



Project Summary

Thermally Modulated Electron Affinity Detector for Priority Pollutant Analysis

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In the area of environmental monitoring, a need exists for a rapid, sensitive, and selective method to analyze for chlorinated organic compounds such as pesticides, PCB, PCDD, and PCDF at trace levels in complex samples.

In response to this need, a program was conducted to determine the feasibility of using a new detector concept in the gas chromatographic analysis of certain priority pollutants. The concept is based on the thermal alteration of a compound's electron affinity in a flow-through reactor, which can be used to modify the selectivity and sensitivity of the ECD to certain compounds. The Thermally Modulated Electron Capture Detector (TM ECD) consists of two ECDs connected by a temperature-controlled reactor. Different classes of organic compounds respond to the reactor conditions in different ways: some compounds exhibit an enhanced ECD response after passing through the reactor; some a diminished signal; and others no change in the magnitude of the signal. The ratio of a compound's response from the postreactor ECD to that obtained from the prereactor ECD appears to be a property characteristic of each compound. This peak area ratio can be used in conjunction with its retention time to increase the confidence level of the identity of a given compound while still taking advantage of the excellent sensitivity characteristics of the ECD.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of

the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The potential for enhancing the selectivity and sensitivity of the ECD to certain compounds was demonstrated in preliminary studies conducted by R.C. Hall at Purdue University in 1973. These studies utilized a detector system comprised of two ECDs and a flow-through reactor. The detectors in this system were arranged in series, but were separated by a reaction chamber. A gold reaction tube and nitrogen carrier gas were used in this design.

It was found that at moderate reactor temperatures (up to 800°C), the response of the second detector was: reduced relative to the first for chlorinated hydrocarbon pesticides; approximately the same for PCBs; and greater for phthalate esters. At high reactor temperatures (950°C), PCBs and phthalates continued to produce a significant response in the second detector; most chlorinated hydrocarbon pesticides exhibited little or no response. The response ratio of the detectors was also found to be compound-specific and useful for confirmation of compound identity.

These phenomena were used to enhance detector selectivity by directly eliminating the response of certain components and by differentially summing the two detector signals to eliminate the response of stable components. These techniques were used to enhance detector selectivity to chlorinated hydrocarbon pesticides in the presence of PCBs and phthalates.

Although these preliminary results were encouraging, this approach was not studied in detail and did not cover a wide variety of compounds. The stability of the system was not verified and actual samples were not investigated. Consequently, funding was solicited to fully investigate the utility of the technique and determine the feasibility of constructing a commercial detector system based on this principle.

This followup program was designed to demonstrate the feasibility of the concept using existing off-the-shelf components. The specific objectives were:

- construct a detection system;
- determine response characteristics for selected compounds as a function of reactor temperature using at least two different materials as reactor tubes;
- investigate response characteristics in different reaction gas compositions including nitrogen, argon/methane, and helium/hydrogen;
- determine the most promising reaction tube/reaction gas combination;
- system evaluate with a limited number of model compounds; and
- evaluate detector specificity.

Hardware Development and Preliminary Evaluation

The chromatographic system used in this study consisted of a Radian 110B Gas Chromatograph modified to accept an experimental detector system which consisted of two modified Tracor ECDs with a flow-through reactor between the two detectors.

The reactor used for this study consisted of a two-hole ceramic tube wrapped with resistance heating wire and enclosed in

ceramic insulation. The reaction tube was inserted through one hole of the ceramic tube and a thermocouple in the other hole. Temperatures of the reactor were controlled $\pm 2^\circ\text{C}$ and were varied from 350°C to 900°C .

A $\frac{1}{8}$ -inch o.d. glass-lined stainless steel column (1.8 mm i.d. \times 168 cm long) was used for all separations. The exit of the column was interfaced to the first detector via a short piece of $\frac{1}{16}$ -inch o.d. (0.035-inch i.d.) gold tubing. Gold was used for this interface to prevent catalytic decomposition of the sample prior to detection.

Seventeen model compounds were selected to determine the TM ECD's response characteristics. The basis for their selection was that they represent electron-capturing analytes from a variety of compound classes including chlorinated hydrocarbon pesticides, PCBs, phthalate esters, organophosphate pesticides, chloroaromatics, nitroaromatics, and chlorophenols. The test compounds were grouped into mixtures each of which contained similar compounds that could be resolved chromatographically under the analytical conditions employed. The mixtures were introduced to the chromatograph in $5\ \mu\text{L}$ injections.

