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RESEARCH ARTICLE

Determination of selected semi-volatile organic compounds in water using automated online solid-phase extraction with large-volume injection/gas chromatography/mass spectrometry

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Abstract A rapid, sensitive, and cost-effective analytical method was developed for the analysis of selected semi-volatile organic compounds in water. The method used an automated online solid-phase extraction technique coupled with programmed-temperature vaporization large-volume injection gas chromatography/mass spectrometry. The water samples were extracted by using a fully automated mobile rack system based on x-y-z robotic techniques using syringes and disposable 96-well extraction plates. The method was validated for the analysis of 30 semi-volatile analytes in drinking water, groundwater, and surface water. For a sample volume of 10 mL, the linear calibrations ranged from 0.01 or 0.05 to 2.5 $\mu g \cdot L^{-1}$, and the method detection limits were less than 0.1 $\mu g \cdot L^{-1}$. For the reagent water samples fortified at 1.0 $\mu g \cdot L^{-1}$ and 2.0 $\mu g \cdot L^{-1}$, the obtained mean absolute recoveries were 70%–130% with relative standard deviations of less than 20% for most analytes. For the drinking water, groundwater, and surface water samples fortified at 1.0 $\mu g \cdot L^{-1}$, the obtained mean absolute recoveries were 50%–130% with relative standard deviations of less than 20% for most analytes. The new method demonstrated three advantages: 1) no manipulation except the fortification of surrogate standards prior to extraction; 2) significant cost reduction associated with sample collection, shipping, storage, and preparation; and 3) reduced exposure to hazardous solvents and other chemicals. As a result, this new automated method can be used as an effective approach for screening and/or compliance monitoring of selected semi-volatile organic compounds in water.

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1 Introduction

Analyses of semi-volatile organic compounds (SOCs) in water samples are primarily performed by using solid-phase extraction (SPE) followed by gas chromatography/mass spectrometry (GC/MS) [1–4]. For drinking water analysis, large volumes of samples are often used to achieve the required sensitivity, and water sample preparation is often the bottleneck because conventional SPE is relatively labor-intensive and time-consuming [5–10]. Automated offline SPE techniques using disposable cartridges or 96-well plates have been well-established. These were recently used for water analyses of SOCs and resulted in improved extraction accuracy, precision, and throughput due to less manipulation [11–13]. However, automated online SPE techniques could be rather complex.

Most current automated SPE techniques are not applicable for online GC/MS analyses of SOCs because water is not a solvent compatible to GC/MS [14]. First, water can quickly deteriorate the stationary phase of a capillary GC column. Secondly, water can cause an ion source vacuum problem that can significantly affect the ionization and sensitivity. Pumping down the ion source is very time-consuming. Thirdly, water is not a suitable solvent to well wet the surfaces of the commonly used retention gaps and pre-columns as well as the commonly used stationary phases of separation columns. The wetting can greatly affect peak shapes and sensitivity, particularly for highly volatile organic compounds. Furthermore, water

has a higher boiling point and can form a much larger volume of vapor per volume of liquid than many organic solvents commonly used for GC, which can make the solvent venting or evaporation process very time-consuming when a large-volume injection (LVI) technique is used. As a result, manual extract drying and evaporative concentration are often required prior to GC/MS analysis [12,13].

LVI is a suitable interface for online SPE because it can improve detection limits without the need for large volumes of samples, it can simplify SPE procedures, and it can eliminate additional evaporation steps for the elution solvent. Researchers have developed several LVI techniques for GC, which include on-column injection [15], loop-type injection [14,16], and programmed-temperature vaporization injection (PTV) [17–20]. The reported automated online SPE/GC and GC/MS included mobile rack systems based on x-y-z robotic techniques using switching valves and disposable small SPE cartridges [21,22], liquid chromatography-like systems using high pressure liquid pumps and switching valves as well as reusable SPE pre-columns or cartridges [23,24], and mobile rack systems based on x-y-z robotic techniques using syringes and disposable 96-well extraction plates [25]. Automated SPE were online coupled with on-column injectors [23,24], loop-type injectors [22], and PTV injectors [21,25]. A fully automated SPE/PTV-LVI/GC/MS method was recently used for the online in situ analysis of SOCs in water [25]. One of the advantages of using disposable small SPE cartridges or 96-well extraction plates is that it can minimize or eliminate carryover contamination.

