An Automated Online SPE-GC-MS System for Water Analysis

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Abstract

A fully automated SPE Twin-PAL system has been developed and coupled with large-volume injection (LVI) GC-MS for online analysis of semi-volatile organic chemicals (SOCs) in water. The method detection limits (MDLs) were lower than 0.1 μg/L. Linear calibrations ranging from 0.01 or 0.05 to 2.5 μg/L have been obtained for most compounds studied. For most analytes studied. the absolute recoveries were 70 to 130%for reagent water, well water, and tap water matrices, and the percent relative standard deviations (%RSDs) were less thant 10%. In general, this new technology provides several advantages over liquid-liquid extraction and macroscale solid-phase extraction GC-MS approaches. These include 1) significant cost reduction associated with sample transportation and storage, chemicals and consumables, waste disposal, and labor hours. Compared with EPA Method 525.2, the developed technology can save 55-80% of costs in sample transportation and preparation, depending on the quantity of samples; 2) greatly improved method accuracy, precision, and sensitivity due to the high degree of automation and online injection capability; and 3) reduced exposure to hazardous solvents and other chemicals.

Introduction

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) technologies, coupled with GC and GC-MS, have been widely used for analysis of organic chemicals in water for decades. However, traditional macroscale LLE and SPE are very costly and not amenable to online analysis due to the use of relatively large sample and solvent volumes. These methods require multi-step manual operational procedures, which often result in large experimental variations [1-4]. SPE is a well-established technique used for the extraction of numerous compound classes in water, which is superior to LLE in both cost savings and extraction efficiency. Microscale LLE and SPE have been developed in place of conventional LLE methods to simplify operational procedures and reduce sample preparation costs [5-7]. Particularly, the automation of SPE operation and the development of new sorbents have significantly improved the extraction speed of samples with equivalent extraction efficiency [8-11].

Large-volume injection (LVI) has become an effective bridge connecting online SPE technology to GC or GC-MS because the LVI can improve detection limits [12,13]. Conventional manual extract evaporation and concentration procedures can be eliminated and replaced by simply injecting a greater amount of the extract. The increased sensitivity can result in the simplification of sample preparation procedures and allow simplification of online SPE operational procedures and reduced sample volumes, which enables the application of online SPE-LVI-GC-MS to the analysis of surface water, groundwater, and even waste water.

Several online automated SPE technologies have been developed to reduce sample preparation costs and minimize operational variations [12]. Switching valve technology has been used in online automated SPE-GC-MS and SPE-LC-MS [13-17]. Several typical LVI interfaces available for online SPE-GC and GC-MS include on-column injection using a column switching technique, loop-type LVI interface using a high pressure switching valve technique connected to a GC precolumn, and programmable temperature vaporization (PTV) injector [13-15]. This paper describes a fully automated SPE Twin-PAL system interfaced with a PTV-LVI-GC-MS system for the online analysis of semi-volatile organic chemicals (SOCs) in water [18,19]. The SPE Twin-PAL is based on x-y-z

robotic technology and is a separate system mounted on the GC. The method sensitivity is improved by injecting a large volume of the eluate [17-20]. Since sample preparation is usually the most labor intensive and costly part of any determination, it can be expected that this new online automated SPE-LVI-GC-MS technique will result in considerable analytical cost savings and significant improvement in quantitation.

Experimental

Chemicals and Materials

The SPE sorbents were SPCC plus 96-well C18AR extraction plates (Ansys Diagnostics, Inc., Lake Forest, CA). The other SPE consumables including eluate collection plates and glass inserts were obtained from MicroLiter Analytical Supplies, Inc. (Suwanee, GA). All the standards including analytes, internal standards and surrogates specified in USEPA Method 525.2 were obtained from AccuStandard Inc.(New Haven, CT). The internal standards included 4,4'-dichlorooctafluorobiphenyl, phenanthrene-d10, and chrysene-d12. The surrogates included 2,4,5,6-tetrachloro-m-xylene, pentachloronitrobenzene, 4,4'-dichlorobiphenyl, and triphenylphosphate. The injection monitoring standard was pyrene-d10. High purity methanol (MeOH), acetonitrile (ACN), dichloromethane (DCM), and ethyl acetate (ETAC) solvents were obtained from AlliedSignal Inc. (Burick&Jackson, Muskegon, MI). Deionized water was obtained from a Milli-Q Ultra-Pure Water System (Millipore Corporation, Bedford, MA) providing reagent water with 18.0-18.1 megaohm resistivity. 40 mL amber borosilcate glass sample vials were obtained from QEC (Beaver, WV). 2 ml amber borosilcate glass vials were obtained from Laboratory Supply Distributors, Corp. (Mt. Laurel, NJ).

