Using Gas Chromatography Coupled to Time-of-Flight Mass Spectrometry for the Analysis of Organochlorine Pesticides to Improve Data Quality in Difficult Samples

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Introduction

Gas chromatographic (GC) analysis of organochlorine pesticides is one of the most common analyses performed by environmental laboratories. This analysis typically uses electron capture detectors (ECD's) to achieve high sensitivity, but ECD's do not allow for identification of the compound producing the signal. For this reason, methods typically employ a dual-column separation where the two columns are of different selectivity. This allows for improvements in data quality, as long as the target compound does not coelute on at lease one of the columns. In difficult matrices, co-extractable interferrents (PCB's, toxaphene, PCN's, etc…) can cause significant difficulties with quantification due to coelution of target compounds with non-targets, thus biasing the results.

In order to gain specificity from the detector used in this analysis, many researchers have performed this analysis using GC-MS. Typical bench-top MS detectors often have a difficult time meeting the sensitivity requirements of most methods, however, so this technique has not been widely adopted. Alternatively high-resolution mass spectrometry (HRMS) has also been used to gain both specificity and sensitivity with the detector. HRMS is both expensive, and also gives information only for predetermined target compounds; identification of unknowns is generally not possible with HRMS.

TOFMS has been used successfully to acquire full-scan information, while maintaining high sensitivity due to the nature of the way the spectra are collected. If GC-TOFMS is capable of meeting the sensitivity requirements of the common GC-ECD methods, it should allow for improved sample characterization with the ability to identify non-target co-extractable compounds.

Experimental

Sample Preparation

Both GC-ECD and GC-TOFMS analyses were performed on the same sample extracts to minimize any variation in results due to sample preparation differences. All samples were prepared by Severn Trent Laboratories (STL, Burlington, VT) according to either USEPA method 3510 for water samples, or USEPA 3550, or 3541for soils. Soil extracts were processed through preparative GPC (J2 Scientific, Columbia MO) according to USEPA method 3640, if applicable, to remove high molecular weight interferrents as well as sulfur. Finally all extracts were processed according to either USEPA method 3620 using 1.0-gm Florisil SPE Cartridges to remove polar contaminants or 3665 (Sulfuric acid cleanup) for PCB-only analysis.

Sample Quantification

Table 1 lists the instrumental conditions for the two separate analyses.

GC-ECD Analysis		
GC	Type	Agilent 6890, or 5890
Detector	Type	Agilent uECD, or ECD
	Temperature	300 C
Columns		1Rtx-CLPesticides 30-M X 0.25 mm i.d. X 0.25 um d.f.

		2Rtx-CLPesticides2 30-M X 0.25 mm i.d. X 0.20 um d.f.
Inlet	Type	Agilent Split/splitless using Restek Uniliner direct injection liner
	Temperature	250 C
Injection	Volume	2 uL
	Solvent	Hexane
Oven	Program	100 (1) 20/min 300
	Runtime	18 minutes
GC-TOFMS Analysis		
GC	Type	Agilent 6890
TOFMS	Type	LECO Pegasus 3
		10 spectra/sec
	stored mass range	45-550 amu
	transfer line	280 C
Column		1Rtx-CLPesticides 10-M X 0.18 mm i.d. X 0.18 um d.f.
Inlet	Type	Agilent Split/splitless using Restek 4-mm Siltek-deactivated single gooseneck liner
	Temperature	250 C
Injection	Volume	2 uL
	Solvent	Hexane
Oven	Program	100 (1) 20/min 300
	Runtime	8 minutes

Table 1: Instrumental Conditions for GC-ECD and GC-TOFMS Analyses

Results:

Calibration of the GC-TOFMS was over a wider range then typical for GC-ECD analysis. Typical GC-ECD calibrations are from 5 to 80 pg/uL for the high-responding compounds (ex. Hexachlorocyclohexane), with the less responsive compounds from 10 to 160 pg/uL (ex. 4,4'-DDT). For the GC-TOFMS, calibration standards of 1-, 2-, 5-, 10-, 20-, 40-, 80-, 200-, 400-, and 800-pg/uL were injected. Extracted ion calibration using tetrabromothiophene at a fixed concentration of 40-pg/uL as an internal standard was used. For most compounds, calibration was successful over the entire range. For compounds that have considerable fragmentation (ex. Endosulfan), the 1-pg and 2-pg calibration standards were dropped. In any event, calibration over a wider range than is common on ECD's was successful. Sensitivity was also as good, or better, than the common ECD methods for analysis (ex. USEPA method 8081). Acceptable calibration for a compound was defined by achieving a 0.999 or greater regression coefficient over the linear calibration.

