Canadian Journal of Chemistry
Revue canadienne de chimie

**Piston Cylinder Based Micro Liquid-Liquid Extraction with
GC-qMS for Trace Analysis of Targeted Chlorinated Organic
Compounds in Water**

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2015-0307.R1
Manuscript Type:	Article
Date Submitted by the Author:	16-Aug-2015
Complete List of Authors:	Luong, Jim; Dow Chemical Canada, Analytical Technology Center Gras, Ronda; Dow chemical Canada, Analytical Technology Center Gras, Kaelyn; University of Alberta, Science Shellie, Robert; University of Tasmania, Chemistry
Keyword:	Micro Liquid Liquid Extraction, Piston cylinder based extraction, planar microfluidics, Triple-axis detector, DB-624UI column

SCHOLARONE™
Manuscripts

Piston Cylinder Based Micro Liquid-Liquid Extraction with GC-qMS for Trace Analysis of Targeted Chlorinated Organic Compounds in Water

J. Luong^{*1,2}, R. Gras^{1,2}, K. Gras³, and R. A. Shellie²

A fast and reliable approach for the measurement of sub parts-per-billion levels of targeted chlorinated compounds like *tetrachloroethane*, *hexachloroethane*, *hexachlorobutadiene*, *pentachlorobenzene*, and *hexachlorobenzene* in various water matrices such as waste water is described. The method employed a novel piston-cylinder based micro liquid-liquid extraction technique with hexane as an extraction solvent. The device, known commercially as the Mixxor substantially accelerates extraction time by a factor of more than 100 times and reduces solvent consumption by a factor of 25 times when compared to the solvent extraction technique with wrist action mechanical agitation. A recently introduced 6% cyanopropyl phenyl 94% dimethyl polysiloxane capillary column offering a high degree of inertness was utilized for the separation of the analytes. A quadrupole mass spectrometer equipped with a triple axis detector was also employed to enhance the instrument detection limit.

With this technique, a complete separation for the analytes mentioned in water can be conducted in less than 10 min with the use of a three-port SilFlow planar microfluidic device for back-flushing. Repeatability of retention times for all compounds were found to be less than 0.04% ($n=10$). The compounds cited can be analyzed over a range from 1 ng/mL to 10 µg/mL with a detection limit and correlation coefficient of at least 0.5 ng/mL and 0.999 respectively. A relative precision of less than 1.2 % RSD ($n=20$) at the 50 ng/mL level with analyte recovery of greater than 99% ($n=3$) over a range from 10 ng/mL to 10 µg/mL was obtained.

¹ Dow Chemical Canada ULC, Highway 15, Fort Saskatchewan, Alberta, T8L 2P4, Canada

² Australian Centre for Research on Separation Science (ACROSS), University of Tasmania, Private Bag 75, Hobart, Tasmania 7001, Australia

³ University of Alberta, 116 Street and 85 Avenue, Edmonton, Alberta T6G 2R3, Canada

22

23 **Key words:**

24

25 *Micro liquid-liquid extraction, piston cylinder based extraction, DB-624UI column, planar*
26 *microfluidics, triple axis-detector*

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43 Introduction

44 Water is technically considered as a renewable resource because it can be used over and over
45 again. However, the sustainability of this renewable resource is questionable. In the next few
46 centuries it is thought that there will be a severe lack of potable water, and this effect can
47 already be observed today even though with less severity. In North America, a large
48 percentage of the population relies on groundwater as a source of potable water [1].
49 Groundwater is also being used extensively in many activities like crop irrigation,
50 manufacturing, oil and gas exploration, and in the production of crude oil from oil sands using
51 steam assisted gravity drainage (SAGD) technology [2-4]. In general, most groundwater is
52 clean, but groundwater can also become contaminated. Any addition of undesirable
53 substances to groundwater caused by human activities is considered to be contamination.
54 These undesirable substances may be caused by agricultural and industrial waste materials and
55 by-products. Prior to the 1970s, the regulation of these pollutants in North America was less
56 stringent. Therefore, they were often disposed of or stored on land where they seeped into the
57 underlying soil and were eventually carried downward, contaminating the underlying
58 groundwater [5,6]. Today, despite substantial improvements in responsible care, human
59 activities such as the production of natural gas using hydraulic fracturing process, also known as
60 “fracking”; spills from industrial operations; tars used in the construction of urban roadways;
61 urban area run-offs; and leaks from landfills can still negatively impact groundwater [7-10].
62 Groundwater contaminants come from two categories: *point sources* or *non-point sources*.
63 Graveyards, Landfills, leaking underground gasoline/diesel fuel tanks, chemicals used at wood
64 preservation facilities, sludge disposal areas at petroleum refineries, and accidental spills are

