EVALUATION AND ENVIRONMENTAL APPLICATION OF GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTION (GC/AED)

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1 ABSTRACT

A hydrocarbon mixture of C_{12} to C_{17} n-alkanes was used to compare splitless injection versus on-column injection for gas chromatography with atomic emission detection (GC/AED). On-column injection was shown to give better and more consistent response than splitless injection resulting in potentially more accurate analyses. On-column injection was then used to evaluate a pesticide standard and shown, in general, to be able to predict molecular formulas and give adequate quantitation. Also, the feasibility of quantitation using non-authentic standards was demonstrated.

Finally, the GC/AED was used to analyze two environmental samples (dimethyl mercury in fish and tetra-n-butyl tin in ground water) for which no authentic standards were available.

2 INTRODUCTION

The atomic emission detector with gas chromatographic separation (GC/AED) uses a microwave-induced plasma to ionize molecules to their atomic constituents for empirical formula elucidation and quantitation. Atoms that can be detected include carbon, hydrogen, oxygen, nitrogen, sulfur, halogens, and certain metals. By monitoring several channels and comparing the outputs with those from standards of known molecular formulas, the empirical formula of an unknown can be deduced.

GC/AED analysis has been shown to be useful for environmental samples *(1)* and is particularly effective at identifying certain elements or classes of compounds in complex chromatograms, such as low-level chlorinated compounds or organometallics. This research was undertaken to evaluate GC/AED analysis and to ascertain its usefulness for environmental samples.

3 EXPERIMENTAL

Standard Solutions

Standard solutions were prepared from two commercially available standards. The Hydrocarbon Test Mix (catalog # 4-8244) and HC Pesticide Mixture (catalog # 4-8913) were purchased from Supelco (Bellefonte, PA). A 10-µL syringe was used to add the appropriate volume directly into a 1.8-mL autosampler vial containing 1.0 mL of either methanol or hexane.

Conditions

After some initial experimentation, the following conditions were used to collect the data for method development.

GC Conditions #1 (injector evaluation)

Initial temperature	**60 °C**	**Initial time**	**1 min**
Temperature rate	**8 °C/min**	**Final temperature**	**284 °C**
Final hold time	**0 min**	**Total run time**	**29 min**
Transfer line	**280 °C**		

GC Conditions #2 (environmental samples)

Initial temperature	**40 °C**	**Initial time**	**1 min**
Temperature rate	**8 °C/min**	**Final temperature**	**152 °C**
Final hold time	**0 min**	**Total run time**	**15 min**
Transfer line	**280 °C**		

Splitless Injection

Temperature	**300 °C**		
Split ratio	**1:1**	**Splitless time**	**1.0 min**
Injection volume	**1.0 µL (delivered by autosampler)**		

On-column Injection

Injection volume	**1.0 to 5.0 µL (delivered by autosampler)**

Column #1 (injector evaluation)

Dimensions	**30 m × 0.32 mm × 0.25 µm film**
Liquid phase	**5% diphenyl-95% dimethyl polysiloxane**
Head pressure	**12 psig helium**
Linear velocity	**40 cm/sec at 60 °C**

Column #2 (environmental samples)

Dimensions	**30 m × 0.53 mm × 1.5 µm film**
Liquid phase	**5% phenyl-95% dimethyl polysiloxane**
Head pressure	**18.6 psig helium**
Linear velocity	**211 cm/sec at 40 °C**

4 CALCULATIONS

Instrument Detection Limit Calculation (IDL) for Methyl Mercury Chloride

This EPA formulated IDL calculation is based on a statistical argument *(2)* and is defined as the minimum concentration of a substance greater than zero that can be measured with 99% confidence. It is calculated from the formula:

IDL = (% rsd × 3.143 × concentration)

where % rsd is the relative standard deviation in per cent, and 3.143 Student's t value, which, in this case, is for seven replicate injections. The method stipulates that the concentration of the replicates must not be greater than five times the resulting calculated IDL.

Dimethyl Mercury Quantitation

Due to the extreme toxicity of dimethyl mercury, methyl mercury chloride was used for the calibration of mercury in fish tissue extracts. The mercury channel (254 nm) was used due to its sensitivity. A comparison of AED results with Automated Mercury Analyzer *(3)* results were highly correlated.

Tetra-n-butyl Tin Quantitation

Since no tetra-n-butyl tin standard was readily available, a tentative quantitation was performed using the average carbon channel response of the hydrocarbon mix standard and back calculating the amount of tetra-n-butyl tin ($C_{16}H_{36}Sn$; M.W. 347) from its carbon channel response *(4)*. No other butyl tins (other than isomers of tetra-n-butyl tin) are gas chromatographable.

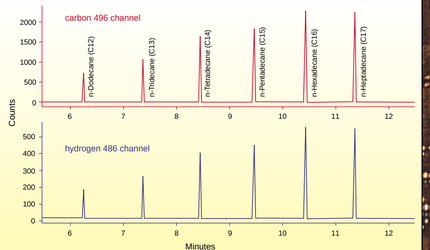


FIGURE 1. GC/AED chromatogram of 6 n-alkanes showing carbon 496 (upper) and hydrogen 486 (lower) channels (see Table I). Number of carbon atoms are shown in parentheses and relative concentrations are in Table I.