Extract Quantification:

Table 2 is a tabulation of the difference in quantification for the results obtained by both methods for a matrix-spiked soil sample. This table represents typical results for the samples indicating that the two methods are equivalent as far as most samples are concerned.

Table 2: Quantification difference for GC-ECD vs. GC-TOFMS

Analyte	STL-BTV GC-ECD	GC-TOFMS	STL-BTV Spike Amount	STL Quant in Sample	STL Corrected Absolute Recovery	GC-TOFMS Quant in Sample	GC-TOFMS Corrected Absolute Recovery	% difference
TCMX	32.9	37.29	40		32.9		37.29	13.3
alpha-HCH	38.8	41.52	20	22.8	16	23.25	18.27	14.2
gamma-HCH	25.8	25.5	20	8	17.8	7.64	17.86	0.3

beta-HCH	65.6	70.92	20	45.3	20.3	47.73	23.19	14.2
delta-HCH	38.8	52.83	20	17.9	20.9	29.45	23.38	11.9
Heptachlor	19.8	19.98	20		19.8		19.98	0.9
Aldrin	20.6	20.24	20		20.6		20.24	-1.7
Heptachlor epoxide	21.6	20.83	20		21.6		20.83	-3.6
Endosulfan I	19.2	13.82	20		19.2		13.82	-28.0
p,p'-DDE	48.3	40.22	40		48.3		40.22	-16.7
Dieldrin	46.6	42.28	40		46.6		42.28	-9.3
Endrin	48.1	44.38	40		48.1		44.38	-7.7
p,p'-DDD	48.8	41.28	40		48.8		41.28	-15.4
Endosulfan II	42.1	38.62	40		42.1		38.62	-8.3
p,p'-DDT	47.7	39.51	40		47.7		39.51	-17.2
Endrinaldehyde	44.5	40.79	40		44.5		40.79	-8.3
Methoxychlor	225	206.8	200		225		206.8	-8.1
Endosulfan sulfate	47.6	42.31	40		47.6		42.31	-11.1
DCB	20	24.52	40		20		24.52	22.6

Where the most dramatic benefit of TOFMS detection versus ECD is apparent is for sample with significant levels of non-target interferences that produce peaks within the retention windows of the target compounds. For samples like this, the ECD method begins to be limited in its ability to either identify or quantify the targets. Figure 3 is the total-ion chromatogram obtained from a sample with significant PCB, and other chlorinated unknown concentration. This sample proved to be beyond the capability of the dual-column ECD method as there were several target compounds identified based upon retention windows that were not found using the GC-TOFMS method. Reported values from the ECD method placed these targets well in the calibration range of the TOFMS experiment, so they would have been found if they were truly present.

Figure 3: Sample “850” tic

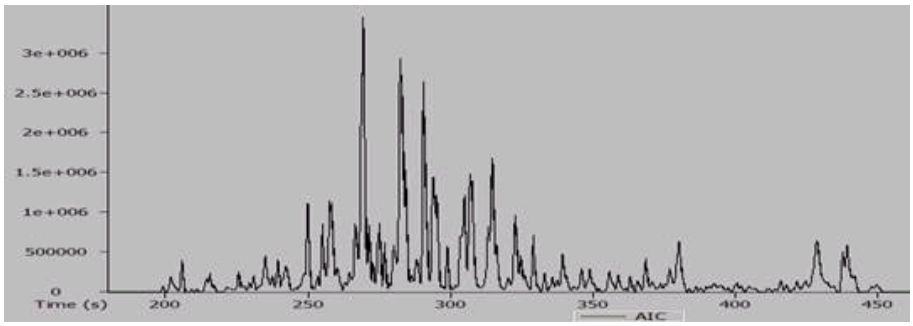

Figure 4 summarizes the target compound comparison for sample “850”.

Analyte	STL-BTV GC-ECD	GC-TOFMS	% difference
TCMX	28.6	31.64	10.6
gamma-HCH	18.8		NA
beta-HCH	10.8		NA
Heptachlor	68.4		NA
Heptachlor epoxide	22.6		NA
gamma-chlordane	18.06	13.4	-25.8
alpha-chlordane	12.38	19.56	58.0
p,p'-DDE	12.86	14.5	12.8
Dieldrin	25.6	22.78	-11.0
Endrin	16.02		-100
p,p'-DDD		7.85	NA
p,p'-DDT	156.8	111.13	-29.1
Endrinaldehyde	40.6		-100

Methoxychlor		6.35	NA
DCB	39.82	64.94	63.1

Summary

GC-TOFMS has been demonstrated to be capable of meeting the analytical requirements of the organochlorine pesticide methods similar to USEPA method 8081, while also providing higher data quality, especially for difficult samples. Especially in samples with PCB, toxaphene, PCN, or other halogenated potential interferrents. This paper will address additional samples, and discuss the technique in more detail.