The objective of this study was to develop a new rapid, sensitive, and cost-effective automated method that could be used for the analysis of SOCs in small volumes of grab water samples. This new method used an automated online mobile rack SPE system coupled with existing PTV-LVI/GC/MS. The various critical experimental conditions were optimized to improve the method sensitivity, accuracy, and precision. The method was validated for the analysis of selected semi-volatile pesticides, herbicides, and other SOCs at concentrations of sub- to low $\mu g \cdot L^{-1}$ in a variety of water matrices.

2 Materials and methods

2.1 Reagents and standards

The stock solutions of mixed analytes at $100\ \mu g \cdot mL^{-1}$, mixed internal standards (IS) at $500\ \mu g \cdot mL^{-1}$, mixed surrogate standards (SS) at $500\ \mu g \cdot mL^{-1}$, and pyrene-d_{10} at $500\ \mu g \cdot mL^{-1}$ (AccuStandard, New Haven, CT, USA). The mixed IS included 4,4'-dichlorooctafluorobiphenyl, phenanthrene-d_{10}, chrysene-d_{12}. The mixed SS included 2,4,5,6-tetrachloro-m-xylene, pentachloronitrobenzene, 4,4'-dichlorobiphenyl, and triphenylphosphate. Pyrene-d_{10} was used to monitor the instrument injection errors. High purity methanol, ethyl acetate (EtAc), and dichloromethane (DCM) were obtained from AlliedSignal (Muskegon, MI, USA). EtAc and DCM were also mixed at a ratio of 1∶1 as the solvent for the automated SPE operation and the standard solution preparation. ACS grade anhydrous sodium sulfite and concentrated hydrochloric acid (HCl) were obtained from Fisher Scientific (St. Louis, MO, USA). Reagent water (18.0–18.1 MΩ·cm resistance) was obtained from a Millipore Milli-Q Ultra-Pure Water System (Bedford, MA, USA).

2.2 Sample collection and preparation

Water samples were collected in 40 mL amber borosilcate glass vials sealed with PTFE-lined silicone septa. For chlorinated tap water, 4 mg sodium sulfite was preloaded into the sampling vial for dechlorination. 0.1 mL of $6\ mol \cdot L^{-1}$HCl was added into the sample for biologic stabilization. The water sample was stored at 1°C–5°C. Before a batch of samples were loaded onto the automated online SPE system for extraction, 0.4 mL methanol and 40 μL of the mixed SS solution at a concentration of $2.0\ \mu g \cdot mL^{-1}$ were manually added into each sample. Methanol was used to improve the SPE efficiency. The SS had a constant concentration of $2.0\ \mu g \cdot L^{-1}$. For the extracted quality control samples, which included fortified reagent water samples called laboratory fortified blanks (LFBs) and fortified real-world water samples called matrix spikes (MS), the analytes were also manually fortified into the samples. The samples were mixed well and warmed up to room temperature before extraction.

2.3 Automated SPE

The automated online SPE was a Twin-PAL system (LEAP Technologies, Carrboro, NC, USA). The extraction was performed by using SPCC PLUS 96-well C18AR extraction plates (Ansys Diagnostics, Lake Forest, CA, USA) and sealed with the polypropylene seal inserts (MicroLiter Analytical Supplies, Suwanee, GA, USA). The eluate was collected in 300 μL glass inserts. A previous report described the detailed functions and procedures of the automated online SPE system [25]. Figure 1 shows the new setup of the automated online SPE/PTV-LVI/GC/MS system used in this study. The 96-well extraction plate was located on the sample extraction tray (ET). The 300 μL glass inserts held in a 96-well deep round collection plate were located on the eluate collection tray (CT). A PTFE container connected to a water waste bottle was located on the CT, which was used to collect the sample passing through the SPE sorbent. The 40 mL sampling vials were set in the water sample tray (WST). Three separate solvent reservoirs (SR) were used to store DCM, methanol, and reagent water, which were used for SPE sorbent cleaning,

conditioning, and pre-extraction rinsing, and post-extraction rinsing, respectively. The 2.5 mL sampling syringe (S1) was automatically rinsed with methanol, EtAc, and DCM before use and after sample delivery. These solvents were stored in three separate 10 mL glass vials located on the wash station (W1). The 100 μL syringe (S2) used for PTV-LVI was automatically rinsed with EtAc, DCM, and DCM again before use and after an elute or standard solution delivery. These solvents were stored in three separate 10 mL glass vials located on the wash station (W2). Unextracted standard solutions were stored in 2 mL amber glass autosampler vials set in the standard solution tray (ST). The system software and Twin-PAL control units (C1 and C2) could provide fully automated and precise control of the SPE and PTV-LVI procedures. Table 1 shows the optimized automated online SPE procedures and experimental conditions.

