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Valve-based comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection: instrumentation and figures-of-merit

Amanda E. Sinha [a], Bryan J. Prazen [a], Carlos G. Fraga [b], Robert E. Synovec [a,*]

[a] *Center for Process Analytical Chemistry, Department of Chemistry, Box 351700, University of Washington, Seattle, WA 98195-1700, USA*
[b] *Department of Chemistry, 2355 Fairchild Dr. Suite 2N225, United States Air Force Academy, Colorado Springs, CO 80840-6230, USA*

Abstract

A valve-based comprehensive two-dimensional gas chromatograph coupled to a time-of-flight mass spectrometer (GC × GC/TOFMS) is demonstrated. The performance characteristics of the instrument were evaluated using a complex sample containing a mixture of fuel components, natural products, and organo-phosphorous compounds. The valve-based GC × GC, designed to function with an extended temperature of operation range, is shown to have high chromatographic resolution, high separation efficiency and low detection limits. Typical peak widths at base are nominally from 100 to 300 ms on column 2 and nominally 10 s on column 1. The injected mass and injected concentration limit of detection (LOD), defined as 3 standard deviations above the mean baseline noise, for three organo-phosphorous compounds (triethylphosphorothioate (TEPT), dimethyl methyl phosphonate (DMMP) and dimethyl phosphite (DMP)) in a complex environmental sample were from 6 to 38 pg, and 3 to 17 ng/ml, respectively. The temperature program for the environmental sample ranged from 40 to 230 °C, a temperature range capable of analyzing semi-volatile compounds. A new compact, stand-alone, valve-pulse generator device has been implemented and is also reported. The valve-based GC × GC instrument, therefore, offers a simple, rugged and less expensive alternative to thermally modulated instruments.

Keywords: Gas chromatography, comprehensive two-dimensional; Mass spectrometry; Modulator, valve-based; Time-of-flight mass spectrometry; Instrumentation; Triethylphosphorothioate; Dimethyl methyl phosphonate; Dimethyl phosphite

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is now a widely accepted powerful technique to analyze complex chemical mixtures and natural products such as petrochemicals, essential oils, fatty acids, and environmental pollutants [1–16]. While the basic concept of comprehensive two-dimensional separations was laid out by Giddings [17,18], a recent summary of the state of comprehensive two-dimensional separations by Liu and Lee demonstrates how ubiquitous two-dimensional separations have become [19]. The heart of a GC × GC instrument is a sample modulator that interfaces two chromatographic columns. The modulator injects

* Corresponding author. Tel.: +1-206-685-2328; fax: +1-206-685-8665.
E-mail address: synovec@chem.washington.edu (R.E. Synovec).

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aliquots of the first column effluent onto the second column at rapid intervals. In practice, the sampling rate for a comprehensive two-dimensional separation should be such that all the components in the sample are analyzed by the second separation even if the entire injected volume is not analyzed [20,21]. In addition, peak shapes and resolution in the first separation should also be preserved in the comprehensive two-dimensional separation, which can be achieved by sampling the first dimension a minimum of three to four times per peak [22]. The first chromatographic column is the longer of the two columns, and often has a non-polar stationary phase resulting in a separation based primarily on boiling point. The second column is shorter, often with a polar stationary phase resulting in a separation based on relative polarity of the components. Thus, GC × GC separations utilize two columns providing complementary separations, which ultimately produce a separation space with a high degree of informational orthogonality [23–25]. This leads to a greatly enhanced utilization of the available peak capacity, which is ideally equal to the multiplicative product of the peak capacity for each dimension [26]. GC × GC is therefore considered more powerful and, in many instances, less time consuming than traditional one-dimensional GC. With the exception of a few reports [27–31], most GC × GC is done with flame ionization detection (FID). In this study we report the development and evaluation of a valve-based GC×GC coupled to a time-of-flight mass spectrometer (TOFMS).

Two categories cover the different approaches for GC × GC modulation: thermal modulators and valve-based modulators. Most GC × GC instruments employ thermal modulation [32–39], but there are a growing number of valve-based GC × GC instruments [5,16,40–43]. One recent advance in valve-based GC × GC instrumentation was adaptation of a new valve-placement that extends the working temperature range of valve-based instruments to ∼250 °C, which is 75 °C above the manufacturer's specified temperature limit of the valve [43]. This advance has extended the applicability of valve-based GC × GC instruments to semi-volatile components [44]. Utilization of this new high-temperature configuration is reported in this paper, in conjunction with TOFMS detection, for the analysis of selected components in a complex environmental sample. Valve-based GC × GC instruments offer a simple, rugged and less expensive alternative to thermally modulated units and have the potential to be portable. A recent instrumentation advance also reported in this paper includes a stand-alone pulse generator to power and control the valve that eliminates the need for a computer and LabView software to drive the valve-based modulator. This development reduces the cost of the valve-based GC × GC and provides an opportunity to simplify the construction of a field-portable GC × GC.