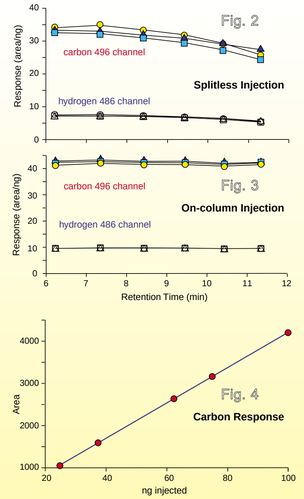


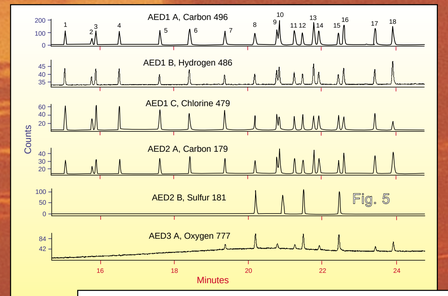
FIGURE 2. Triplicate injections of hydrocarbon mix showing response versus retention time for carbon 496 channel (closed symbols) and hydrogen 486 channel (open symbols) using splitless injection.

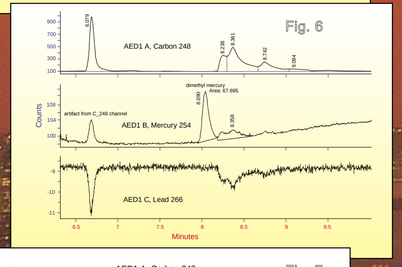
FIGURE 3. Triplicate injections of hydrocarbon mix showing response versus retention time for carbon 496 channel (closed symbols) and hydrogen 486 channel (open symbols) using on-column injection (see Table I).

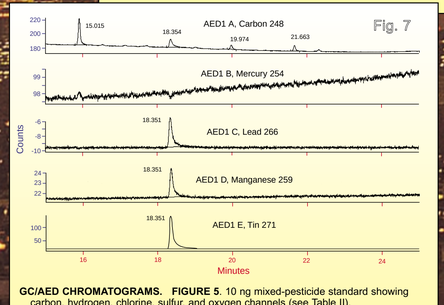
FIGURE 4. Calibration curve of carbon channel response (area) versus amount injected (ng) from a single injection of hydrocarbon mix.

TABLE I. Compound, retention time, formula, amount, area, response, and C to H response ratio of n-alkanes. Precision (% rsd) for last three columns shown at the bottom.

compound	time	formula	amount	C_{496nm}	H_{486nm}	C_{496nm}	H_{486nm}	C : H response ratio
	min		ng	area	area	area/ng	area/ng	
n-dodecane	6.24	$C_{12}H_{26}$	25.0	1032	240	41.28	9.60	4.30
n-tridecane	7.36	$C_{13}H_{28}$	37.5	1567	367	41.79	9.79	4.27
n-tetradecane	8.44	$C_{14}H_{30}$	62.5	2596	608	41.54	9.73	4.27
n-pentadecane	9.46	$C_{15}H_{32}$	75.0	3114	729	41.52	9.72	4.27
n-hexadecane	10.43	$C_{16}H_{34}$	100.0	4111	959	41.11	9.59	4.29
n-heptadecane	11.35	$C_{17}H_{36}$	100.0	4166	966	41.66	9.66	4.31
					% rsd =	0.6%	0.8%	0.4%







GC/AED CHROMATOGRAMS. FIGURE 5. 10 ng mixed-pesticide standard showing carbon, hydrogen, chlorine, sulfur, and oxygen channels (see Table II). **FIGURE 6.** Dimethyl mercury from fish tissue extract showing carbon, mercury, and lead channels. Peak corresponds to 467 ng/g in fish tissue. *(2)* **FIGURE 7.** Tetra-n-butyl tin from a ground water extract showing carbon, mercury, lead, manganese, and tin channels. Concentration in extract calculated to be 2 ppm (see Calculations).

TABLE II. GC/AED of mixed pesticides (10 ng each) showing compound number, compound, formula, molecular weight, retention time, calculated recovery, empirical formula by channel, and deviation from theoretical formula by channel. Errors from theoretical (> 0.5 atoms) are shown in bold.