examples of potential point sources. Infiltration from farm land treated with pesticides and fertilizers and dry atmospheric fall-outs are illustrations of potential non-point sources. In all cases, groundwater often spreads the negative effects of contamination far beyond the point of origin. Using contaminated groundwater can be hazardous to public health through poisoning or the spreading of diseases. One of the classes of contaminants found in groundwater is chlorinated compounds. Some examples of chlorinated compounds are *tetrachlorethane (TCE)*, *hexachloroethane (HCE)*, *hexachlorobutadiene (HCBD)*, *pentachlorobenzene (QCB)*, and *hexachlorobenzene (HCB)*. These compounds are often encountered in the wood preservative sector or as by-products of chlorinated solvents used in dry-cleaning or degreasing businesses [11-15]. Amongst these targeted compounds, QCB and HCB have a high negative impact on human health with HCB being an animal carcinogen and considered to be a probable human carcinogen [15]. Many of the methodologies published by *The United States Environmental Protection Agency (USEPA)* can be adapted for use in the monitoring of the targeted analytes. However, these methods, like *USEPA 525.3* or *USEPA 8270D*, are geared mainly for the open characterization of a wide range of semi-volatile contaminants with an analysis time of 30 to 40 min [16,17]. In general, they can be cost ineffective to implement and maintain for routine analysis in point source monitoring. As a result, there is a need for an easy to implement, fast, and reliable method for the characterization of the compounds mentioned in water for monitoring and remediation activities.

As stated earlier, the characterization of the analytes mentioned in various matrices have been reported extensively in the literature. For instance, a common approach was the use of gas

chromatography (GC) with detectors like electron capture (ECD), flame ionization (FID), and photo-ionization (PID) [18-20]. Mass spectrometry was also employed for structural elucidation and for quantitative analysis in selected ion monitoring modes [16,17]. Common sample enrichment and clean up techniques involve the use of liquid-liquid extraction (LLE), solid phase extraction (SPE), stir-bar sorptive extraction (SBSE), and solid phase micro-extraction (SPME).

In the present article, we introduce a fast and practical ultra-trace GC method based on mass spectrometry detection in selected ion monitoring mode, capable of detecting sub parts-per-billion of the targeted analytes in groundwater for point source monitoring and remediation. We believe the present article is the first report in the literature of the use of Mixxor extraction device to extract the targeted chlorinated compounds for groundwater monitoring and remediation purposes. Separation of analytes was conducted with a recently commercialized highly inert 6% cyanopropyl phenyl 94% dimethyl polysiloxane capillary column. A mass spectrometer equipped with a triple-axis-detector (TAD) was used to improve the instrument detection limit. The use of a SilFlow three-port planar microfluidic device and a mid-point pressure source affords back-flushing to be conducted.

Experimental

An Agilent 7890B gas chromatograph (Agilent Technologies, Wilmington, USA), equipped with an Agilent 7693B auto-sampler, one ultra-inert split/splitless inlet, one pressure control module (PCM), and an Agilent 5975C Inert XL Mass Selective Detector equipped with a triple-axis-detector (TAD) and a high performance turbo pump PN# G3172A (Agilent Technologies,

Wilmington, USA) was used. The GC was also equipped with a three-port SilFlow planar microfluidic device, PN#123725 (SGE Analytical Science, Ringwood, Australia) for back-flushing purpose. **Figure 1** shows a schematic diagram of the apparatus used.

Figure 1: Schematic Diagram of the Analytical System

Gas chromatographic conditions used are as follows:

A 5 m × 0.25 mm-id × 1.4 μm DB-624UI Ultra Inert column was connected to a 25 m × 0.25 mm-id × 1.4 μm DB-624UI Ultra Inert column with a three-port SilFlow planar microfluidic device. These two columns were cut from a 30m × 0.25 mm-id × 1.4 μm DB-624UI Ultra Inert column, PN#122-1334UI (Agilent Technologies, Folsom, USA).