This paper is the first report of a GC × GC/TOFMS using a valve-based modulator. By coupling mass spectrometry to GC × GC, identification of components is possible using mass spectral database searches or a handful of highly selective ions for specific components. Conclusive identification of analytes without the use of standards is often not possible with commonly used universal detectors such as flame ionization detection. The most common types of mass spectrometers for GC detection have been quadrupole instruments. The scanning speed of most quadrupole mass selective detectors (MSD) (∼0.5 s for *m*/*z* 40–400) [45] is not fast enough to use as a detector for GC × GC instruments in which the second column peak widths are routinely around 100 ms. GC × GC with MSD can be used for qualitative analysis using limited mass range scanning, but the precision of the quantitative analysis is compromised at the slow scanning rate. Recently available TOFMS analyzers that are able to store 500 full spectra per second are perfectly suited for GC × GC detection and have been demonstrated with thermal modulation instruments [27–31]. The pressure and flow conditions for thermal modulation and valve-based GC × GC instruments are substantially different providing some unique coupling challenges for valve-based instruments to TOFMS detectors. Therefore, the development and evaluation of a valve-based GC × GC/TOFMS instrument is reported herein. A complex environmental sample was analyzed to investigate the separation and performance characteristics of this novel system.

2. Experimental

An Agilent 6890 Gas Chromatograph equipped with an Agilent 7683 Auto-injector (Agilent Technologies,

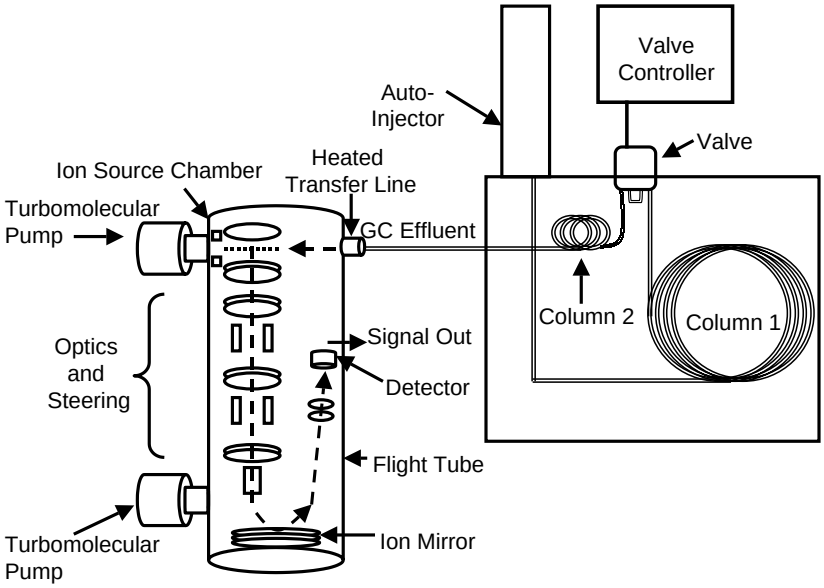

Fig. 1. Valve-based GC × GC/TOFMS instrument schematic. Both columns are housed inside the same oven. A stand-alone pulse generator (valve controller) is utilized in the system to simplify the instrumentation and to promote portability. Modulation occurs via a sample loop on a six-port high-speed mini-diaphragm valve.

Palo Alto, CA, USA) was modified to a valve-based GC × GC by mounting the wetted portions of the high-speed six-port micro diaphragm valve (VICI, Valco Instruments Co. Inc., Houston, TX, USA) inside the oven and the remaining portions outside the oven [43]. The second column was connected to a LECO Pegasus III TOFMS (LECO Corporation, St. Joseph, MI, USA) via the heated transfer line (Fig. 1). A GC × GC/TOFMS analysis was performed on a complex environmental sample. The environmental sample, an acetone extract from a contaminated landfill site of a proprietary nature, originally contained a mixture of fuel components and natural products. Three organo-phosphorous pesticides: triethylphosphorothioate (TEPT) (Accu-Standard Inc., New Haven, CT, USA), dimethyl methyl phosphonate (DMMP) (Sigma–Aldrich, St. Louis, MO, USA), and dimethyl phosphite (DMP) (Sigma–Aldrich) were spiked into the environmental sample. These compounds can sometimes be found in similar environmental samples; however, they were not detected prior to addition in this particular sample.