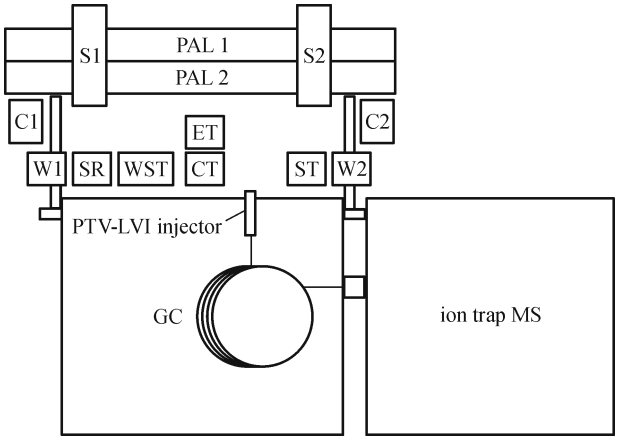

Fig. 1 Schematic diagram of the automated SPE Twin-PAL PTV-LVI/GC/MS system. S1: upper PAL head and syringe (2.5 mL); S2: lower PAL head and syringe (100 μL); C1: upper PAL control unit; C2: lower PAL control unit; W1: wash station for upper PAL syringe S1; W2: wash station for lower PAL syringe S2; ST: standard solution tray; ET: sample extraction tray; CT: eluate collection tray; WST: water sample tray; and SR: solvent reservoirs

2.4 PTV- LVI/GC/MS

This work used a Varian Saturn II GC/MS equipped with a Star 3400 GC system and a 1078 Universal Capillary Injector (Varian, Inc., Walnut Creek, CA, USA). The separation was carried out using a Restek RTX-5 fused silica capillary column (30 m length × 0.25 mm I.D × 0.25 μm film thickness) connected to a 1 m Siltek deactivated fused silica guard column (Restek, Bellefonte, PA, USA). The Siltek deactivated PTV-LVI injector liner (2 mm I.D.) was packed with Siltek deactivated glass wool. The similar PTV-LVI/GC/MS conditions reported previously were used for the data acquisition [25]. A selected ion storage (SIS) function was used to improve the signal-to-noise ratios by ejecting background ions resulting from the PTV-LVI and the column bleeding. The injection volume was 50 μL.

3 Results and discussion

3.1 Calibration and quantitation

The calibration standard solutions were prepared in the 1:1 mixed solvent in a series of 1.0 mL volumetric flasks. The analyte concentrations ranged from 0.01 to 2.5 $\mu g \cdot L^{-1}$, the SS concentrations ranged from 0.5 to 5.0 $\mu g \cdot L^{-1}$, and the IS concentration was 2.0 $\mu g \cdot L^{-1}$ in terms of 10 mL sample and 100 μL extract. Internal standard calibrations were used for quantitative determination of the analytes and SS using the peak areas of the selected characteristic quantitation ions. External standard calibrations were used for the determination of the IS. The IS quantitation ion masses were 212, 296, 188, and 240 for pyrene-d_{10},

