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EVALUATION OF A PHOTOIONIZATION DETECTOR FOR MICROBORE COLUMN SUPERCRITICAL FLUID CHROMATOGRAPHY IN ENVIRONMENTAL ANALYSIS

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by

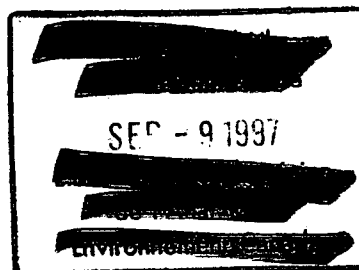Francis I. Onuska, and K.A. Terry

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MANAGEMENT PERSPECTIVE

This manuscript examines the application of a photoionization detector in supercritical fluid chromatography employing microbore columns for environmental analysis.

Ten polychlorinated biphenyl isomers and three chlorinated phenoxyacetic acid esters were selected as model compounds. Sensitivity of the photoionization detector was compared to a flame ionization detector as a current standard and found to be equivalent or marginally worse. However, the detector is more selective, especially for aromatic compounds.

Dr. J. Lawrence

Director

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PERSPECTIVE-GESTION

Dans ce manuscrit, on examine l'application du détecteur à photo-ionisation à l'analyse d'échantillons environnementaux par chromatographie en fluide supercritique avec des micro-colonnes.

On a choisi comme composés modèles dix isomères de polychlorobiphényles et trois esters chlorés de l'acide phénoxyacétique. On a comparé la sensibilité du détecteur à photo-ionisation à celle du détecteur à ionisation de flamme qui servait d'étalon; le détecteur à photo-ionisation possède une sensibilité équivalente ou à peine moindre que le détecteur à ionisation de flamme. Toutefois, il est plus sélectif, en particulier dans le cas des composés aromatiques.

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SUMMARY

A photoionization detector (PID) has been evaluated for its applications in supercritical fluid chromatography using microbore columns. The PID is a non-destrutive detector which is sensitive to the concentration of the analyte present. Thus, maximum sensitivity is obtained at low flow-rates. The PID dynamic range in supercritical fluid chromatography is approx. 10^4 which is much smaller than in gas chromatography. Although the PID appears to complement the flame ionization detector (FID) in many respects, it should be considered of limited value in environmental trace analyses due to the large cell volume.

RÉSUMÉ

On a évalué un détecteur à photo-ionisation (DPI) en vue de l'appliquer à la chromatographie en fluide supercritique avec des micro-colonnes. Le DPI est un détecteur non destructif qui est sensible à la concentration d'analyte. Ainsi, la sensibilité maximale est obtenue à de faibles débits. La gamme dynamique du DPI en chromatographie en fluide supercritique est d'environ 10^4, ce qui est beaucoup plus petit que la gamme dynamique en chromatographie en phase gazeuse. Bien que le DPI semble compléter le détecteur à ionisation de flamme (DIF) à bien des égards, sa valeur est limitée, estime-t-on, pour l'analyse des éléments-traces, en raison du grand volume de la cellule.

INTRODUCTION

Since the introduction of supercritical fluid chromatography as an analytical technique, the flame ionization detector (FID) has been the most frequently used detector because of its sensitivity, selective response to carbon-containing compounds and wide dynamic range of operation. However, the analysis of complex mixtures can require the use of a more selective detector such as a photometric detector for analytes containing either sulfur or phosphorus (1) or more expensive but universal detectors such as an ion mobility detector (2) or a mass spectrometric detector (3).

The photoionization detector (PID) was first developed by Lossing and Tamaka (4) and significantly improved by Driscoll (5). Applications have been largely in gas chromatography. There have been conflicting reports on the application of photoionization detectors in supercritical fluid chromatography (6). The applicability of the PID in supercritical fluid chromatography has been demonstrated by Sim et al (7). In their work a conventional-size 4.6 mm i.d. packed column was used and the PID cell volume was not modified. The PID showed advantages over FID in terms of increased selectivity to polycyclic aromatic hydrocarbons as well as sensitivity and detector signal stability when subjected to high gas flow rates. Although many

advances in design have improved the performance of the PID, few modifications have addressed the fundamental optical shortcomings observed when used in SFC (8).