The first column of the GC × GC/TOFMS was a 60 m × 250 μm i.d. capillary column with a 0.5 μm 5% diphenyl/95% dimethyl polysiloxane film (DB-5; J&W Scientific/Agilent Technologies). The second column was a 3 m × 180 μm i.d. capillary column with a 0.05 μm 90% biscyanopropyl/10% phenylcyanopropyl film (RTX-2330; Restek Corp., Bellfonte, PA, USA). Helium was used as the carrier gas. Column 1 was operated with a constant flow of 1.0 ml/min. Column 2 was operated with a constant pressure of 138 kPa. The injector set point was 275 °C and 2.0 μl injections of the sample were split-less for 0.5 min. The oven was held at 40 °C for 0.5 min, ramped to 80 at 20 °C/min, ramped to 210 at 5 °C/min, then ramped to 230 at 20 °C/min and held for 4 min. The valve coupling columns 1–2 was equipped with a 5 μl sample loop and actuated every 2.5 s with a 60 ms injection pulse width. Under these experimental conditions, it is estimated that 10% of the sample is transferred from the first column to the second column. Essentially, this is equivalent to a 1:10 split at the injector onto column 1. A stand-alone pulse generator that was designed and built in-house

was used to control the valve actuation (valve controller in Fig. 1). This new hardware allows the user to set the pulse width, the period of the actuations, and the total duration of the analysis. This new development in the valve-based GC × GC instrument replaces the LabView program and counter/timer board thus reducing the cost and enabling field-portability. The mass spectrometer had a transfer line temperature of 250 °C and an ion source temperature of 200 °C. The filament bias voltage was −70 V and the detector voltage was −2000 V. All other MS parameters were set from the results of an automatic optimization sequence controlled by the LECO software using perfluorotributylamine (PFTBA) as the standard. Data were collected from *m/z* 40–300 at a nominal rate of 5 kHz and averaged to 50 full spectra/s by the LECO software, resulting in more than 4 mass spectra per second dimension peak (column 2). Data were then exported as a comma separated value (csv) file and loaded into Matlab 6.0 R12 (The Mathworks, Natick, MA, USA) for data processing.