The column ensemble outlet flow was 2.0 mL/min Helium, in constant flow mode. The inlet pressure was 17.7 psig @ 60 °C, while the auxiliary pressure was 14.2 psig @60°C to deliver the flow required. During the back-flush state, the inlet pressure was lowered to 10.0 psig at a rate of 99.0 psig/min while the mid-point pressure was kept steady at 14.2 psig. This delivered a back-flush flow of -2.5 mL/min on the 5 m column section while maintaining a positive flow of 2.0 mL/min on the 25 m column section. The inlet temperature was 250 °C, operating in split mode at a ratio of 10:1 and equipped with an Ultra-inert liner PN# 5190-2294 (Agilent Technologies, Folsom, USA). The temperature was programmed from 60 °C (0.5 min) to 250 °C @ 20°C/min, and maintained at 250 °C for 1 min.

The mass spectrometer draw-out lens was a 3 mm standard aperture; the solvent delay time was 2.5 min, with scan range from 20 to 300 Da, a threshold of 150, a sampling rate of 3, and scan rate of 2.60/s. The quadrupole temperature was 150°C, the Inert XL ion source temperature was 250°C, the transfer line temperature was 250°C, the tune type was standard tune using perfluoro tributylamine (PFTBA) as a calibrant, with the electron multiplier gain factor set at 5 and trace ion detection set to ON. **Table 1** lists the parameters for monitoring the compounds under the simultaneous *SCAN/SIM* mode.

Chromatographic data obtained were collected using ChemStation version B.02.02.SP1 (Agilent Technologies, Waldbronn, Germany). Ultra-clean helium (99.9999%) was acquired from Air Liquide (Edmonton, Canada).

A certified mixed standard of 200 $\mu\text{g/mL}$ each of tetrachloroethane (CAS 79-34-5), hexachloroethane (CAS 67-72-1), hexachlorobutadiene (CAS 87-68-3), pentachlorobenzene (CAS 608-93-5), and hexachlorobenzene (CAS 118-74-1) in hexane was obtained from Restek Corporation (Bellefonte, USA). The rest of the standards were serially diluted with n-hexane from the certified stock standard.

Solvents such as n-hexanes (95% hexane), acetone, dichloromethane, iso-propanol, all of ACS grade, were obtained from Fisher Scientific (Edmonton, Canada). Groundwater samples were obtained from local residential areas in the county of Strathcona, Canada. A sample of water used in the “shampooing” of a car engine for the removal of transmission fluids, coolants, and brake fluids was obtained from a car engine repair and refurbishing centre in Edmonton, Canada.

A Mixxor glass extraction device, NBS PN# MXLK00002 (Haifa, Israel) with a nominal volume of 2 mL was used for the micro liquid-liquid extraction. As a liquid-liquid glass extraction device, the Mixxor has two portions: a reservoir and a vertical mixer-separator. The mixer-separator has a channel that traverses the entire length of the mixer-separator in the vertical axis. The purpose of the channel is to maximize mass transfer between the two counter-current flow fluids, with the denser chemical such as water in the outside and the less dense liquid-like n-hexane in the center of the channel [21]. From an operational standpoint, the two virtually immiscible liquids: a) water and b) n-hexane are added to the reservoir. The phases are thoroughly mixed by moving the mixer-separator in and out of the reservoir. Once the extraction is completed,

the upper phase (n-hexane) is removed with a Pasteur glass pipette by removing the vessel cap, pushing the mixer-separator down to a point where the lower phase reaches the top part of the channel, and locking in place the position of the mixer-separator with the Teflon locking collar provided. The principle of operation of the Mixxor is graphically depicted in **Figure 1S** (*supplementary materials*).