The response ratios determined experimentally at various temperatures with argon/methane carrier and a gold reaction tube are presented in Table 1. The ratios shown are the average of three determinations. The standard deviations for the determinations are also shown. These ratios are based on the assumption that the responses of ECD#1 and ECD#2 are equal for all compounds with an ambient reactor temperature. An ambient temperature for the reactor, however, was impossible to at-

tain due to the temperature of the detectors (340°C each). Therefore, equal response was assumed and a reactor temperature of 350°C was used as the minimum temperature.

At 350°C , the response ratios were not equal to 1.0 for all compounds. This indicates that some rearrangement takes place either in the first detector or in the reaction tube at 350°C . The compounds altered the most were toxaphene, chlordane (both chlorinated hydrocarbons), and the phthalates.

As the temperature of the reactor was increased, the chlorinated pesticides were degraded to species less responsive to the electron capture detector. This resulted in response ratios less than 1.0. The most thermally stable chlorinated pesticides were *p,p'*-DDE and *p,p'*-DDT. Toxaphene and chlordane, both aliphatic chlorinated hydrocarbons, were found to be very unstable.

PCBs, nitrobenzene, 1,2,4-trichlorobenzene and 2,4-dichlorophenol exhibited high thermal stability. The thermal stability of PCBs is well documented. Therefore, the response ratios were expected to be close to 1.0 and show little change as a function of temperature. The stability of nitrobenzene, 1,2,4-trichlorobenzene and 2,4-dichlorophenol was surprising. These compounds, particularly nitrobenzene and 2,4-dichlorophenol, are chemically reactive and were therefore expected to exhibit thermal instability.

Phthalates and the parathions were found to be thermally unstable. The organophosphate pesticides, methyl and ethyl parathion, were thermally degraded to products having very little electron affinity. As a result, the response ratios were quite

Table 1. Response Ratios¹ At Various Temperatures With Ar/CH₄ Carrier And A Gold Reaction Tube

Compound	Reactor Temperature ($^\circ\text{C}$)					
	350	600	700	800	850	900
1. Lindane	0.93 ± 0.01	0.93 ± 0.01	0.90 ± 0.01	0.11 ± 0.01	0.05	0.04
2. Heptachlor	0.82 ± 0.01	0.77 ± 0.01	0.41 ± 0.06	0.05	0.02	0.02
3. Heptachlor Epoxide	0.82 ± 0.01	0.82 ± 0.01	0.77 ± 0.02	0.17 ± 0.01	0.08 ± 0.01	0.05
4. <i>p,p'</i> -DDE	0.81 ± 0.01	0.83 ± 0.01	0.82 ± 0.01	0.59 ± 0.02	0.48 ± 0.01	0.40 ± 0.01
5. <i>p,p'</i> -DDT	0.78 ± 0.01	0.78 ± 0.05	0.54 ± 0.03	0.21 ± 0.03	0.25 ± 0.03	0.15 ± 0.01
6. Aroclor 1016	0.98 ± 0.02	1.00 ± 0.01	0.98 ± 0.02	0.92 ± 0.03	0.92 ± 0.01	0.85 ± 0.01
7. Aroclor 1254	0.94 ± 0.06	1.01 ± 0.01	1.01 ± 0.02	0.92 ± 0.03	0.89 ± 0.03	0.77 ± 0.04
8. Toxaphene	0.61 ± 0.06	0.64 ± 0.02	0.05 ± 0.03	< 0.01	< 0.01	< 0.01
9. Chlordane	0.72 ± 0.01	0.69 ± 0.02	0.27 ± 0.10	0.03	0.01	< 0.01
10. Diethyl Phthalate	1.54 ± 0.30	1.58 ± 0.10	1.82 ± 0.01	3.48 ± 0.04	6.55 ± 0.04	8.09 ± 0.15
11. Dibutyl Phthalate	1.61 ± 0.24	1.55 ± 0.04	1.57 ± 0.04	1.86 ± 0.05	2.52 ± 0.02	3.16 ± 0.02
12. bis(2-Ethylhexyl)Phthalate	1.84 ± 0.39	1.80 ± 0.05	1.85 ± 0.07	2.04 ± 0.05	2.44 ± 0.08	3.03 ± 0.12
13. Methyl Parathion	0.90 ± 0.01	0.89 ± 0.01	0.31 ± 0.01	0.09 ± 0.01	0.08 ± 0.01	0.07 ± 0.01
14. Ethyl Parathion	0.92 ± 0.01	0.91 ± 0.01	0.26 ± 0.01	0.09 ± 0.01	0.09 ± 0.01	0.08 ± 0.01
15. Nitrobenzene	1.00 ± 0.02	0.84 ± 0.01	0.90 ± 0.03	0.84 ± 0.02	0.85 ± 0.01	0.90 ± 0.02
16. 1,2,4-Trichlorobenzene	0.82 ± 0.01	1.02 ± 0.02	0.97 ± 0.01	0.92 ± 0.01	0.93 ± 0.01	0.91 ± 0.01
17. 2,4-Dichlorophenol	1.07 ± 0.03	1.04 ± 0.01	0.90 ± 0.05	0.85 ± 0.03	0.75 ± 0.01	0.77 ± 0.03