For a PID-detector, the most frequent contribution to spurious performance arises from impurity of the supercritical fluid. The impurities change the light intensity by quenching that affects sensitivity of the detector. In general, the photoionization detector utilizes a high energy UV-lamp adjacent to an ionization chamber which contains an accelerating and a collecting electrode. Analytes eluted from the SFC column absorb the photons having a maximum energy of 10.2 eV (979.2 kJ/mole) and are ionized as follows :

$$R + hv = R^+ + e^-$$
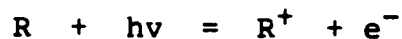
where hv is a 979.2 kJ/mole photon (an energy greater than the ionization potential of analytes R). Ions formed during the photoionization reaction are driven to the collector electrode by an electrical field. The resulting current is then amplified and measured.

We report evaluation of a PID using microbore column SFC. Determination of detection limits, linearity and linear range for selected PCB-isomers and 2,4-D esters are presented to illustrate performance of the system.

EXPERIMENTAL

Instrumentation

The chromatographic system consisted of a Lee Scientific Co. computer-controlled pumping and injection system using Lee Scientific Co. software running on an IBM-XT personal computer (Lee Scientific Co., Salt Lake City, Utah, U.S.A.), a gas chromatographic oven (Dani 3900 GC oven, Monza, Italy), a 500 nL sample loop injection valve (Valco Instruments, Houston, TX) and a PID Model P152-02 HT (HNU Systems) using a high temperature glass-lined detection cell. The 10.2 eV HNU detector has a relatively simple design with a cell volume of 40 uL. Photons emitted from the lamp are absorbed by the analytes in the sample cell, resulting in a decrease in the photon flux measured by the photodiode detector.

The entire detector assembly was positioned inside the split-splitless injector cavity of the chromatograph. All the detector connections were made inside the chromatographic oven. The detector was connected to the HNU-electrometer and was installed on the DANI gas chromatograph, a Model 3900 modified for supercritical fluid chromatography as described earlier (9). A microbore column was employed to reduce the column flow rate when using CO_2 and CO_2+methanol as the mobile phases. The PID detector was coupled directly to the microbore

column via a 10 cm length of 30 um i.d. restriction capillary tubing in the GC-oven.

Chemicals

All solutions were prepared from reagent grade chemicals. SFC-grade carbon dioxide (Linde Specialty Gases, Oakville, Ont.), was used with the addition of methanol or acetonitrile modifiers for some tests. Modifier was added by introducing specified volumes of solvent through stainless steel capillary tubing directly into the pump.

1. Chlorinated Phenoxyacetic Acid Esters.

A mixture of three chlorinated phenoxyacetic acid esters (2,4-D isopropyl ester, 2,4-D n-butyl ester and 2,4,5-T isopropyl ester) was prepared in pesticide grade methylene chloride at 6 different concentration levels of 50, 100, 250, 500, 1000 and 2500 ng/uL (see Table 1). A Deltabond-Phenyl microbore column (Keystone Scientific Inc., Bellefonte, PA) 250mm x 1 mm i.d. was used. An oven temperature of 60° C was maintained constant during the pressure programming operation. A Valco internal volume injector (0.5 uL) was used to inject the sample onto the column. The pressure was held at 120 atm for 2 minutes, ramped at 2 atm per minute to 150 atm and then maintained at 150 atm for 10 minutes. The PID detector temperature was set at 240° C during analyses. Helium was added to the end of the microbore column at 20 mL/min.

2. Polychlorinated Biphenyl Mixture

A mixture of five chlorinated biphenyl congeners was prepared at 4 different concentration levels from 25 to 500 ng/uL in methylene chloride (Table 2). All chromatograms were recorded using the above described instrumentation. An oven temperature of 80° C was employed.

RESULTS AND DISCUSSION

If it is intended to use a commercially available PID detector with microcolumns, it is of primary importance to keep the extra-column contributions to peak broadening to a minimum. These contributions originate from the dead volume of the inlet tube and the cell volume of the detector. The HNU PID-detector has an undesirably large dead volume for microbore and capillary column work (approx. 40 uL). Modifications to reduce this volume are needed. For this study volume reduction was achieved by means of packing small fractured pieces of calcium fluoride inside the detector cell. Calcium fluoride has the same optical density as the lamp windows and it provides sufficient reduction of the cell volume. It was estimated that the inner volume was decreased by approx. 40 percent. An improvement was observed for the peak shape, showing less than 10

percent tailing after the modification. This is illustrated in Figure 1.

The application of the microbore columns in supercritical fluid chromatography using a photoionization detector was also explored with a mixture containing chlorinated phenoxyacetic acid esters. A chromatogram illustrating their separation is shown in Figure 2.