Table 1 Automated online SPE procedures and conditions

procedure	condition and description
sorbent cleaning	add 0.5 mL of 1:1 EtAc:DCM at 10 $\mu L \cdot s^{-1}$ and soak for 30 s to clean the sorbent
sorbent drying	apply nitrogen gas at 0.15 MPa pressure for 30 s to dry the sorbent
sorbent conditioning	add 0.5 mL methanol at 10 $\mu L \cdot s^{-1}$ and soak for 60 s to condition the sorbent
sorbent rinsing	add 0.5 mL reagent water at 20 $\mu L \cdot s^{-1}$ to rinse the sorbent
sample extraction	load 10 mL sample (4 × 2.5 mL) at 20 $\mu L \cdot s^{-1}$ to extract the sample
post-extraction rinsing	add 1.0 mL reagent water at 20 $\mu L \cdot s^{-1}$ to rinse the sorbent
sorbent drying	apply nitrogen gas at 0.15 MPa pressure for 5 min to dry the sorbent
analyte elution	add 160 μL of 1:1 EtAc:DCM at 10 $\mu L \cdot s^{-1}$ and elute the analytes into a 300 μL glass insert when the PTV-LVI/GC/MS was ready for injection
eluate concentration	apply nitrogen gas at 0.15 MPa pressure for 5 s to concentrate the eluate to approximately 90 μL
IS addition	add 10 μL of 2.0 $\mu L \cdot mL^{-1}$ IS solution into the eluate and mix well by using 5–10 syringe plunger strokes
online GC/MS injection	inject 50 μL extract mixture onto the PTV-LVI at 2 $\mu L \cdot s^{-1}$

Note: The syringe cleaning processes are not included

4,4'-dichlorooctafluorobiphenyl, phenanthrene-d_{10}, and chrysene-d_{12}, respectively. The SS quantitation ion masses were 207, 237, 150, and 325 for 2,4,5,6-tetrachloro-m-xylene, 4,4'-dichlorobiphenyl, pentachloronitrobenzene, and triphenylphosphate, respectively. Table 2 describes the selected characteristic quantitation ion(s), retention time, studied calibration linear range, mean response factor, and correlation coefficient (R^2) of each analyte included in this study.

The calibration linearity was dependent on both the target analytes and the PTV-LVI/GC/MS conditions. As shown in Table 2, all the studied analytes except cyanazine had a linear calibration with a correlation coefficient (R^2) of 0.995 or better. Cyanazine had a correlation coefficient (R^2) of 0.981, which could result from its relatively low sensitivity. The obtained mean response factor of cyanazine was 0.054, which was significantly lower than that of other analytes.

3.2 Sensitivity, accuracy, and precision

The method detection limits (MDLs) were measured from seven replicate acidified laboratory reagent water samples fortified at 0.1 $\mu g \cdot L^{-1}$, which was near the limits of detection [26]. As shown in Table 3, the obtained MDLs were not greater than the target concentration of 0.1 $\mu g \cdot L^{-1}$ and were not less than one-tenth of the target concentration for each analyte. However, bromacil, cyanazine, and diazinon had relatively higher MDLs. The relatively higher MDL of bromacil could be rationalized as a result

Table 2 Quantitation ions, retention times, and calibration curves of analytes

analyte	ion/(m/z)	RT/min	LR/($\mu g \cdot L^{-1}$)	mean RF	CC/R^2
acetochlor	146	14.3	0.05–2.5	0.236	0.998
alachlor	45, 160, 188	14.6	0.01–2.5	1.096	0.997
aldrin	66, 263	15.8	0.01–2.5	0.323	0.999
atrazine	200	12.2	0.01–2.5	0.542	0.997
benzo[a]pyrene	252	29.7	0.05–2.5	0.354	0.996
bromacil	205, 207	15.5	0.01–2.5	0.433	0.999
butachlor	160, 176, 188	18.4	0.01–2.5	1.523	0.996
chlordane, alpha	373, 375	18.5	0.01–2.5	0.807	1.000
chlordane, gamma	373, 375	18.0	0.01–2.5	0.858	0.998
cyanazine	212, 225	16.0	0.05–2.5	0.054	0.981
diazinon	179	12.8	0.01–2.5	0.375	0.997
dieldrin	79	19.3	0.01–2.5	0.280	0.998
endosulfan I	159, 195, 241	18.5	0.05–2.5	0.244	0.997
endosulfan II	159, 195, 241	20.5	0.05–2.5	0.168	0.996
endrin	81, 243, 245	20.1	0.05–2.5	0.210	0.998
fenamiphos	154, 303	18.7	0.05–2.5	0.317	0.990
heptachlor	100, 272	14.7	0.05–2.5	0.315	0.996
heptachlor epoxide	81, 353, 355	17.2	0.01–2.5	0.689	0.997
hexachlorobenzene	284	11.8	0.01–2.5	0.192	0.995
lindane	181, 183	12.6	0.01–2.5	0.486	0.997
methoxychlor	227	24.0	0.01–2.5	0.290	0.996
metolachlor	168, 238	15.8	0.01–2.5	2.612	1.000
metribuzin	198	14.3	0.05–2.5	0.647	0.997
nonachlor, trans	407, 409	18.6	0.01–2.5	0.313	0.999
pendimethalin	252	17.1	0.05–2.5	0.437	0.995
prometon	168, 210	12.0	0.05–2.5	0.748	0.995
propachlor	120	10.3	0.01–2.5	0.734	0.998
simazine	201	12.1	0.05–2.5	0.394	0.999
terbufos	57, 231	12.5	0.05–2.5	1.079	0.998
trifluralin	264, 306	11.0	0.05–2.5	1.043	0.998