¹Based on equal response of ECD #1 and ECD #2.

small. The phthalates were also very unstable. However, the products formed during the thermal degradation of the phthalates had a greater electron affinity than the parent compounds.

In general, the results with nitrogen as the carrier were similar to those obtained with argon/methane. The chlorinated pesticides, the parathions, and the phthalates were again found to be thermally unstable. The PCBs, nitrobenzene, trichlorobenzene, and dichlorophenol, were found to be more thermally stable.

The response ratios for the helium/hydrogen gas composition were obtained by using a carrier of 30 mL/min helium and a makeup gas of 30 mL/min hydrogen. The makeup gas was added to the column effluent immediately prior to entering the first detector.

Response ratios obtained with a helium/hydrogen carrier gas did not yield reproducible results for the chlorinated pesticides or for the phthalates. Reproducible results were obtained for the PCBs, 2,4-dichlorophenol, and 1,2,4-trichlorobenzene. Toxaphene, chlordane, nitrobenzene and the parathions had very low response ratios at all temperatures and were not studied in great detail.

Heating the reactor to temperatures above 800°C with helium/hydrogen carrier caused an apparent activation of the reaction tube. The reactor would require several days to return to its original level of activation once the temperature had been reduced. This activation caused very poor reproducibility, especially for the chlorinated pesticides and phthalates. The reactor activation was postulated to be due to a temperature dependent reaction between the hydrogen and some substance coating either the inside of the ECDs or the reaction tube.

Replacement of the gold reaction tube with a nickel tube did not alleviate the problems observed with gold and helium/hydrogen. All compounds, except diethyl phthalate, were completely destroyed at a reactor temperature of 900°C. The activation of the reactor was again observed at high temperatures. After reducing the reactor temperature, several days were required for restoration of the original activity level.

Response ratios determined with a nitrogen carrier and a nickel reaction tube were found to be lower at 350°C for every compound except the phthalates and nitrobenzene. The phthalates were observed earlier to have larger response ratios due to the formation of a degradation product with a greater electron affinity. The increased degradation of all compounds at 350°C with nitrogen/nickel suggested that

catalytic reactions were occurring (i.e., the gold tube is more inert than the nickel tube). The nickel tube displayed another difference from the gold tube with nitrogen. At temperatures >800°C all compounds were degraded including the normally thermally stable PCBs, chloroaromatics and nitroaromatics. In addition, the response ratios of the phthalates were smaller, suggesting that the intermediate species formed by the thermal degradation of the phthalates were degraded further to species which have small electron affinities. Due to these difficulties, this system was not investigated further.

Response ratios obtained using an argon/methane carrier and a nickel reaction tube at 350°C are very similar to those observed for a nitrogen carrier when a nickel tube is employed as the reactor. The reactivity of the nickel tube appears to increase more rapidly with a corresponding increase in temperature when argon/methane is used in place of nitrogen as the carrier.

At a reaction temperature of 800°C the response ratios of all the compounds except the phthalates were extremely small for the argon/methane system, whereas the response ratios of the chlorinated compounds and the phthalates resulting from the nitrogen system were significantly greater at the same temperature. The response ratios for the organophosphate pesticides, the chloroaromatics, and the nitroaromatics are very similar for both systems at this temperature.

In the case of the chlorinated pesticides, these data may be indicative of the occurrence of free radical formation in the argon/methane atmosphere within the nickel reactor, followed by subsequent recombination reactions in which species that have lower electron affinities are formed. The nickel tube appears to act as a catalyst under these conditions since the test compounds exhibit much greater thermal stability when argon/methane is used in conjunction with a gold reaction tube. Because of these characteristics, this system was not selected for further study.