The results for the sensitivity determination are shown in Table 3 for selected PCB congeners expressed as mean values from triplicate measurements. The detection limit for PCBs, at S/N = 3 is approx. 6 ng/uL. Under identical chromatographic conditions, the detection limit for 2,4-D and 2,4,5-T esters at S/N = 3 is 1.5 ng/uL. In all experiments using a microbore column connected to the PID, a helium purge (20 mL/min) was used and no substantial decrease in performance was observed. From the chromatograms shown in Figures 1 and 2, it can be seen that the detector, as currently constructed, is suited to microbore columns because of the higher flow-rates and greater sample capacity.

Photoionization detector responses to selected PCB-isomers and chlorinated phenoxyacetic acid esters are shown in Tables 3 and 4. The upper limit of responses for the 10.2 eV source was determined by injecting up to 2.5 mg of an analyte into a microbore

column. Chromatograms at this concentration level did not show any appreciable overloading. The lower concentration limit was determined by making measurements at the same attenuation for various analytes, is shown in Figures 3 and 4. From the concentration dependent responses of a PID, it is evident that this type of detector is well suited for microbore columns. Linearity of detector response over a wide range of concentrations indicates its suitability for compounds containing an aromatic moiety. The linearity of the detector was determined by measuring the peak area versus peak mass of integrated solute. The detector gave a linear response over the range 10 to 25,000 nanograms. The signal to noise level at 12 ng was about 25:1.

A pressure-programmed analysis of a sediment extract is shown in Figure 5. The magnitude of the baseline drop was acceptable, and the peak widths indicated that a minimum detector cell dead volume was present.

Methanol modified carbon dioxide (2 percent by weight) showed substantial loss of sensitivity of the detector due to quenching. It was demonstrated that the addition of methanol to carbon dioxide is not a practical choice because of a substantial loss of sensitivity for all analytes. However, up to 2 percent of acetonitrile added to the supercritical carbon dioxide improved the sensitivity for all analytes tested to approx. 35% of the values for CO_2 alone.

The use of nitrous oxide as a supercritical fluid was also investigated. The ionization potential (12.9 eV) for nitrous oxide indicated that it might be useful as a carrier fluid. However, first results showed a reduction in the PID background current due to increased quenching by nitrous oxide itself or its impurities. As discussed by Senum (10), the quenching of the photoionization detector response by absorption of the excitation energy is 50 fold greater than that of carbon dioxide. Sensitivity however, is restored almost immediately after switching back to carbon dioxide.

The PID detector may find some applications using more exotic supercritical fluids such as xenon, sulfur hexafluoride or freons for very specific analyses. This speculation must be evaluated but the most important requirement for its successful implementation in SFC would be a smaller volume of the PID cell.

CONCLUSIONS

The SFC-PID system is an effective tool for detection of analytes containing a phenyl ring in the molecule. The optimal use of a PID requires that a negligible excitation absorption and electron capture rate be exerted in order to have an acceptable sensitivity even for aromatic compounds. First impressions of the

PID's performance in SFC would suggest that it does not match sensitivities of other detectors in gas chromatography. Our results confirm that the PID offers a detection system with modest

sensitivity to aromatic compounds, which can be used with both packed and microbore packed columns in SFC.   However, the tested commercially available PID-detector is not suitable in its present design to be employed with capillary SFC.

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Table 1. Retention Data and Concentrations of 2,4-D and 2,4,5-T
         Esters.

Compound	M.W.	R.T.(min)	Conc.(mg/mL)
2,4-D isopropyl ester	263.5	5.12	5.0
2,4,5-T isopropyl ester	297.6	6.18	5.0
2,4-D n-butyl ester	277.5	5.85	5.0

Table 2. Retention Data and Concentration of Model Polychlorinated
Biphenyl Congenrs.

Isomer (-chlorobiphenyl)	M.W.	R.T.(min)	Conc.(mg/mL)
2,6 di	223.1	15.40	5.0
3',4 di	223.1	16.37	5.0
2,3,6 tri	257.5	18.04	5.0
2,5,3',4' tetra	292.0	19.43	5.0
2,4,6,3' tetra	292.0	20.59	5.0
2,4,6,2',5' penta	326.4	21.72	5.0
2,4,6,2',4',6' hexa	360.9	25.68	3.3
2,3,4,5,6,2'3'4'5' nona	464.2	35.80	2.6
Decachlorobiphenyl	498.7	36.98	1.4

Table 3. Variation of the PID Molar Responses with Concentration for Selected PCB Congeners.