SPE Twin-PAL

The SPE Twin-PAL system (LEAP Technologies, Carrboro, NC) can provide fully automated functionalities including sorbent cleaning and conditioning, sampling, post-extraction washing, sorbent drying, analyte elution, solvent evaporation, reagent addition and mixing, and online injection into a GC, GC-MS, LC, or LC-MS system. The upper PAL holds a large syringe and is responsible for sorbent cleaning, conditioning, extraction, washing, drying, and elution. The lower PAL holds a small syringe and is responsible for mixing the eluate with the standard solutions and injecting the mixture into the LVI injector. The 96-well extraction plate is sealed with specially designed inserts sealed with septa so that the system can use a positive-pressure flow control to deliver liquids. Nitrogen gas flowing through the syringe connected to a solenoid valve is used to dry the sorbents. Variable liquid volumes, injection speed, drain or soak time, and drying time are precisely controlled by the system software. The system is also able to perform multi-step operations for conditioning, sampling, elution, washing, and injection.

40 mL vials were used to collect samples. 96-well SPE plates were used for the extraction of samples which was performed during the GC-MS cycle time. The optimized SPE operating time for a 10 mL sample was shorter than the cycle time of the GC-MS. The SPE operation would automatically stop after extracting a sample and washing the sorbent followed by drying the sorbent. The elution began after the GC-MS was ready to start a new acquisition. After each sample, reagent water was used to wash away the matrix interference, and then nitrogen gas was applied to dry the sorbent. Multi-step elution was developed to provide more efficient elution. After elution, a flow of nitrogen gas was automatically applied to push the eluate out of the sorbent. The eluate was automatically collected into a 300 µL glass insert set in the 96-well deep round block. The eluate volume was about 90 uL based on the optimized SPE experimental conditions as shown in Table 1. A 1.0 or 2.5 mL syringe was used for the liquid delivery. 10 mL samples were extracted by repeatedly loading an aliquot unto the sorbent.

The SPE Twin-PAL provided the online injection of calibration standard solutions or eluate into the LVI-GC-MS system. A 100 µL injection syringe was programmed to have a filling speed of 10 µL/s, a plunger pullup delay of 20 s, a injection speed of 2 µL/s, and a penetration depth of 45 mm. For the measurement of method

calibrations, 50 μL standard solutions were directly taken and injected into the LVI-GC-MS instrument. The analyte calibration standard solutions were prepared at a concentration range of 0.01 to 25 μg/L and contained 2 μg/L internal standards in 1:1 DCM and ETAC. The surrogate standard solutions were prepared at a concentration of 0.5 to 5 μg/L and contained 2 ug/L internal standards in 1:1 DCM and ETAC. For the analysis of water samples, 10 μL internal standard solution at a concentration of 2.0 ng/uL was taken into the elute and mixed by controlling the syringe strokes. Then the mixture of 50 μL was injected into the LVI-GC-MS instrument. In this way, the absolute recoveries of analytes could be measured. For the measurement of ongoing calibrations, a 50 μL continuous calibration check standard solution (CCC) was directly injected into the LVI-GC-MS instrument. The CCC solutions contained analytes at a concentration of 1 to 5 μg/L, surrogates at a concentration of 2 μg/L, and an internal standard at a concentration of 2 μg/L.

LVI-GC-MS

The calibration standards and eluate were injected into a Varian Star 3400 GC with a 1078 Universal Capillary Injector (Varian Analytical Instruments, Walnut Creek, CA). A 2 mm ID Siltek deactivated liner was packed with 10 mg Siltek deactivated glass wool (Restek, Bellefonte, PA). A temperature ramp mode for the PTV injector was performed to vent the solvent vapor and inject the analytes into a 1 m Siltek deactivated fused silica guard column connected to a 30 m x 0.25 mm x 0.25 um RTX-5 column (Restek, Bellefonte, PA). The guard column was used to reduce the solvent effects on the separation column and refocus more volatile sample constituents. The peak shape of relatively low volatility components could be sharpened by cold (low temperature) trapping. The injector temperature was set to 80 ^{o}C for 1 min, 80-280 ^{o}C at 300 ^{o}C/min, and 280 ^{o}C for 35 min. The solvent vent exit solenoid valve was set to be open at 0-0.6 min to remove the solvent vapor, close at 0.6-3.5 min to inject the sample components into the separation column, and then open at 3.5-37 min to remove the remaining traces of solvent vapor from the liner. The oven temperature was set 45 ^{o}C for 3 min, 45-160 ^{o}C at 50 ^{o}C/min, 160-260 ^{o}C at 5 ^{o}C/min, 260-330 ^{o}C at 6 ^{o}C/min, and 330 ^{o}C for 1 min.