no.	compound	formula	MW amu	time min	recovery ng	C_{496nm} atom	H_{486nm} atom	Cl_{479nm} atom	O_{777nm} atom	S_{918nm} atom	C	H	Cl	O	S
1	a-BHC	$C_6H_6Cl_6$	291	15.05	10.32	6.00	6.03	5.99			0.0	0.0	-0.0		
2	b-BHC*	$C_6H_6Cl_6$	291	15.78	5.05	6.00	6.04	6.05			0.0	0.0	0.1		
3	g-BHC	$C_6H_6Cl_6$	291	15.89	10.46	6.00	5.98	6.08			0.0	-0.0	0.1		
4	d-BHC	$C_6H_6Cl_6$	291	16.53	10.11	6.00	5.98	6.02			0.0	-0.0	0.0		
5	heptachlor	$C_{10}H_5Cl_7$	373.5	17.62	10.10	10.00	5.29	6.95			0.0	0.3	-0.1		
6	aldrin	$C_{12}H_8Cl_6$	365	18.42	10.07	12.00	8.06	6.00			0.0	0.1	-0.0		
7	heptachlor epoxide	$C_{10}H_5Cl_7O$	389.5	19.38	10.06	10.00	5.12	6.98	1.00		0.0	0.1	-0.0	-0.0	
8	endosulfan I	$C_9H_6Cl_6O_3S$	407	20.19	10.16	9.00	6.21	5.99	3.19	0.97	0.0	0.2	-0.0	0.2	-0.0
9	dieldrin	$C_{12}H_8Cl_6O$	381	20.79	9.46	12.00	**8.76**	**6.72**	1.42		0.0	**0.8**	**0.7**	0.4	
10	DDE	$C_{14}H_8Cl_4$	318	20.85	10.86	14.00	**7.36**	3.78			0.0	**-0.6**	-0.2		
11	endrin	$C_{12}H_8Cl_6O$	381	21.26	8.69	12.00	7.79	5.98	1.03		0.0	-0.2	-0.0	0.0	
12	endosulfan II	$C_9H_6Cl_6O_3S$	407	21.49	10.32	9.00	5.87	5.94	3.10	0.99	0.0	-0.1	-0.1	0.1	-0.0
13	DDD	$C_{14}H_{10}Cl_4$	320	21.79	9.99	14.00	9.97	4.00			0.0	-0.0	0.0		
14	endrin aldehyde	$C_{12}H_8Cl_6O$	381	21.93	9.43	12.00	7.81	5.95	0.90		0.0	-0.2	-0.0	-0.1	
15	endosulfan sulfate	$C_9H_6Cl_6O_4S$	423	22.46	10.06	9.00	6.07	5.98	3.94	0.98	0.0	0.1	-0.0	-0.1	-0.0
16	DDT	$C_{15}H_9Cl_5$	354.5	22.60	9.94	14.00	8.67	5.00			0.0	-0.3	-0.0		
17	endrin ketone	$C_{12}H_8Cl_6O$	381	23.44	10.65	12.00	8.12	5.86	0.84		0.0	0.1	-0.1	-0.2	
18	methoxychlor	$C_{16}H_{15}Cl_3O_2$	345.5	23.92	9.52	16.00	**14.40**	3.01	2.02		0.0	**-0.6**	0.0	0.0	

*outlier (on basis of recovery) omitted from calibrations

5 DISCUSSION

Figure 1 shows the hydrocarbon mix chromatogram collected using the carbon and hydrogen channels. This mixture and method were used to evaluate on-column and splitless injection. The results (in Figures 2 and 3) demonstrate that splitless injection clearly discriminates especially for higher molecular weight compounds as compared to on-column injection. Precision of on-column injection (Table I) is also excellent (< 1% rsd). The fact that the response of an element/channel does not vary appreciably with the compound or retention time (Figure 4) makes it feasible to calibrate using a single run (instead of multiple runs) and quantitate without authentic standards.

To further test the concept, a pesticide standard was run monitoring for the appropriate elements (Figure 5) and processed as an unknown to measure the accuracy of the molecular formula information and check the quantitation. Table II shows only four deviations (> 0.5 atoms) from the correct molecular formulas, three of which are hydrogen atoms.

Figures 6 and 7 show two examples of environmental analyses by GC/AED. In the case of dimethyl mercury in fish extract, a calibration was performed for methyl mercury chloride using the sensitive mercury channel. This channel was much more sensitive than the corresponding carbon channel for this compound which is why a response for C is not evident. The instrument detection limit in the extract was determined to be < 0.25 ppb. The tentative identification of tetra-n-butyl tin in groundwater concentrates was based on the tin channel response and the fact that tetra-n-butyl tin (or any of its isomers) are the only tin compounds that are likely to be gas chromatographable. Quantitation was accomplished using the carbon channel and comparing it to the standard n-alkane mixture. The positive responses in the lead and manganese channels which coincide with the tin channel response were deemed to be artifacts due to their low levels and the close proximity of the three channels.

6 CONCLUSIONS

1) **Unlike splitless injection, on-column injection showed no compound discrimination and therefore adds to the precision and utility of GC/AED results.**
2) **When analyzing standards, GC/AED was shown to give adequate molecular formula and quantitation information.**
3) **Response curves from a single injection using a common channel/element from different compounds are possible making quantitation without authentic standards feasible.**
4) **Two practical examples are shown, demonstrating applicability of GC/AED for analyzing environmental samples.**

7 REFERENCES

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3) **Hinners T. A., J. V. Cizdziel, and S. M. Pyle (unpublished data).**
4) **Jones-Lepp T. L., K. E. Varner, M. McDaniel, and L. Riddick.** *Applied Organometallic Chemistry.* **13, 881–889 (1999).**