Isomer (-chlorobiphenyl	Amount(ng)	Conc.(uM/L)	Area (count/uM)
2,5,2'4'-tetra	12.5	42.8	1075
	25.0	85.6	888
	75.0	257.0	767
	250.0	1027.0	747
2,4,6,3'-tetra	12.5	42.8	1521
	25.0	85.6	1053
	75.0	257.0	1031
	250.0	1027.0	980
2,4,6,2'5'-penta	12.5	31.9	1805
	25.0	63.8	1317
	75.0	191.5	1237
	250.0	765.9	1236
2,4,6,2'4'6'-hexa	12.5	69.3	760
	25.0	138.5	555
	75.0	417.0	540
	250.0	1385.0	540
2,3,4,6,2'4'-hexa	12.5	69.3	703
	25.0	138.5	600
	75.0	417.0	547
	250.0	1385.0	430
2,3,4,5,6,2'3'4'5'-nona	12.5	53.9	332
	25.0	107.7	325
	75.0	323.1	318
	250.0	1076.4	318
Decachlorobiphenyl	12.5	50.0	230
	25.0	100.2	227
	75.0	300.8	222

Table 4. Variation of the PID Molar Responses vs. Concentration for
Selected 2,4-D and 2,4,5-T Esters.

Compound	Amount (ng)	Amount (pM)	Conc.. (uM/L)	Area (counts/pM)
2,4-D isopropyl	50	190.0	0.379	65.2
	100	397.5	0.759	64.0
	250	949.0	1.898	58.0
	500	1898.0	3.795	52.0
	1,000	3795.0	7.591	53.0
	2,500	9488.0	18,979	49.0
2,4-D butyl	50	180.0	0.360	67.0
	100	360.0	0.720	66.1
	250	901.0	1.802	61.7
	500	1802.0	3.603	56.7
	1,000	3604.0	7.207	55.4
	2,500	9009.0	18.018	52.6
2,4,5-T isopropyl	50	168.0	0.336	67.3
	100	336.0	0.672	64.6
	250	840.0	1.680	58.3
	500	1680.0	3.360	51.6
	1,000	3360.0	6.720	51.4
	2,500	8403.0	16.800	47.4

CAPTIONS

Figure 1. Separation of selected PCB-isomers.

Conditions: elution order and identification in Table 2. Microbore column 250 mm x 1 mm i.d. Deltabond-Phenyl bonded silica (5 mm particle size); mobile phase CO_2 at 80 C; pressure programmed from 120 atm, held 2 min. to 250 atm at 2 atm/min/ Detail in the text.

Figure 2. Separation of selected 2,4-D and 2,4,5-T esters.

Conditions: elution order and identification in Table 1. Microbore column 250 x 1 mm i.d. Deltabond-Phenyl bonded silica (5 mm particle size); mobile phase CO_2 at 60 C; pressure programmed from 120 atm, held 2 min., to 200 atm at 2 atm/min. Details in the text.

Figure 3. Calibration graph for 2,4-D and 2,4,5-T esters.---2,4-D isopropyl ester; 2,4-D n butyl ester; 2,4,5-T isopropyl ester.

Figure 4. Calibration graph for selected PCB congeners.

2,3'4',5; tetrachlorobiphenyl; 2,3',4,6-tetrachlorobiphenyl; 2,2',4,5',6-pentachlorobiphenyl; 2,2',4,4',6,6'-hexachlorobiphenyl.

Figure 5. Sediment spiked extract of AROCLOR 1232.

