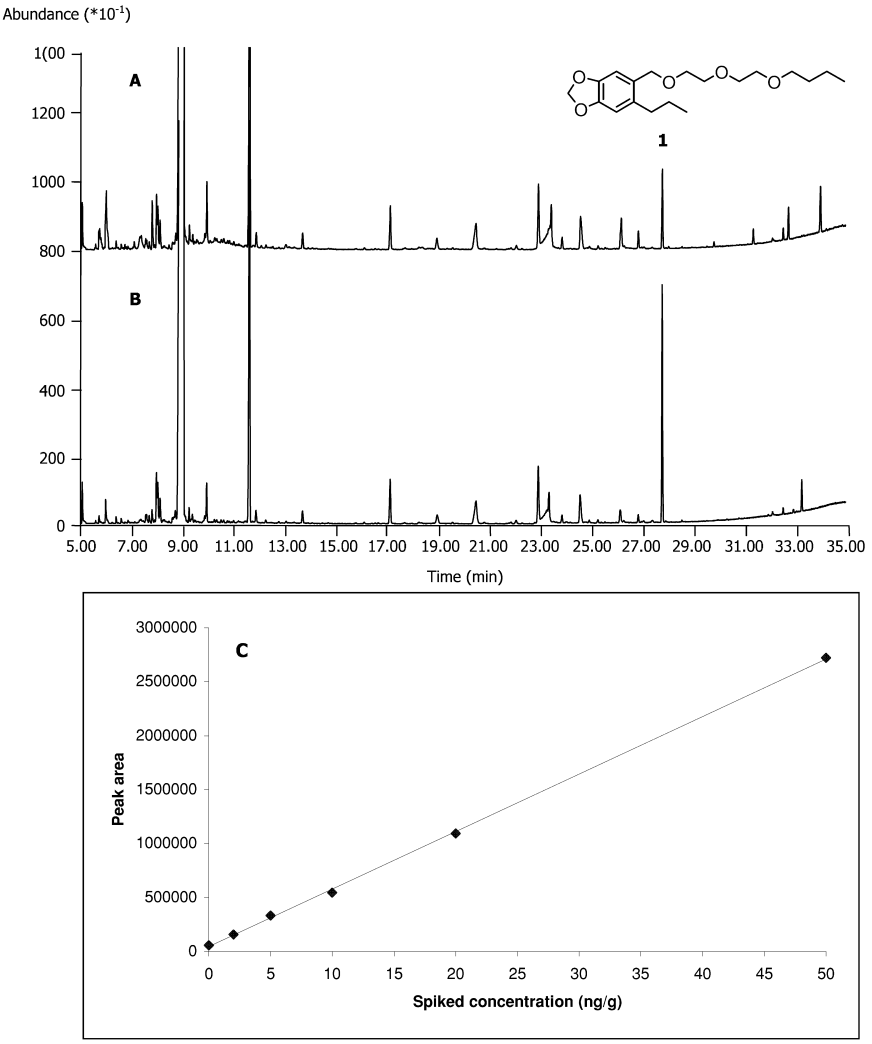

Fig. 8. Selected ion chromatograms at m/z 176 for piperonyl butoxide (peak 1) in the extract of an unspiked (A) and a spiked (2 μg/kg) baby food sample (B). Standard addition curve of piperonyl butoxide in the concentration range between 2 and 50 μg/kg (C). For sampling and chromatographic conditions, see text.