Notes: RT = retention time; LR = linear range; RF = response factor; and CC = correlation coefficient

of the difficulty in accurately integrating the peak areas. Wide and tailing peaks were observed for bromacil. It was also known that the active sites on the packed PTV-LVI liner, the guard column, and the separation column could cause the degradation of bromacil, which would make it more difficult to achieve reproducible peak area integration for this compound at low concentrations. The relatively higher MDL of cyanazine could result from the spectral interferences that had a great impact on the low concentration measurements, as discussed above, the sensitivity of cyanazine was significantly lower than that of other analytes included in this work. The relatively higher MDL of diazinon could result from its coelution with both SS pentachloronitrobenzene and IS phenanthrene-d_{10}, which made it difficult to accurately integrate the peak areas.

The method accuracy and precision were measured as the mean percent absolute recovery and percent relative standard deviation (RSD) of replicate fortified acidified laboratory reagent water samples. For the seven LFBs at 0.1 $\mu g \cdot L^{-1}$, the obtained mean absolute recoveries were 50%–150% for all analytes except prometon. The low mean recoveries of prometon could be rationalized as a result of its known rapid degradation in acidified samples [5,10,25]. For the seven LFBs at 1.0 $\mu g \cdot L^{-1}$ and 2.0 $\mu g \cdot L^{-1}$, most analytes had a mean absolute recovery of

Table 3 Method sensitivity, accuracy, and precision

analyte	MDL/($\mu g \cdot L^{-1}$)	% mean absolute rec.±% RSD [a)]	% mean absolute rec.±% RSD [b)]	% mean absolute rec.±% RSD [c)]
acetochlor	0.045	122±11.7	95±4.9	102±5.1
alachlor	0.060	116±16.5	91±4.7	99±6.7
aldrin	0.053	85±19.8	74±4.8	67±4.2
atrazine	0.054	73±23.5	105±6.8	92±4.6
benzo[a]pyrene	0.027	108±8.0	68±0.4	57±17.0
bromacil	0.099	87±36.2	92±7.7	87±4.0
butachlor	0.073	108±21.5	97±8.8	102±10.1
chlordane, alpha	0.040	86±14.8	72±3.3	72±5.5
chlordane, gamma	0.019	86±7.0	79±4.4	71±4.1
cyanazine	0.087	129±17.4	98±3.2	113±2.3
diazinon	0.096	108±28.3	111±6.5	102±5.3
dieldrin	0.046	106±13.8	85±2.0	81±7.0
endosulfan I	0.021	119±5.6	107±7.1	113±10.1
endosulfan II	0.047	137±10.9	92±2.0	92±6.7
endrin	0.071	142±15.9	102±3.4	95±8.8
fenamiphos	0.023	138±5.3	94±5.4	88±0.7
heptachlor	0.031	132±7.5	67±3.0	62±2.9
heptachlor epoxide	0.031	104±9.5	93±3.8	84±5.2
hexachlorobenzene	0.024	94±8.1	61±4.8	57±4.8
lindane	0.024	132±5.8	80±5.3	74±6.2
methoxychlor	0.045	96±14.9	74±5.2	61±11.1
metolachlor	0.057	110±16.5	104±5.6	117±9.5
metribuzin	0.039	99±12.5	82±9.5	75±8.6
nonachlor, trans	0.015	73±6.5	75±4.8	67±5.0
pendimethalin	0.048	121±12.6	90±4.5	89±3.2
prometon	0.023	18±40.7	65±7.5	54±53.3
propachlor	0.031	108±9.1	101±2.6	90±5.8
simazine	0.039	117±10.6	86±5.2	141±17.1
terbufos	0.043	99±13.8	71±4.3	70±4.0
trifluralin	0.022	114±6.1	90±2.6	76±2. 7