Conditions: as in Fig.1. Concentration 11.2 ng/mL.
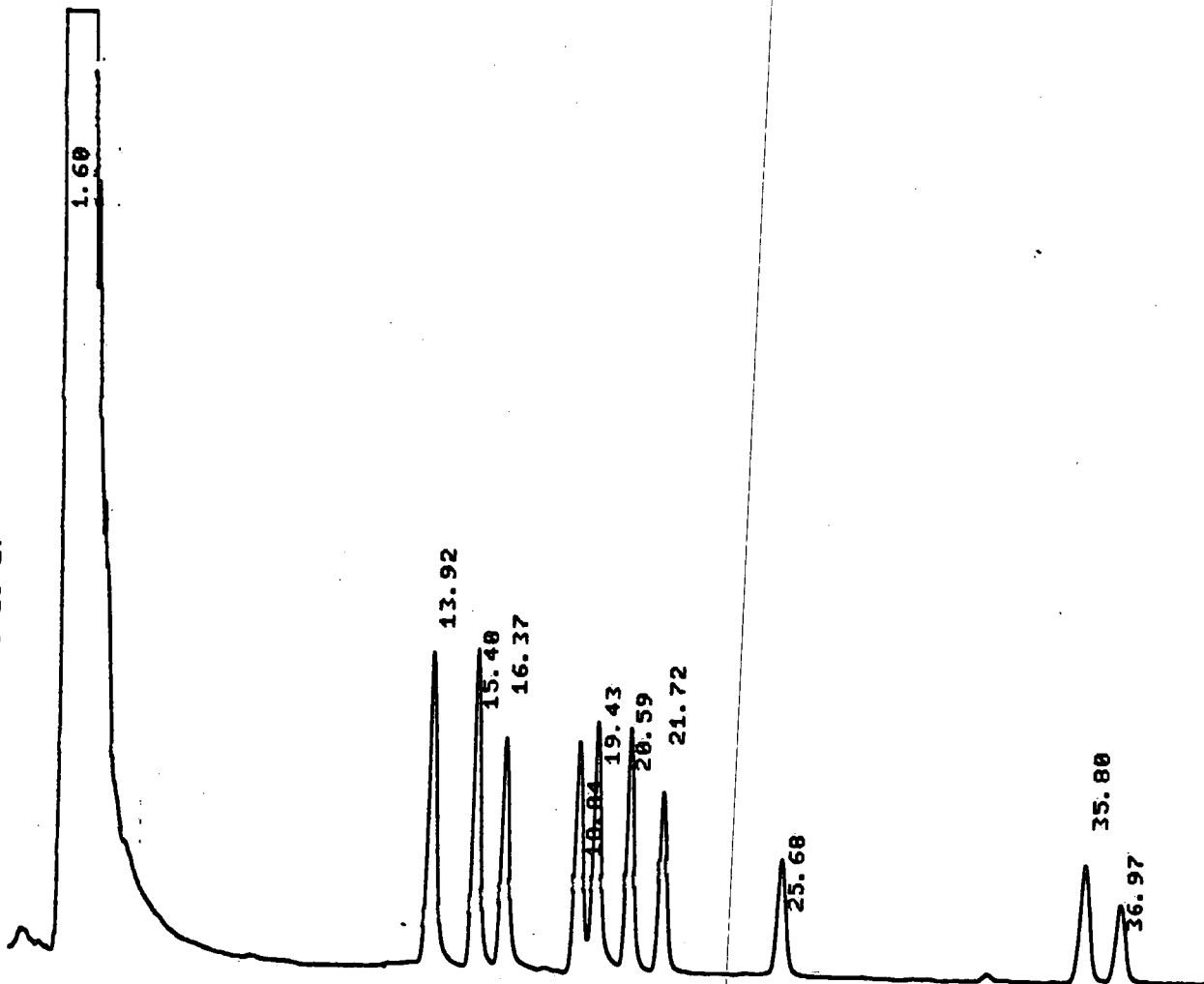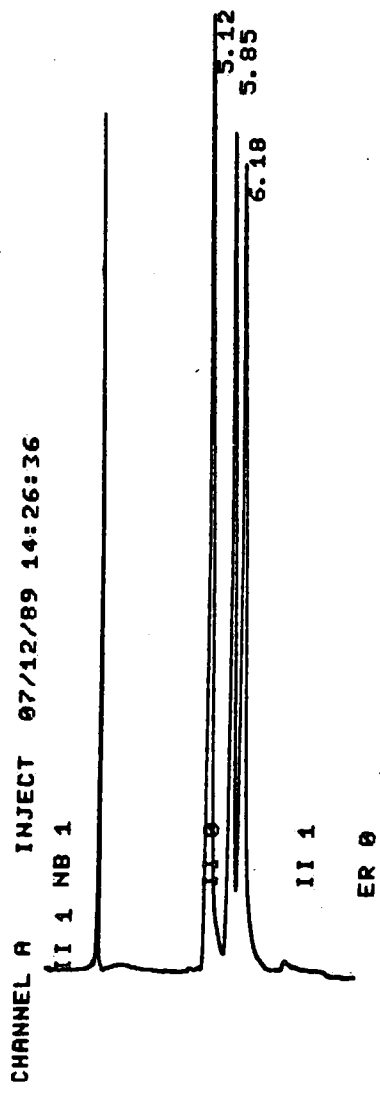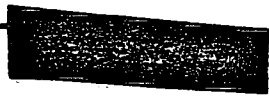