Method Evaluation Study

The optimum experimental configuration was determined to be a gold catalyst at 850°C with a total flow rate of 60 mL/min of 5% methane/95% argon. This configuration was selected for further study. The target compounds selected for use in the method evaluation study included phthalate esters and toxaphene. The evaluation study itself was based on the analytical procedures employed in USEPA Method 608 for organochlorine pesticides and PCBs. The study was conducted based

on the assumption that the phthalate esters were to act as interferents in the analysis of water samples for toxaphene.

The following phthalate esters were selected for use in the method evaluation: di-*n*-butyl phthalate, benzyl butyl phthalate, and bis(2-ethylhexyl) phthalate.

Twenty 1-L samples of reagent water were fortified with a 1.0 mL aliquot of spiking solution containing appropriate concentrations of toxaphene and the three phthalate esters. After spiking, the 20 water samples were extracted according to the protocol detailed in USEPA Method 608. Briefly, this involved extracting the sample with three 60-mL portions of methylene chloride, drying the combined extracts on an anhydrous sodium sulfate column, and concentrating the dried extracts followed by solvent exchange into hexane. After extraction, the samples were analyzed on both a conventional ECD and TM ECD.

After analysis, the extracts were cleaned up on Florisil®* columns using the procedure recommended in USEPA Method 608. The 6% diethyl ether in hexane eluate fraction was analyzed under the same chromatographic conditions. Prior to beginning this phase of the study, the Florisil® elution pattern for toxaphene was established using standard solutions.

A comparison of the two detectors in terms of accuracy and precision for both the pre- and post-cleanup methods demonstrated that the commercial ECD and the TM ECD work equally well for the analysis of toxaphene in fortified reagent water samples. This is true for both pre- and post-cleanup methods.

Industrial wastewater samples (1L volumes) known to contain toxaphene as a contaminant were extracted and analyzed according to USEPA Method 608. The analyses were conducted prior to and after Florisil® column cleanup using both detection systems.

Four toxaphene-containing wastewater samples were obtained for use in the evaluation study. One of the samples was divided into three 1-L aliquots. Two of the aliquots were extracted and analyzed as previously described. The third aliquot was fortified with a toxaphene spiking solution at a level that would yield an equivalent sample concentration of 86 µg/L as a method recovery check. The three other industrial wastewater samples were each treated as single determinations. One of these samples contained phthalate levels so high that measurements of background

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

toxaphene concentrations (before cleanup) had to be made using a single toxaphene peak.

The results of the method recovery check are listed in Table 2 and indicate quantitative recovery of toxaphene from the fortified industrial waste sample. As was illustrated for the reagent water samples, the TM ECD appears to be equivalent in this particular application.

An additional series of analyses using the TM ECD were performed in an attempt to identify the mechanism responsible for the enhanced phthalate response. It was hypothesized that phthalate esters were being converted to phthalic anhydride within the heated reactor and that the enhanced signal was the result of the relatively greater electron affinity of the anhydride.

The phthalic anhydride chromatographic peak tailed so badly, however, that it was impossible to get an accurate comparison. Nevertheless, it was found that phthalic anhydride was more sensitive than the phthalate ester. The difference between the sensitivities of the anhydride and the ester was approximately the same as the elevated response observed for the ester after passing through the reactor at 850°C. Thus, the formation of phthalic anhydride is a plausible reaction mechanism.

Recommendations

The evaluation of the detector prototype has demonstrated the validity of the TM ECD concept. A final determination of the detector's potential for widespread application in the area of environmental monitoring is not possible without additional work. The following areas merit continued investigation:

- determine the reaction products responsible for the post-reactor signals;
- determine molecular positional effects on the response factors of various isomers;
- utilize capillary columns in conjunction with the TM ECD;
- define the limits of matrix effects on TM ECD response ratios; and
- optimize TM ECD selectivity and sensitivity for PCD and PCDF.

Table 2. Method Recovery Check

Parameter	Concentration ($\mu\text{g/L}$)			
	Pre-Cleanup ECD	Pre-Cleanup TMECD	Post-Cleanup ECD	Post-Cleanup TMECD
Average toxaphene concentration (duplicates)	122	114	120	108
Toxaphene spiking level ($\mu\text{g/L}$)	86	86	86	86
Predicted toxaphene concentration ($\mu\text{g/L}$)	208	200	206	194
Analyzed toxaphene concentration ($\mu\text{g/L}$)	235	195	196	183
% toxaphene recovery	113	98	95	94

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The complete report, entitled "Thermally Modulated Electron Affinity Detector for Priority Pollutant Analysis," (Order No. PB 85-158 145/AS; Cost: \$10.00, subject to change) will be available only from:

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