In terms of sample preparation, 2 mL of a water sample was first filtered with a 0.2 μm nylon filter for particulate removal and transferred directly into the extraction vessel. 400 μL of hexane was subsequently added to the vessel with an Eppendorf automated pipette to carry out the extraction. The sample was extracted for 1 min with 15 strokes and allowed to settle. A 200 μL aliquot of the top layer (hexane) was transferred to a 2 mL auto-sampler vial equipped with a 250 μL limited volume insert (Agilent Technologies, Delaware, USA) for analysis. 1 μL of the sample was injected into the gas chromatograph with the syringe rinsed twice before and twice after the injection with n-hexane.

For liquid-liquid extraction with mechanical agitation experiments, 50 mL of the aqueous sample was extracted with 10 mL of hexane in a 100 mL I-Chem vial. The vial was shaken with a Burrell wrist action mechanical shaker model 75 (Pittsburgh, PA, USA) for a pre-determined amount of time as stated in the Results and Discussions section. Once the extraction was completed and a clear phase separation was obtained, 1.5 mL of hexane (top layer) was transferred to a 2 mL auto-sampler vial for analysis. 1 μL of the sample was injected into the

gas chromatograph with the syringe rinsed twice before and twice after the injection with n-hexane.

Results and Discussions

Various extraction techniques like liquid-liquid solvent extraction (LLE), solid phase extraction (SPE), solid phase micro-extraction (SPME), stir-bar sorptive extraction (SBSE) have been reported in the extraction of chlorinated compounds from aqueous matrices like potable water, groundwater, river water, municipal and industrial wastewater to name a few [16,17,20,22]. A rate determining step associated with the techniques is the extraction time to achieve adequate extraction efficiency. As such, sample preparation tends to be the biggest bottleneck for the analytical workflow. This constraint can not only hinder the overall sample throughput, but also delay the availability of analytical results, critical for making informed and data-driven decisions in the event of a spill or an emergency. In the present article, we introduced a fast liquid-liquid extraction approach to expediently and efficiently extract the analytes from the water matrix. The fast micro liquid-liquid extraction approach was based on the piston-extraction principle as described by *Cais and Shimoni* as the Mixxor [21,23].

The extraction efficiency of targeted chlorinated compounds with the Mixxor device was compared to a standard technique such as solvent extraction with wrist action mechanical agitation. With a “stroke” rate of 15 strokes per min, in 1 min extraction, recoveries of greater than 98% were obtained for all the analytes over a range of concentrations from 1 ng/mL to 10

$\mu\text{g/mL}$. In contrast, with the same solvent, it took almost 120 min for the solvent extraction with mechanical agitation technique to achieve the same rate of recovery. **Figure 2** plots the results obtained for HCB using the two techniques with a 100 $\mu\text{g/mL}$ mixed standard. Similar results were also obtained for the rest of the analytes.

Figure 2: Extraction efficiency of 100 $\mu\text{g/mL}$ HCB in a mixed standard using Mixxor and LLE/Mechanical agitation technology

Figure 3 shows an overlay of reconstructed chromatograms of two extractions of a 8 µg/mL each of TCE, HCE, HCB, QCB, and HCB standard mixture compared to a system blank extraction. As shown in **Figure 3**, respectable chromatographic performance was obtained with no carry over detected under the conditions used.

Figure 3: Overlay of reconstructed chromatograms of two extractions of 8 µg/mL each of TCE, HCE, HCB, QCB, and HCB standard mixture (black and blue traces) compared to a system blank extraction (red trace).

Parameters that have been optimized for the application include the number of strokes/unit of time, the length of time required to achieve the highest level of extraction efficiency for the

target compounds, the ratio of volume of sample to the volume of extraction solvent, the type of extraction solvents including hexane, hexane/acetone, and dichloromethane. The manufacturer of the Mixxor had recommended 4-7 strokes/min for a complete extraction. 15 strokes/min was found to be ideal to achieve reliable and reproducible extraction performance. Less than 0.2 mL of the solvent use for extraction is not recommended as this might cause difficulty in removing the solvent from the extraction vessel once the extraction is completed. A larger amount of solvent can be used with the reduction of sample size to prevent the overfilling of the extraction vessel. As expected, with a larger amount of solvent used, the concentration factor of the analyte also decreases accordingly.