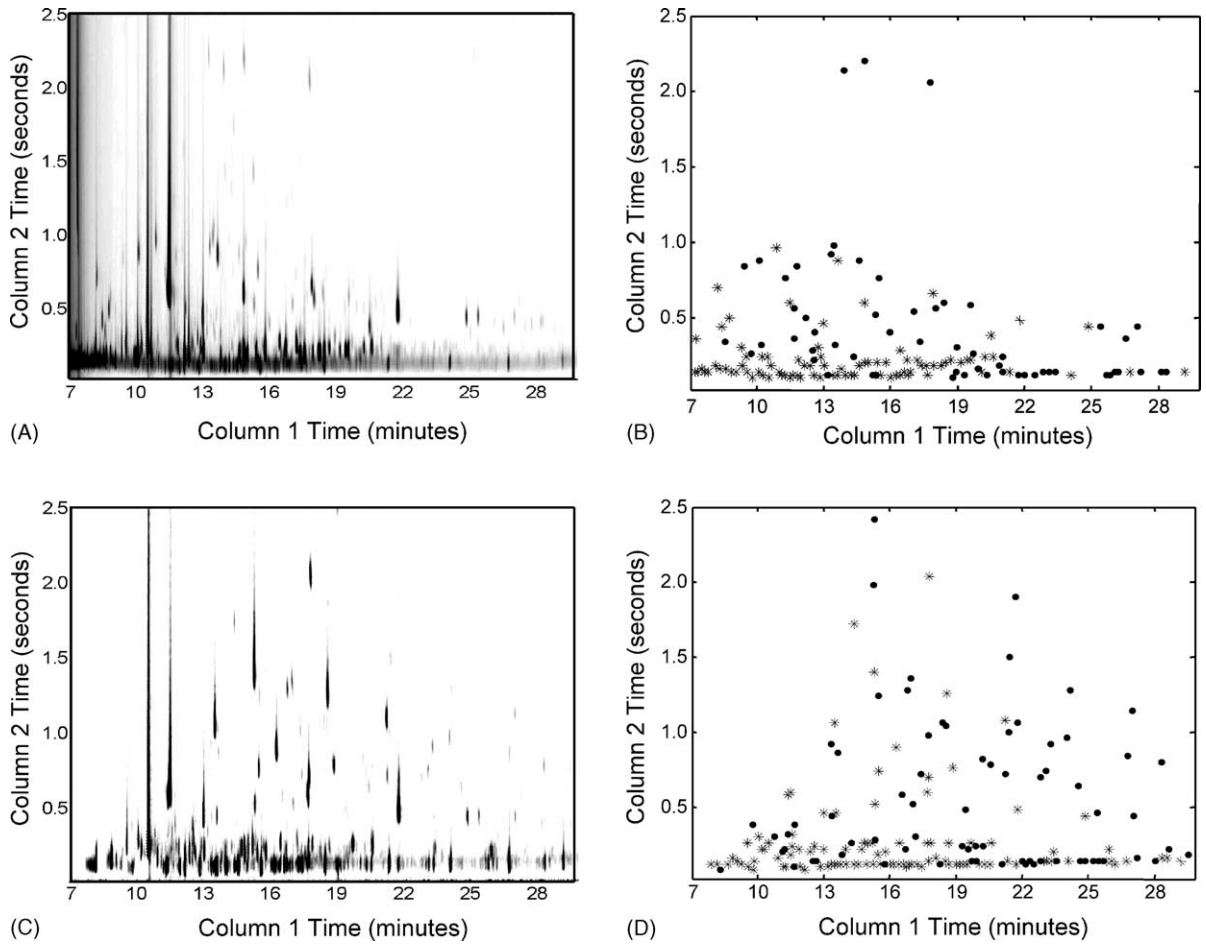

Fig. 2. (A) TIC chromatogram of a complex environmental sample. (B) Peak locations of the total ion current chromatogram generated with a program that identifies local peak maxima: (∗) indicates peaks of heights 40–100% of the maximum peak height (i.e. largest peak in the chromatogram), and (●) indicates peaks with heights 5σ to 40% of the maximum peak height. (C) Chromatogram of *m/z* 99. This demonstrates the selectivity of GC × GC/TOFMS in that this chromatogram and the TIC have very different peak distributions. (D) Peak locations of the chromatogram of *m/z* 99 generated with a program that identifies local peak maxima: (∗) indicates peaks of heights 40–100% of the maximum peak height, and (●) indicates peaks with heights 5σ to 40% of the maximum peak height.

3. Results and discussion

Fig. 2A depicts the two-dimensional total ion current (TIC) chromatogram for the environmental sample analyzed for the purpose of investigating instrumental performance. The complexity of the sample was such that a 30 min first column separation time was required. A column 2 separation time of 2.5 s was used. The column 2 flow rate is constrained by the 10 ml/min maximum flow allowed for the TOFMS. With these parameters, at least four injections onto column 2 during the elution of a peak from column 1 were achieved. Since the TIC is a sum of all of the mass channels at each point in the two-dimensional separation space, only the largest peaks are visible in this image. Note that high-concentration compounds eluting at about 11–12 min overload column 2, resulting in the broad peaks with apparent breakthrough. A peak location plot for the TIC is shown in Fig. 2B. The TIC plot was generated by an algorithm written in-house that locates and marks peak maxima. A representative GC × GC chromatogram and a peak locator plot of *m*/*z* 99 for this sample are shown in Fig. 2C and D in order to further illustrate the sample complexity and near-full use of available peak capacity. It can be seen that the individual *m*/*z* 99 mass channel and the TIC chromatograms exhibit different patterns of peaks. It can also be seen from *m*/*z* 99 that there are peaks filling a large percentage of the separation space. The peak capacity of this separation space was estimated to be ∼2000 using a resolution of 1. The *m*/*z* 99 chromatogram was chosen, because it contains a pattern of peaks that are not seen in the TIC chromatogram, further illustrating the use of nearly all the available peak capacity. Other mass channels exhibit different peak patterns emphasizing the high selectivity of GC × GC/TOFMS and extreme complexity of this sample, but were not shown for brevity.

Fig. 3 is a sub-region of the TIC chromatogram containing approximately 20 peaks. This figure illustrates the separation efficiency of the valve-based GC × GC coupled with TOFMS in greater detail than the previous figures. As can seen in Fig. 3, the nominal peak widths at the base in the column 2 dimension are from 100 to 300 ms, thus indicating an efficient column 2 separation, similar to what is achieved with thermal modulation-based GC × GC systems.