The mass spectrometer was a Saturn II GC/MS (Varian Analytical Instruments, Walnut Creek, CA). The electron multiplier voltage and filament emission current were tuned to obtain a gain of 10^5 and the mass resolution required by EPA Method 525.2. Selected ion storage (SIS) was added into the data acquisition. The filament and electron multiplier were delayed for 6 min. The peak threshold was set to 2 counts. The scan rate was set to 1 scan/s. The data acquisition was set to 37 min. Segment 1 was set to 2 min with a mass range of 56-250 m/z and the masses to eject were 61 m/z (100%), 73 m/z (100%), and 89 m/z (100%). Segment 2 was set to 2.8 min with a mass range of 56-300 m/z and the masses to eject were 61 m/z (100%), 73 m/z (100%), and 84 m/z (100%). Segment 3 was set to 19.2 min with a full scan mass range of 50-450 m/z. Segment 4 was set to 8 min with a mass range of 50-450 m/z and the masses to eject were 73 m/z (100%) and 207 m/z (100%).

Results and Discussion

Method Calibration

Table 2 demonstrates the calibration linearity and average response factors. In general, linear calibrations at a range of 0.01 or 0.05 to 2.5 μg/L (sample concentrations) have been obtained for most compounds studied. Nonlinear calibrations have been obtained for 2,6-dinitrotoluene, 2,4-dinitrotoluene, trifluralin, heptachlor, cyanazine, and benzo(a)pyrene at a concentration of 0.01 or 0.05 to 2.5 μg/L. These compounds were analyzed by using a quadratic fit. Di(2-ethylhexyl)phthalate had a nonlinear calibration at a concentration higher than 5 μg/L and a quadratic fit could be applied. A quadratic fit was also applicable for di(2-ethylhexyl)adipate. However, di(2-ethylhexyl)phthalate at a concentration of lower than 5 μg/L could not be accurately measured because of the system contamination. Relatively volatile compounds, such as hexachlorocyclopentadiene and isophorone, had lower response factors because these compounds were potentially discriminated in the solvent vent process. It was also observed that the packing of the injector liner played an important role in the method sensitivity and

reproducibility of these low boiling compounds. Therefore, highly volatile analytes could not be effectively analyzed by this online SPE-LVI-GC-MS method unless alternate packing materials having a higher affinity to these compounds can be used.

Method Sensitivity, Accuracy and Precision

Table 3 shows the method detection limits (MDLs), average percent absolute recoveries (%Abs. R) and percent relative standard deviations (%RSD) of the compounds of interest. The MDLs were determined through the measurement of seven replicate reagent water spikes at a concentration of 0.1 µg/L. The reagent water spikes contained 1.0% methanol to assist the extraction and were not dechlorinated and acidified. The reagent water spikes were stored under 4 °C for more than 12 hours to achieve an even distribution of analytes in the sample. The MDL was calculated as a product of the standard deviation of the replicate analyses and the student's t value with a 99% confidence level and a n-1 degree of freedom. The absolute recoveries and relative standard deviations were measured from four reagent water spike replicates at a concentration of 1.0 µg/L.

MDLs lower than 0.1 µg/L have been obtained for most compounds studied. Benzo(a)pyrene could not be accurately determined because of the surface adsorption loss. It was found that this compound, similar to many other heavy polynuclear aromatic hydrocarbons (PAHs), were lost as aresult of adsorption on the wall of the glass container. The surface adsorption loss also increased with the increasing in holding time. Absolute recoveries in a range of 70-130% with RSDs of lower than 10% have been obtained for most SOCs studied. 2,6-Dinitrotoluene and 2,4-dinitrotoluene show relatively large %RSDs, which can be rationalized as the effects of inconsistent discrimination of relatively low boiling compounds. These compounds had a relatively high potential of being discriminated in the solvent vent process under the optimized conditions, which could result in a large variation of analyte injection into the system. careful quality control of the packing of the injector liner can be considered an effective way to solve this problem. Bromacil and cyanazine often resulted in a wide, tailing peak. Bromacil easily degraded due to the active sites on the injector liner, packing material, and guard column. The wide and tailing peaks made it difficult to accurately and precisely quantitate bromacil and cyanazine. Therefore, relatively large %RSDs were observed for these compounds. Metribuzin, propachlor, and trans-nonachlor sometimes had a slightly low recovery for unknown reasons.