With a 2 mL Mixxor extraction vessel and hexane as an extraction solvent, the optimal conditions were 15 strokes/min for 1 min and a sample-to-solvent ratio of 2 mL to 0.4 mL. 0.4 mL of solvent was employed with this technique. The minimal amount of solvent helped in minimizing both solvent cost and more significantly, the cost of used solvent disposal. Further, with the analyte being concentrated five times by the sample-to-solvent ratio, this substantially improved the method detection limit. The method is 120 times faster and 25 times less in solvent use when compared to an in-house solvent extraction technique with wrist action mechanical agitation; adapted from USEPA SW-846 sample preparation protocols [24].

A newly commercialized inert capillary column technology was evaluated with critical industrial applications including the separation of the analytes mentioned [25]. Based on 6% cyanopropyl phenyl and 94% dimethyl polysiloxane, the DB-624UI Ultra Inert offers some important

performance advantages in that its polymer structure facilitates immobilization via both cross-linking and surface bonding, and the polymer used as a stationary phase is clean, free of any monomers and catalysts. The unique selectivity of this stationary phase affords excellent separation of the target compounds as well as other known chlorinated overlapping pairs that would have co-eluted on a 100% dimethyl polysiloxane stationary phase like *1,1,2-trichloroethylene* and *bromodichloroethane*, and on a 14% cyanopropyl phenyl 86% dimethyl polysiloxane stationary phase (DB-1701) like *chloroform* and *1,2-dichloroethane* [25-27]. This column stationary phase was found to be highly suitable for use with chlorinated compound analysis with a respectable thermal stability temperature of up to 260 °C [25-27]. **Figure 4** shows an overlay of reconstructed chromatograms with a duplicate analysis of a 2.5 ng/mL standard mixture in SIM mode, demonstrating peak symmetries for all compounds of greater than 0.98 based on UPS tailing factor with a low column bleed profile at elevated temperature. As a result, this column technology was selected for the application described. As shown in **Figure 4**, there was a step change in the baseline at 4.9 min as a result of column flow change when back-flush was initiated. However, this baseline change does not interfere with the measurement of the analytes of interest. Also, other compounds with *m/z* of 83 Da between *t_r* of 3.0 to 3.8 min were detected between tetrachloroethane and hexachloroethane. These are hydrocarbons in the solvent used for extraction. As stated earlier in the experimental section, the solvent used is hexanes with 95% hexane purity.

Figure 4: Overlay of reconstructed chromatograms of a duplicate analysis of 2.5 ng/mL each of a mixed standard in SIM mode.

In this application, a TAD and a triple channel electron multiplier for the mass spectrometer were employed to improve instrument detection limit (IDL). The triple-axis orientation placed the high energy dynode-electron multiplier (HED-EM) doubly off-axis from the axis of the transmission quadrupole. The instrument design change afforded ion collection to be maximized which led to an increased signal for the analyte while neutral noise to be reduced below standard off-axis detector [28]. The net result was an improvement in IDL as evidenced in the low detection limits attained for the analytes involved.

Despite the high degree of selectivity provided by the extraction solvent, if present in the sample, residual high molecular weight organic compounds such as anti-foaming agents and surfactants can be found in the hexanes extract along with the analytes of interest. A simple technique was implemented to minimize the issue encountered. This involved the use of a short 5 m column coupled to a 25 m column with a SilFlow three-port planar microfluidic device. A mid-point pressure was introduced via the PCM module. **Figure 1** shows the configuration employed. The 5 m column acted as a guard column with the main purpose of retaining heavier components. Once the analytes of interest reached the 25m column, the inlet pressure was decreased to 10.0 psig with the mid-point pressure maintained at 14.2 psig. Residual high molecular weight organic materials such as anti-foam agents, surfactants, if they exist in the sample, are back-flushed to vent while separation of the analytes continues on the 25 m column. The incorporation of back-flushing improves sample throughput. Further, with back-flushing, extensive exposure of the stationary phase to excessive temperature programming to remove the residual material/matrix can be reduced substantially [29]. With this design, a complete analysis can be conducted in less than 10 min.