Notes: a) based on seven replicate acidified reagent water samples fortified at 0.1 $\mu g \cdot L^{-1}$; b) based on four replicate acidified reagent water samples fortified at 1.0 $\mu g \cdot L^{-1}$; c) based on four replicate acidified reagent water samples fortified at 2.0 $\mu g \cdot L^{-1}$; and RSD = relative standard deviation

70%–130% with a RSD of less than 20%. However, mean recoveries of less than 70% were also obtained for benzo [a]pyrene, heptachlor, hexachlorobenzene, metoxychlor, trans-nonachlor, and prometon [10,25].

A major reason for the reduced recoveries could be due to the surface adsorption losses of the analytes on the wall of the glass sampling vials because the automated online SPE method did not have the capability of rinsing the sampling vials. A mass balance experiment conducted separately indicated that a significant amount of low polarity analytes could be lost on the wall of the sampling vials, which could vary with the holding time and concentration levels [25]. In addition, like conventional methods, the low mean recoveries of benzo[a]pyrene could be in part rationalized as a result of the combination of several factors, which might include the photo-degradation, glass surface adsorption losses, and difficulty in peak area integration because it appeared as tailing peaks for the LFB at 2.0 $\mu g \cdot L^{-1}$ [10,25]. Moreover, the low mean recoveries of prometon could be due to the unpredictable degradation in acidified water samples as described above [5,10,25]. Water samples preserved with hydrochloric acid could not provide accurate analysis of prometon.

3.3 Real water sample studies

The automated online SPE/PTV-LVI/GC/MS method was validated for analyzing real water samples. The mean absolute recoveries and RSDs were measured for the selected drinking water, groundwater, and surface water

Table 4 Demonstration of matrix effects based on four replicate water matrix spikes

analyte	% mean absolute recovery±% RSD [a)]	% mean absolute recovery±% RSD [b)]	% mean absolute recovery±% RSD [c)]
acetochlor	84±3.5	83±5.5	76±1.4
alachlor	73±4.8	67±1.7	67±1.7
aldrin	46±7.7	54±2.4	49±8.4
atrazine	86±5.1	80±6.1	82±2.7
benzo[a]pyrene	54±2.8	72±26.4	53±19.6
bromacil	78±3.4	119±10.5	79±5.2
butachlor	79±4.8	80±2.5	71±5.5
chlordane, alpha	54±5.1	63±3.6	60±3.4
chlordane, gamma	50±2.9	60±1.6	59±2.9
cyanazine	101±2.7	89±1.3	85±4.6
diazinon	98±2.7	102±10.1	100±2.6
dieldrin	66±4.1	71±4.3	68±2.4
endosulfan I	83±8.2	75±10.0	88±6.0
endosulfan II	77±6.2	89±9.1	80±4.8
endrin	79±4.0	89±4.8	94±5.5
fenamiphos	112±5.1	98±3.2	102±1.6
heptachlor	48±1.7	44±15.2	57±1.6
heptachlor epoxide	68±3.9	83±9.4	108±11.2
hexachlorobenzene	47±3.5	41±4.4	47±4.4
lindane	72±3.4	90±4.6	81±4.2
methoxychlor	87±5.5	125±11.0	106±11.1
metolachlor	84±4.5	78±5.3	79±1.1
metribuzin	62±1.1	86±6.5	71±4.9
nonachlor, trans	49±3.4	59±2.6	56±7.0
pendimethalin	86±4.4	78±4.8	76±3.3
prometon	83±5.4	79±6.0	81±3.3
propachlor	71±4.3	82±7.0	75±5.7
simazine	67±5.8	67±6.1	60±5.2
terbufos	62±1.8	35±8.9	59±5.0
trifluralin	63±5.9	65±4.0	59±7.9