Matrix Effects

The absolute recoveries and RSDs for well water and tap water spikes were determined based on four replicate spikes at a concentration of 1.0 µg/L. The well water samples were not preserved with hydrochloric acid. The tap water samples were dechlorinated with sodium sulfite and then acidified with hydrochloric acid. The results are shown in Table 4. These water spikes contained 1% methanol and were stored under 4 °C for more than 12 hours.

The results indicate that the online automated SPE-LVI-GC-MS method can provide sufficient recoveries and precision for most compounds in the filtrated well water and tap water, compared with the results of the reagent water spikes shown in Table 3. For tap water, prometon resulted in a low recovery and an extremely high %RSD, which was due to the rapid degradation of this compound under the preservation condition at pH < 2. Lindane (gamma-BHC) had a relatively high recovery for unknown reasons in this particular set of measurements. Slightly lower recoveries were also observed for most compounds studied in the untreated well water, which was likely due to the biological degradation of these analytes because the samples were not preserved.

Conclusions

The online automated SPE-LVI-GC-MS was free of manual intervention steps, which provided several advantages over conventional LLE- and SPE-GC-MS methods. First, the high degree of automation provided

consistent sorbent conditioning, sampling, elution and injection. Lower than 20% RSDs have been obtained for most compounds spiked in reagent water, well water, and tap water. Secondly, LVI greatly improved the method sensitivity. Lower than 0.1 μg/L MDLs have been obtained for the studied analytes. Linear calibrations at a range of 0.01 or 0.05 to 2.5 μg/L have been obtained for most compounds studied. A quadratic fit provided accurate and precise quantitation when needed. Thirdly, considerable analytical cost savings are realized due to reduction of labor, sample transportation and storage, consumables, and waste disposal. Compared with manual macroscale SPE, this new technology will be able to save 55-80% costs in sample transportation and preparation, depending on the quantity of samples. Finally, the high degree of automation and the use of reduced volumes of samples largely reduced exposure to hazardous solvents and other chemicals. This new technology also resulted in 70 -130% absolute recoveries for most SOCs studied, which meets many needs for screening and monitoring a large number of water samples with significantly reduced analytical costs. The new technology can greatly increase laboratory productivity. After starting the sample preparation analysis and data acquisition lists, people can walk away.

Several approaches to improve the injection consistency and sensitivity for relatively low boiling compounds and reduce the surface adsorption losses of high molecular weight PAHs are under investigation. These include using alternate packing materials, precisely controlling the packing of the injector liners, and adding organic solvents to increase the solubility of PAHs in water. Future studies will also include online in-situ analysis of SOCs in waters.

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Table 1 Online automated SPELVI-GC-MS Method Conditions

SPE sequence	Condition
Sorbent cleaning	500 µL 1:1 dichloromethane:ethyl acetate, 10 µL/s, 30 s for draining
Apply pressure	30 s, 1.5 bar pressure (N_2)
Sorbent conditioning	1) 500 µL methanol, 10 µL/s, 60 s for draining 2) 500 µL reagent water, 20 µL/s
Sample extraction	10 mL (4 x 2.5 mL or 10 x 1.0 mL), 20 µL/s
Syringe cleaning	2 solvents for the sample prep syringe
Washing	1.0 mL reagent water or other solutions, 20 µL/s
Apply pressure/drying	5 min, 1.5 bar pressure (N_2)
Elution	160 µL 1:1 dichloromethane:ethyl acetate, 10 µL/s (70 µL, soak for 60 s; 30 µL, soak for 30 s;30 µL, soak for 30 s;30 µL, soak for 30 s;30 µL, soak for 30 s.)
Apply pressure	5 s, 1.5 bar pressure (N_2)
Addition of standards	Take 10 µL internal standard solution (3 strokes) and mix with eluate (5-10 strokes).
Online injection	Take 50 µL of the mixture solution and inject it at 2 µL/s.
Syringe cleaning:	3 solvents for the injection syringe