The chromatographic performance of the system was found to be reliable under the conditions established. Reproducibility of retention times for all compounds were found to be less than 0.04% ($n=10$). The compounds cited can be analyzed over a range from 1 ng/mL to 10 µg/mL with detection limits of 0.5 ng/mL each for tetrachloroethane, hexachloroethane, hexachlorobutadiene, 0.2 ng/mL for pentachlorobenzene and hexachlorobenze, and correlation coefficients of at least 0.999 for all analytes. A relative precision of less than 1.2 % RSD ($n=20$)

at 10 ng/mL level with analyte recovery of greater than 99% ($n=3$) over a range from 10 ng/mL to 10 $\mu\text{g/mL}$ were obtained. **Figure 5** shows an overlay of reconstructed chromatograms of groundwater known to be uncontaminated versus a sample of the same groundwater spiked with 0.5 ng/mL each of the targeted compounds. As illustrated in **Figure 5**, no detectable amount of the targeted compound was found in the uncontaminated groundwater while the presence of the targeted compounds in the spiked sample was accurately identified and quantitated.

Figure 5: An overlay of reconstructed chromatograms of a groundwater sample known to be uncontaminated (blue trace) and a duplicate of the same sample spiked with 0.5 ng/mL each of a mixed chlorinated standard (red and black trace)

Figure 6 shows a reconstructed chromatogram of a recycled water sample taken from a local car engine repair/rebuilding centre where car engines are often “shampooed” with commercially available degreasers after engine repair work. Shampooing the engines is needed to remove engine oils, transmission fluids, and anti-freezes as these chemicals can damage engine seals and gaskets upon prolonged contact. No chlorobenzenes or hexachlorobutadiene were detected in the sample, while the presence of tetrachloroethane and hexachloroethane were positively identified. This demonstrated the utility of the method, not only capable of analyzing the targeted compounds in groundwater for point source monitoring and remediation, but also it can be leveraged for use in the characterization of the analytes in water from other sources.

Figure 6: Reconstructed chromatogram of a recycled water sample taken from a local car engine repair/rebuilding centre where car engines are often

333

334 **Conclusions**

335 A fast and practical analytical approach has been successfully developed and implemented for
336 the determination of parts-per-billion levels of TCE, HCE, HCB, QCB, and HCB in water for
337 point source monitoring and remediation. A completed analysis can be completed in less than
338 10 minutes. The use of piston-cylinder based micro liquid-liquid extraction technique
339 substantially accelerates extraction time (by a factor of more than 100 times) and decreases
340 solvent consumption (by a factor of 25 times) when compared to conventional solvent
341 extraction technique with mechanical agitation. The use of an inert and low bleed capillary
342 column in combination with a triple-axis-detector enhanced IDL.

343 **Acknowledgements**

344 We dedicate this manuscript to Dr. Martine Stolk on the occasion of her retirement from the
345 Dow Chemical Company. The authors would like to express their gratitude to Martine for her
346 leadership, for her effort in promoting science and technology, and for her passion in cultivating
347 the next generation of chromatographers.

348

349 Dr. JD Tate, and Dr. Matthias Pursch, Analytical Technology Center are acknowledged for their
350 support and help in preparing the manuscript. Dr. Gary Lee and Dr. Allen Vickers of *Agilent*
351 *Technologies* are acknowledged for providing the pre-commercialized DB-624UI columns for
352 evaluation.

353

354 Robert Shellie is the recipient of an Australian Research Council Australian Research Fellowship
355 (project number DP110104923).