The injected mass and injected concentration limit of detection (LOD) for three organo-phosphorous compounds (TEPT, DMMP, DMP), were determined (see Table 1) using the standard addition method by spiking known amounts of the pure components into

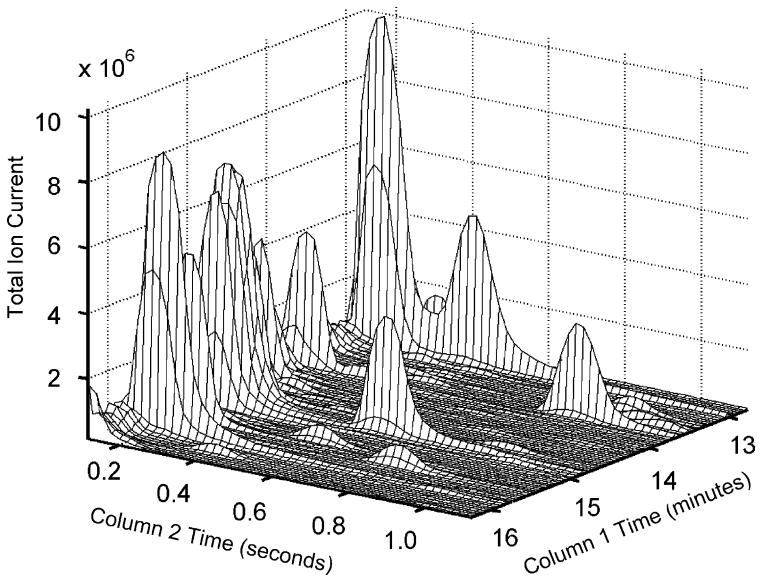

Fig. 3. Subsection of the environmental sample GC × GC chromatogram illustrating separation efficiency and resolution. Note that the axis is rotated to make more peaks visible.