Notes: a) St. Joseph River water fortified at 1.0 $\mu g \cdot L^{-1}$; b) Mishawaka well water fortified at 1.0 $\mu g \cdot L^{-1}$; c) South Bend tap water fortified at 1.0 $\mu g \cdot L^{-1}$, and RSD = relative standard deviation

samples, based on four replicates fortified at a concentration of 1.0 μg·L^{-1}. The drinking water sample was tap water from a local water utility. The groundwater sample was collected from a local private well. The surface water sample was collected from the St. Joseph River flowing through the local area. These water samples were not acidified because they were quickly analyzed after collection. As shown in Table 4, the obtained mean absolute recoveries and RSDs for the three different water matrices were comparable. Compared with the results shown in Table 3, reduced mean absolute recoveries were observed from these sample matrices but the RSDs did not change significantly. The mean absolute recoveries were over 50% with RSDs of less than 10% for most analytes. Several analytes had mean absolute recoveries of less than 50% in some measurements, which included aldrin, heptachlor, hexachlorobenzene, trans-nonachlor, and terbufos. The matrix effects on recoveries could result from a combination of factors, which might include the insufficient dechlorination of the tap water samples, the adsorption on the container inner surfaces, and the adsorption on the particles potentially existing in the river water and well water. Sufficient absolute recoveries were obtained for prometon when the samples were not preserved at a low pH of less than 2.0 [5,10,25].

3.4 Ruggedness and variability

The ruggedness and variability of the automated online SPE/PTV-LVI/GC/MS method were evaluated based on the performance of 58 acidified reagent water samples fortified at a concentration of 1.0 μg·L^{-1} over 30 days. As shown in Table 5, the calculated mean percent absolute recoveries had a trend basically similar to the results observed in Tables 3 and 4. The RSDs of these 58 replicates were less than 30% for all the analytes except prometon and methoxychlor. The extremely high RSD for prometon was due to its unpredictable degradation in the acidified reagent water samples [5,10,25]. However, the variation of methoxychlor remained unclear. The data indicated that the automated online SPE/PTV-LVI/GC/MS method was generally rugged and reproducible. However, a routine check of the large sampling syringe was necessary to maintain a reproducible delivery of aliquots. The syringe plunger could deteriorate because of the multiple deliveries of aliquots for the automated online preparation of a sample. In addition, the instrument and system software was relatively easy to operate.

Table 5 Statistic accuracy and precision based on 58 acidified reagent water samples fortified at 1.0 μg·L^{-1} over 30 days

analyte	% mean absolute recovery	% RSD
acetochlor	93.3	14.2
alachlor	82.0	13.6
aldrin	56.2	15.8
atrazine	89.8	17.3
benzo[a]pyrene	50.9	28.3
bromacil	90.5	18.7
butachlor	91.6	17.5
chlordane, alpha	61.9	14.5
chlordane, gamma	59.1	14.7
cyanazine	97.9	14.8
diazinon	105.3	14.3
dieldrin	72.3	13.9
endosulfan I	95.2	18.3
endosulfan II	86.2	16.7
endrin	86.3	19.5
fenamiphos	93.8	21.8
heptachlor	60.9	17.9
heptachlor epoxide	73.6	12.8
hexachlorobenzene	49.6	23.1
lindane	82.7	9.9
methoxychlor	58.6	62.7
metolachlor	90.8	16.6
metribuzin	67.5	21.0
nonachlor, trans	57.8	15.1
pendimethalin	82.5	14.3
prometon	45.0	57.4
propachlor	82.5	12.4
simazine	72.1	23.4
terbufos	61.9	19.2
trifluralin	66.8	14.8

Note: RSD = relative standard deviation

4 Conclusions

This paper has demonstrated a new automated online SPE/PTV-LVI/GC/MS method with a few characteristics for the analysis of SOCs. First, it was rapid, sensitive, and capable of analyzing selected SOCs at sub- to low μ·L^{-1} levels in a variety of water matrices. Second, it required only minimal manipulation. Many experimental variations could be minimized or eliminated due to being free of manual intervention steps after fortifying samples with the SS. Third, compared with conventional manual SPE methods, it could provide a significant cost savings associated with sample collection, shipping, storage, and preparation. Furthermore, it could significantly reduce human exposure to hazardous solvents and other chemicals. This method was applicable for the screening analysis of the selected SOCs and/or for the compliance analysis of some of the selected SOCs water. However, it could not be effectively

used for analyzing highly volatile compounds because of the evaporation losses in the PTV-LVI process.

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