356

Draft

357 **References**

- 358 1. Harris, P. *Environ. Geol.*, **1995**, 26, 262-268.
- 359 2. Pionke, H.; Urban, J., *Groundwater*, **1985**, 23, 68-80.
- 360 3. Ayars, J.; Christen, E.; Soppe, R.; Meyer, W. *Irrig. Sci.*, **2006**, 24, 147-160.
- 361 4. Barson, D.; Bachu, S.; Esslinger, P. *B. Can. Petrol. Geol.*, **2001**, 49, 376-392.
- 362 5. Sudicky, E.; Cherry, J.; Fry, E. *J. Hydrol.*, **1983**, 63, 81-87.
- 363 6. Barnes, K.; Christenson, S.; Kolpin, D.; Focazio, M.; Furlong, E.; Zaugg, S.; Meyer, M.; Barber,
364 L. *Ground Water Monit. R.*, **2004**, 24, 119-126.
- 365 7. Baccante, D. *Fisheries*, **2012**, 37, 40-41.
- 366 8. Abrams, R.; Loague, K., *Hydrogeol. J.*, **2000**, 8, 594-607.
- 367 9. Gibert, O; Ferguson, A.; Kalin, R.; Doherty, R.; Dickson, K.; McGeough, K.; Robinson, J.;
368 Thomas, R. *Environ. Sci. Technol.*, **2007**, 41, 6795-6801.
- 369 10. Singh, U; Kumar, M; Chauhan, R.; Jha, P.; Ramanathan, A.; Subramanian, V. *Environ. Monit.*
370 *Assess.*, **2008**, 141, 309-321.
- 371 11. Mendoca, R. *Br. J. Ind. Med.*, **1963**, 20, 50-56.
- 372 12. Selden, A.; Nygren, Y.; Westberg, H.; Bodin, L. *Occup. Environ. Med.*, **1997**, 54, 613-618.
- 373 13. Kogan, L. *Russian Chemical Reviews*, **1964**, 33, 176-188.
- 374 14. Carrizo, D.; Grimalt, J. Fito, N.; Torrent, M.; Sunyer, J. *Ecotox. Environ. Safe*, **2008**, 71, 260-
375 266.
- 376 15. Bailey, R. *Chemosphere*, **2001**, 43, 167-182.
- 377 16. USEPA, Method 525.3, *Determination of semi-volatile organic chemicals in drinking water*
378 *by solid phase extraction and capillary column gas chromatography/mass spectrometry*

(GC/MS), Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio, Revision 1.0, February 2012.

17. USEPA, Method 8270D, *Semi-volatile organic compounds by gas chromatography/mass spectrometry (GC/MS)*, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio, Revision 4.0, February 2007.

18. Driscoll, J.; Atwood, E. *J. Chromatogr. A*, **1993**, 642, 435-443.

19. de Wit, J.; Jorgenson, J. *J. Chromatogr. A*, **1987**, 411, 201-212.

20. Eisert, R.; Levsen, K. *J. Chromatogr. A*, **1996**, 733, 143-157.

21. Peleg, I.; Vromen, S. *Chem. Ind.*, **1983**, 15, 615-616.

22. Popp, P.; Bauer, C.; Hauser, B.; Keil, P.; Wennrich, L. *J. Sep. Sci.*, **2003**, 26, 961-967.

23. Cais, M.; Shimoni, M. US patent# 4,545,231, 12.06.1984.

24. USEPA, Method SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, Environmental Monitoring Systems Laboratory, Office of Research and Development, USEPA, Cincinnati, Ohio, Revision 6.0, February 2007.

25. Gras, K.; Gras, R.; Luong, J.; Hayward, T. in CASSS (Ed.), *Proceedings of the 37th International Symposium on Capillary Chromatography, Poster*, Palm Springs, CA, CASSS Publisher, 2013.

26. Gras, K.; Gras, R.; Luong, J.; Lee, G.; Vickers, *Agilent J&W DB-624 UI Ultra Inert GC Capillary Column for Challenging Industrial Applications*, Agilent Publication 5991-5197EN, November 2014.

27. Gras, K.; Gras, R.; Luong, J.; Cortes, H.J.; Shellie, R.A. *J. Chromatogr. A*, **2014**, 1362, 43-48.

28. Prest, H.; Foote, J. *The Triple-Axis-Detector – Attributes and Operating Advice*, Agilent Technologies, Publication 5989-7655N, January 2008.

401 29. Klee, M. *J. Sep. Sci.*, **2009**, 32, 88-98.

402

403

Draft

404 **Table 1:** Parameters for Monitoring Target Compounds by GC-MS with Triple-Axis-Detector

Compound	Time (min)		Target Ion (Da)	Qualifier Ions (Da)
	t_r (min)	SIM Start Time (min) Dwell: 100 ms		
Tetrachloroethane (TCE)	2.75	2.55	83	117,133
Hexachloroethane (HCE)	4.00	3.80	117	199,201
Hexachlorobutadiene (HCBd)	5.01	4.80	225	223,227
Pentachlorobenzene (QCB)	7.13	6.90	250	215,252
Hexachlorobenzene (HCB)	8.27	8.00	284	142,249

405