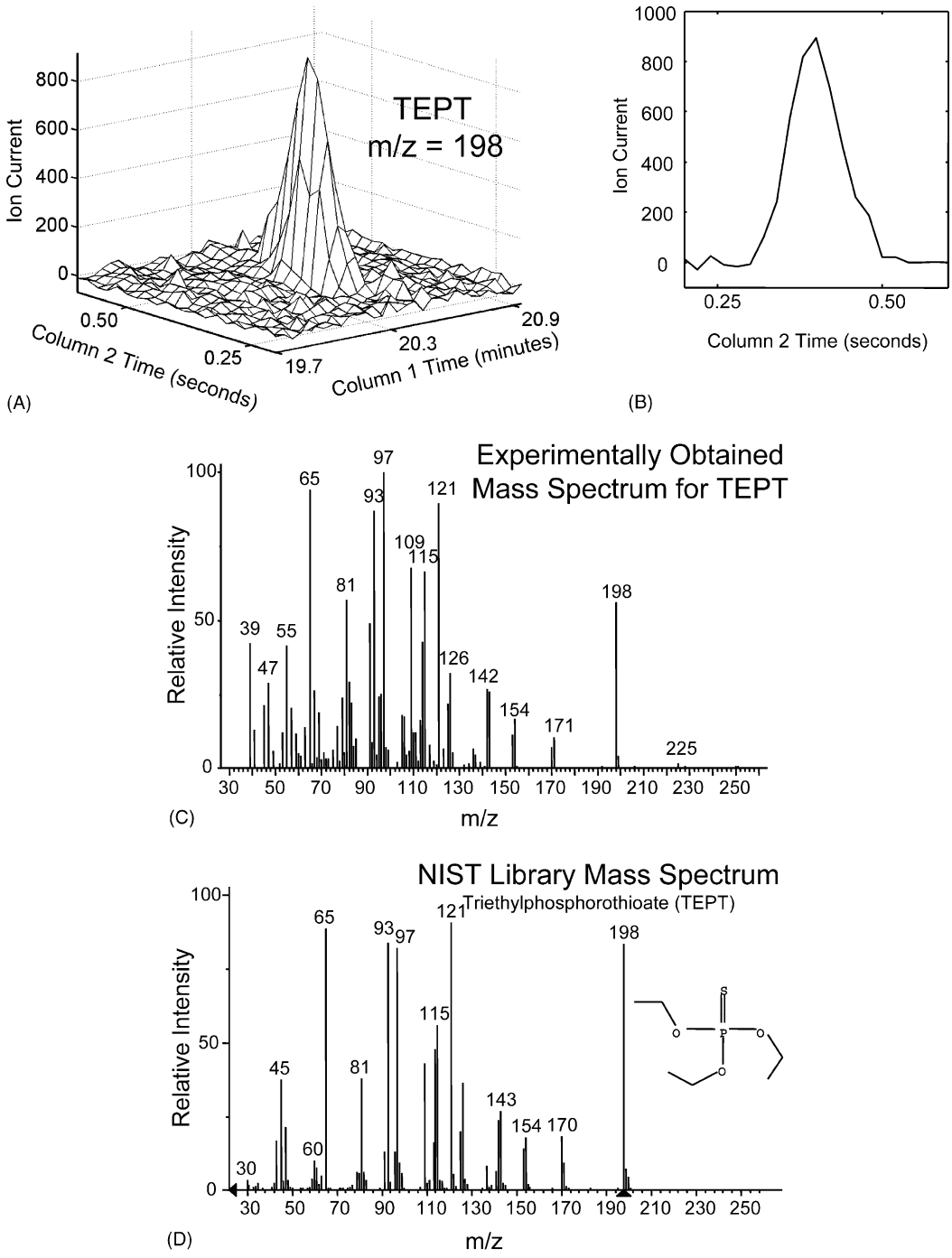

Fig. 4. (A) 3D region of chromatogram of *m*/*z* 198 of TEPT peak at an injected concentration of 70 ng/ml. (B) Highest second column chromatogram of *m*/*z* 198 for the TEPT peak. LOD was calculated at 3σ using an average of the standard deviations of four adjacent column 2 chromatograms consisting entirely of baseline noise. The LOD was calculated to be 3 ng/ml. (C) Experimentally obtained spectrum of TEPT at 70 ng/ml. (D) NIST library matched spectrum for TEPT.

Table 1
Analytical figures-of-merit for three organo-phosphorous pesticides: triethylphosphorothioate (TEPT), dimethyl methyl phosphonate (DMMP), and dimethyl phosphite (DMP) determined from three replicate samples analyzed with standard addition

Analyte	*m*/*z*	Concentration (ng/ml) injected	Column 1 retention time (min)	Column 2 retention time (s)	Column 1 width (s)	Column 2 width (ms)	LOD (3σ) (ng/ml)	LOD (3σ) (pg)
DMP	47	878	10.51 ± 0.02	1.037 ± 0.005	7.4 ± 0.6	218 ± 10	17 ± 3	38 ± 6
DMMP	94	273	12.25 ± 0	1.04 ± 0	7.4 ± 0.7	293 ± 50	7 ± 1	14 ± 2
TEPT	198	70	20.38 ± 0	0.403 ± 0.005	8.8 ± 0.5	156 ± 19	3.2 ± 0.2	6.4 ± 0.4

Concentrations of the analytes of interest ranged from 25 to 50 times the LOD. The limit of detection was determined from the peak height of the maximum column 2 chromatogram and three times the average standard deviation of four adjacent rows of noise. The *m*/*z* used for quantitation was the most abundant and/or selective ion for each analyte. The limit of detection is listed in concentration injected and in absolute mass injected for a 2 μl injection. Peak widths were measured at peak base. For each entry the standard deviation is also indicated.

the environmental sample. The locations of the target compounds are not directly identified in any of the GC × GC plots in Fig. 2, however their retention times are listed in Table 1. Three replicate data sets were collected in order to gauge the reproducibility of the instrument. The LOD is based on the most abundant and/or the most selective mass channels for each analyte (Table 1). The three-dimensional signal region for *m*/*z* 198 containing TEPT is shown in Fig. 4A. The signal intensity was determined as the height of the largest column 2 peak above the mean baseline (Fig. 4B). The LOD for each analyte was defined as 3σ, where σ was determined from the average standard deviation of four column 2 chromatograms (i.e. sections of baseline, absent of peaks) adjacent to the peak consisting only of baseline noise. The injected mass and injected concentration LODs were from 6 to 38 pg, and 3 to 17 ng/ml, respectively. This LOD range is comparable to results recently reported using thermal modulation GC × GC/TOFMS [29] for trace analysis.