Ten baby food samples were analyzed and, in four samples, pesticide traces between 0.5 and 2 ppb were detected by the described method, namely piperonyl butoxide, pyrimethanil (two samples) and bromopropylate. As an illustration, the analysis of a baby food containing vegetables, complete rice and chicken using the described method is presented. Preliminary screening was performed with the mass spectrometric detector in the scan mode, thereby elucidating the presence of small traces of piperonyl butoxide. The pesticide shows high affinity for PDMS ($\log K_{o/w}$ 4.29) and can be extracted from 1:10 diluted methanol in water with a recovery of 48% (REC3 in Table 1). For accurate quantitation, the MSD was used in the selected-ion monitoring (SIM) mode at m/z 176. Six sub-samples of the baby food sample were spiked with a piperonyl butoxide standard in methanol at concentrations of 0, 2, 5, 10, 20 and 50 μg/kg. Fig. 8 shows the selected ion chromatogram at m/z 176 of an unspiked sample and of a sample spiked at 2 μg/kg piperonyl butoxide. The correlation coefficient of the standard addition curve was $R^2 > 0.99$ (Fig. 8C) and the concentration in the sample was calculated at 1.1 μg/kg.

4. Conclusion

Stir bar sorptive extraction (SBSE) in combination with thermal desorption-RTL-locked capillary GC–MS is a versatile and cost-effective method for the elucidation and quantification of over 350 pesticides in different foodstuffs down to sub-ppb levels.

Acknowledgements

Gerstel GmbH and Agilent Technologies are thanked for supporting our SBSE pesticide research. B.T. thanks the Institute for Scientific Technology, Flanders, Belgium, for a study grant.

References

[1] C.D.S. Tomlin (Ed.), The Pesticide Manual, 12th ed., The British Crop Protection Council, Farnham, Surrey, 2000.
[2] C. Schenzler, H.-P. Their, Food Addit. Contam. 18 (10) (2001) 875.
[3] M.A. Luke, J.E. Froberg, G.M. Doose, H.T. Masumoto, J. Assoc. Off. Anal. Chem. 64 (1981) 1187.
[4] G. Becker, in: Manual of Pesticide Residue Analysis, Vol. 2, VCH, Weinheim, 1992, p. 313.
[5] W. Specht, in: Manual of Pesticide Residue Analysis, Vol. 2, VCH, Weinheim, 1992, p. 317.
[6] P. Cunniff (Ed.), 16th ed., Official Methods of Analysis of AOAC International, Vol 1, AOAC, Arlington, VA, 1995, p. 1.
[7] P. van Zoonen (Ed.), Analytical Methods for Pesticide Residues in Foodstuffs, Part 1, General Inspectorate for Health Protection, RIVM, Bilthoven, Netherlands, 1996.
[8] J. Fullion, www.chem.agilent.com/cag/peak/peak1-96/pesticide.html.
[9] E. Baltussen, C.A. Cramers, P. Sandra, Anal. Bioanal. Chem. 373 (2002) 3.
[10] J. Pawliszyn, Solid Phase Microextraction. Theory and Applications, Wiley–VCH, New York, 1997.
[11] E. Baltussen, P. Sandra, F. David, C.A. Cramers, J. Microcol. Sep. 11 (1999) 737.
[12] K.-W. Yang, R. Eisret, H. Lord, J. Pawliszyn, in: J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, RSC, Hertfordshire, UK, 1999, p. 435.
[13] A.A. Boyd-Boland, M. Chai, Y.Z. Luo, Z. Zhang, J. Pawliszyn, T. Gorecki, Environ. Sci. Technol. 28 (1994) 596A.
[14] P. Sandra, B. Tienpont, J. Vercammen, A. Tredoux, T. Sandra, F. David, J. Chromatogr. A 928 (2001) 117.
[15] Ph. Wylie, B. Quimby, Agilent Application Note 5967-5860E (2000), www.agilent.com/chem.
[16] C. Kai Meng, Agilent Application Note 5988-4392EN (2001), www.agilent.com/chem.
[17] W.M. Meylan, P.H. Howard, J. Pharm. Sci. 84 (1995) 83.
[18] Gerstel Application Notes 2/2001, 9/2001, 3/2002 and 4/2002 at www.gerstel.de.
[19] A. Tredoux, H. Lauer, T. Heideman, P. Sandra, J. High Resolut. Chromatogr. 23 (2000) 644.
[20] J. Zrostlikova, J. Hajslova, M. Godula, K. Mastovska, J. Chromatogr. A 937 (2001) 73.