Table 2 Calibrations of Representative Semi-volatile Organic Compounds

Compound	Quantiation Mass	Linear Range mg/L	Response Factor	Correlation Coefficient
Propachlor	120	0.01-2.5	0.734	0.998
Hexachlorobenzene	284	0.01-2.5	0.192	0.995
Prometon	168+210	0.05-2.5	0.748	0.995
Simazine	201	0.05-2.5	0.394	0.999
Atrazine	200	0.01-2.5	0.542	0.997
Lindane (gamma-BHC)	181+183	0.01-2.5	0.486	0.997
Metribuzin	198	0.05-2.5	0.647	0.997
Alachlor	45+160+188	0.01-2.5	1.096	0.997
Bromacil	205+207	0.01-2.5	0.433	0.999
Aldrin	66+263	0.01-2.5	0.323	0.999
Metoachlor	162+238	0.01-2.5	2.612	1.000
Heptachlor Epoxide	81+353+355	0.01-2.5	0.689	0.997
gamma-Chlordane	373+375	0.01-2.5	0.858	0.998
alpha-Chlordane	373+375	0.01-2.5	0.807	1.000
Butachlor	160+176+188	0.01-2.5	1.523	0.996
trans-Nonachlor	407+409	0.01-2.5	0.313	0.999
Dieldrin	79	0.01-2.5	0.280	0.998
Endrin	81+243+245	0.05-2.5	0.21.	0.998
Methoxychlor	227	0.01-2.5	0.290	0.996

Table 3 Method Sensitivity, Accuracy, and Precision

Compound	MDL, µg/L	%Abs. R	%RSD
2,6-Dinitrotoluene	0.069	119.7	15.9
2,4-Dinitrotoluene	0.075	94.7	25.1
Propachlor	0.051	115.6	3.9
Trifluralin	0.066	121.9	3.7
Hexachlorobenzene	0.044	60.0	3.7
Prometon	0.074	109.2	4.5
Simazine	0.043	101.2	5.9
Atrazine	0.030	95.8	6.4
Lindane (gamma-BHC)	0.052	126.6	2.2
Metribuzin	0.018	68.7	13.4
Alachlor	0.043	108.5	7.2
Heptachlor	0.066	90.7	5.7
Bromacil	0.066	57.1	16.0
Aldrin	0.037	64.6	14.8
Metoachlor	0.038	108.4	2.3
Cyanazine	0.054	93.2	15.7
Heptachlor Epoxide	0.033	95.8	7.3
gamma-Chlordane	0.027	66.8	10.2
alpha-Chlordane	0.028	75.5	6.3
Butachlor	0.036	95.2	1.4
trans-Nonachlor	0.027	54.5	10.2
Dieldrin	0.031	90.4	6.6
Endrin	0.019	86.5	5.5
Methoxychlor	0.044	116.9	4.9

Table 4 Matrix Effects on Method Accuracy and Precision

Compound	Untreated Well Water %Abs. R	%RSD	Filtrated Well Water %Abs. R	%RSD	Tap Water %Abs. R	%RSD
2,6-Dinitrotoluene	39.0	3.9	94.6	8.4	80.3	15.0
2,4-Dinitrotoluene	69.2	6.6	67.5	14.4	82.2	11.5
Propachlor	67.9	2.4	50.4	7.9	134.5	10.6
Trifluralin	27.5	4.0	95.4	8.7	134.5	10.8
Hexachlorobenzene	43.3	2.8	70.5	12.7	66.5	6.5
Prometon	83.0	4.6	116.4	6.0	34.1	68.8
Simazine	68.9	8.6	97.4	3.7	93.5	8.1
Atrazine	78.3	5.4	120.0	4.1	103.9	13.5
Lindane	88.7	3.2	105.8	15.6	186.1	8.0
Metribuzin	57.0	3.0	86.0	6.5	71.4	4.9
Alachlor	74.6	2.8	96.5	14.1	115.7	7.8
Heptachlor	91.2	3.1	99.4	17.1	110.5	4.8
Bromacil	60.6	13.6	108.3	6.2	103.0	7.2
Aldrin	66.6	3.2	86.4	13.5	74.5	5.9
Metoachlor	84.6	4.1	111.7	13.7	114.1	5.4
Cyanazine	91.7	3.4	105.9	3.8	115.2	3.6
Heptachlor Epoxide	77.1	5.4	82.7	9.4	108.3	11.2
gamma-Chlordane	64.5	4.0	99.7	10.4	64.2	6.1
alpha-Chlordane	70.5	3.2	93.9	8.7	70.6	8.2
Butachlor	71.6	2.8	104.1	5.5	98.2	7.2
trans-Nonachlor	54.5	10.2	98.8	11.2	55.9	7.0
Dieldrin	67.0	4.0	98.8	3.4	97.8	7.2
Endrin	59.1	11.5	72.1	11.2	75.0	16.3
Methoxychlor	131.1	3.1	124.5	11.0	106.3	11.1