An experimentally obtained mass spectrum for TEPT at ∼25 times the LOD and the resultant identity search NIST library spectrum show a significant degree of similarity even at such a low concentration (Fig. 4C and D). There are multiple factors that one can use to evaluate the quality of a spectral match in the NIST MS Search program. The match factor evaluates how closely the target spectrum and the database spectrum correlate. It is calculated by taking the inner product of the two spectra, with lower *m*/*z* peaks having less weight than higher *m*/*z* peaks. Values are reported on a scale from 1 to 1000 where a perfect match is 1000. The reverse match factor ignores impurity peaks in the experimental spectrum, that is, peaks that are not present in the library spectrum. This is also reported on a scale of 1–1000. The probability of the unknown spectrum arising from the same compound that generated the library spectrum is listed on a scale from 1 to 100. For the experimental spectrum of TEPT (Fig. 4C), a library search resulted in a match value of 735, a reverse match of 793, and a probability of 78.7. Extracted spectra at higher concentrations of TEPT result in higher match factors, but considering the low concentration the spectral match quality is very high. Along with the speed that makes TOFMS amenable to GC × GC detection, the added selectivity of full spectral detection lends more credence to analyte identification. Mass spectral analysis of the other two pesticides was also successful with the results not shown for brevity. If an analyst requires higher match values, it may be prudent to design your own library with analyte standards. This would minimize spectral variation due to differences in the ionization source for the NIST system relative to the TOFMS in use. Indeed, ionization source difference is the cause for the match values with the TEPT study falling below the ideal.

4. Conclusions

It was demonstrated that valve-based GC × GC/TOFMS is a selective and sensitive instrument for the analysis of complex samples. Detection limits for organo-phosphorous compounds in a complex sample were determined to be between 6 and 38 pg and typical column 2 peak widths ranged from 100 to 300 ms. Furthermore, the GC × GC/TOFMS instrument provides the unambiguous identification of compounds

based on their full mass spectra. In addition to the attributes just listed, valve-based GC × GC/TOFMS provides the opportunity to use unique chemometric signal deconvolution techniques. Our previous work demonstrated GC × GC peak deconvolution using techniques like generalized rank annihilation method (GRAM) [5,16,40,46,47]. GRAM and other chemometric deconvolution techniques utilize the bilinear structure of GC × GC data to separate unresolved chromatographic peaks. GRAM requires the comparison of a sample data set and a standard data set for deconvolution and quantitation. The unique structure of GC × GC/TOFMS data, which is known as third-order data (i.e. a trilinear data structure), allows for signal deconvolution without the comparison of data sets [48]. This eases the retention time precision requirements, and thus simplifies signal deconvolution. Indeed, we recently reported the deconvolution of GC × GC/TOFMS signals using trilinear decomposition (TLD) coupled with parallel factor analysis (PARAFAC) at the First International Symposium on Comprehensive Multidimensional Gas Chromatography.

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References

[1] H.J. de Geus, I. Aidos, J.d. Boer, J.B. Luten, U.A.Th. Brinkman, J. Chromatogr. A 910 (2001) 95.
[2] H.J. de Geus, R. Baycan-Keller, M. Oehme, J. de Boer, U.A.Th. Brinkman, J. High Resolut. Chromatogr. 21 (1998) 39.
[3] P.J. Marriott, R. Shellie, J. Fergeus, R. Ong, P. Morrison, Flavour Frag. J. 15 (2000) 225.
[4] R. Shellie, P.J. Marriott, C. Cornwell, J. Sep. Sci. 24 (2001) 823.
[5] B.J. Prazen, K.J. Johnson, A. Weber, R.E. Synovec, Anal. Chem. 73 (2001) 5677.
[6] M. Harju, P. Haglund, J. Microcol. Sep. 13 (2001) 300.
[7] J. Beens, J. Dalluge, M. Adahchour, R.J.J. Vreuls, U.A.Th. Brinkman, J. Microcol. Sep. 13 (2001) 134.
[8] G.S. Frysinger, R.B. Gaines, E.B. Ledford Jr., J. High Resolut. Chromatogr. 22 (1999) 195.
[9] G.S. Frysinger, R.B. Gaines, J. Sep. Sci. 24 (2001) 87.
[10] C.G. Fraga, B.J. Prazen, R.E. Synovec, Anal. Chem. 72 (2000) 4154.
[11] J.-M.D. Dimandja, S.B. Stanfill, J. Grainger, J. Donald, G. Patterson, J. High Resolut. Chromatogr. 23 (2000) 208.
[12] W. Bertsch, J. High Resolut. Chromatogr. 23 (2000) 167.
[13] A.C. Lewis, N. Carslaw, P.J. Marriott, R.M. Kinghorn, P. Morrison, A.L. Lee, K.D. Bartle, M.J. Pilling, Nature 45 (2000) 778.
[14] A.L. Lee, K.D. Bartle, A.C. Lewis, Anal. Chem. 73 (2001) 1330.
[15] P.J. Marriott, R. Shellie, Trends Anal. Chem. 21 (2002) 573.
[16] K.J. Johnson, B.J. Prazen, R.K. Olund, R.E. Synovec, J. Sep. Sci. 25 (2002) 297.
[17] J.C. Giddings, Anal. Chem. 56 (1984) 1258A.
[18] J.C. Giddings, J. High Resolut. Chromatogr. Chromatogr. Commun. 10 (1987) 319.
[19] Z. Liu, M.L. Lee, J. Microcol. Sep. 12 (2000) 241.
[20] M.M. Bushey, J.W. Jorgenson, Anal. Chem. 62 (1990) 161.
[21] M.M. Bushey, J.W. Jorgenson, Anal. Chem. 62 (1990) 978.
[22] R.E. Murphy, M.R. Schure, J.P. Foley, Anal. Chem. 70 (1998) 1585.
[23] Z. Liu, D.G. Patterson Jr., M.L. Lee, Anal. Chem. 67 (1995) 3840.
[24] P.J. Slonecker, X. Li, T.H. Ridgway, J.G. Dorsey, Anal. Chem. 68 (1996) 682.
[25] C.J. Venkatramani, J. Xu, J.B. Phillips, Anal. Chem. 68 (1996) 1486.
[26] J.C. Giddings, in: H. Cortes (Ed.), Multidimensional Chromatography: Techniques and Applications, Marcel Dekker, New York, 1990, p. 1.
[27] J. Dallüge, L.L.P. van Stee, X. Xu, J. Williams, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 974 (2002) 169.
[28] J. Dallüge, M. van Rijn, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 965 (2002) 207.
[29] J. Dallüge, R.J.J. Vreuls, J. Beens, U.A.Th. Brinkman, J. Sep. Sci. 25 (2002) 201.
[30] R. Shellie, P.J. Marriott, P. Morrison, Anal. Chem. 73 (2001) 1336.
[31] M. van Deursen, J. Beens, J. Reijenga, P. Lipman, C. Cramers, J. Blomberg, J. High Resolut. Chromatogr. 23 (2000) 507.
[32] J.B. Phillips, R.B. Gaines, J. Blomberg, F.W.M. van der Wielen, J.M. Dimandja, V. Green, J. Granger, D. Patterson, L. Racovalis, H.J. de Geus, J. de Boer, P. Haglund, J. Lipsky, V. Sinha, E.B. Ledford Jr., J. High Resolut. Chromatogr. 22 (1999) 3.
[33] J.B. Phillips, J. Xu, J. Chromatogr. A 703 (1995) 327.
[34] H.J. de Geus, A. Schelvis, J. de Boer, U.A.Th. Brinkman, J. High Resolut. Chromatogr. 23 (2000) 189.
[35] P.J. Marriott, R.M. Kinghorn, Anal. Chem. 69 (1997) 2582.
[36] R.M. Kinghorn, P.J. Marriott, J. High Resolut. Chromatogr. 23 (2000) 245.

[37] E.B. Ledford Jr., E.B.C. Billesbach, J. High Resolut. Chromatogr. 23 (2000) 202.
[38] J. Beens, M. Adahchour, R.J.J. Vreuls, K. van Altena, U.A.Th. Brinkman, J. Chromatogr. A 919 (2001) 127.
[39] P. Korytar, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, J. Chromatogr. A 958 (2002) 203.
[40] C.A. Bruckner, B.J. Prazen, R.E. Synovec, Anal. Chem. 70 (1998) 2796.
[41] J.V. Seeley, F. Kramp, C.J. Hicks, Anal. Chem. 72 (2000) 4346.
[42] J.V. Seeley, F.J. Kramp, K.S. Sharpe, S.K. Seeley, J. Sep. Sci. 25 (2002) 53.
[43] A.E. Sinha, K.J. Johnson, B.J. Prazen, S.V. Lucas, C.G. Fraga, R.E. Synovec, J. Chromatogr. A 983 (2003) 195.
[44] Terms of Environment: Glossary, Abbreviations, and Acronyms, EPA/OA/Office of Communications, Education, and Media Relations, 1997.
[45] R. Shellie, L. Mondello, P. Marriott, G. Dugo, J. Chromatogr. A 970 (2002) 225.
[46] C.G. Fraga, C.A. Bruckner, R.E. Synovec, Anal. Chem. 73 (2001) 675.
[47] C.G. Fraga, B.J. Prazen, R.E. Synovec, Anal. Chem. 73 (2001) 5833.
[48] K.S. Booksh, B.R. Kowalski, Anal. Chem. 66 (1994) 782A.