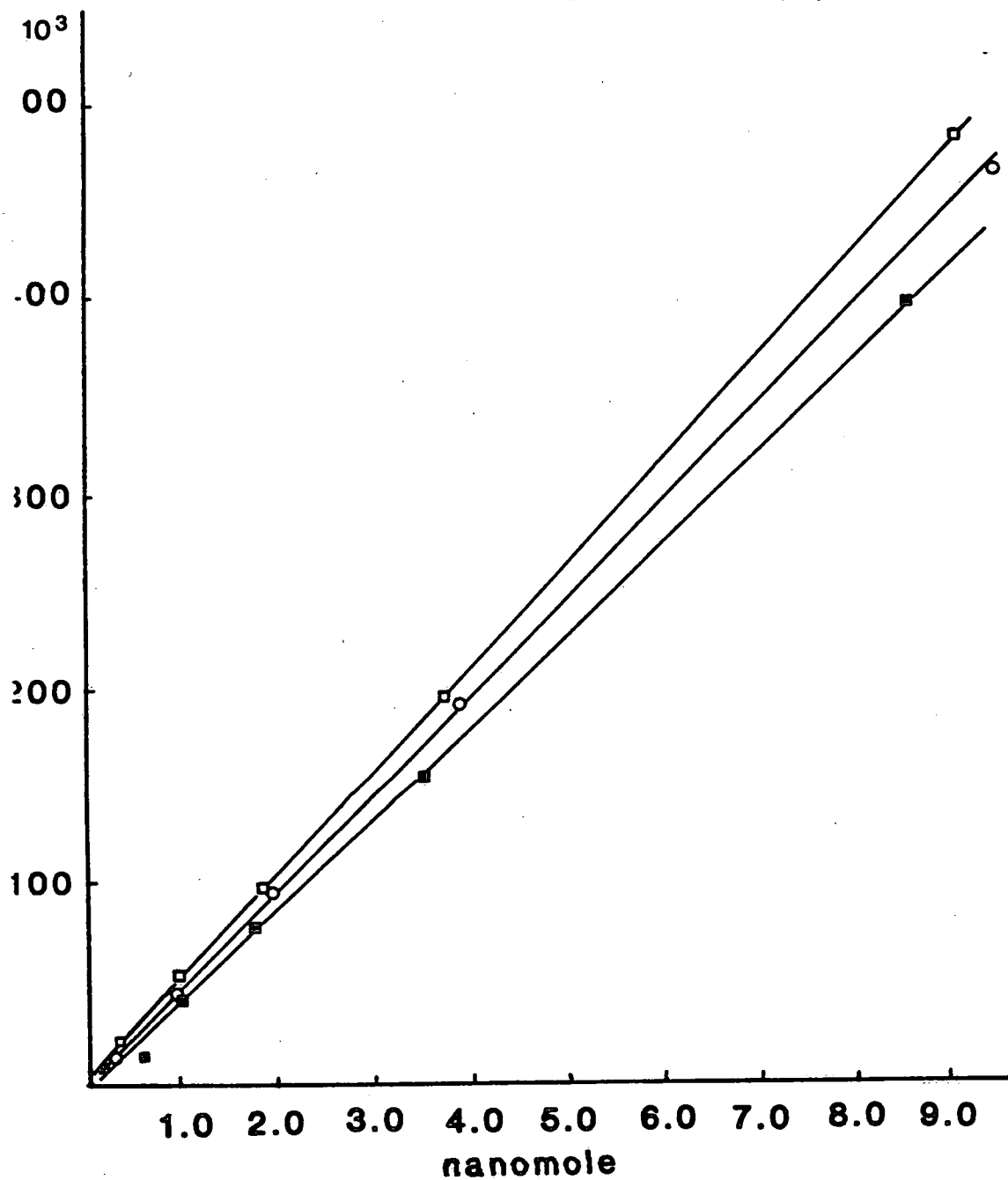CHANNEL A   INJECT   00:16:27

Fig. 1

Fig. 2

CHANNEL A   INJECT 07/12/89 14:26:36

II 1 NB 1

II 0

5.12
5.85
6.18

II 1

ER 0

Fig. 2

LINEARITY GRAPH FOR 2,4-D AND 2,4,5-T ESTERS
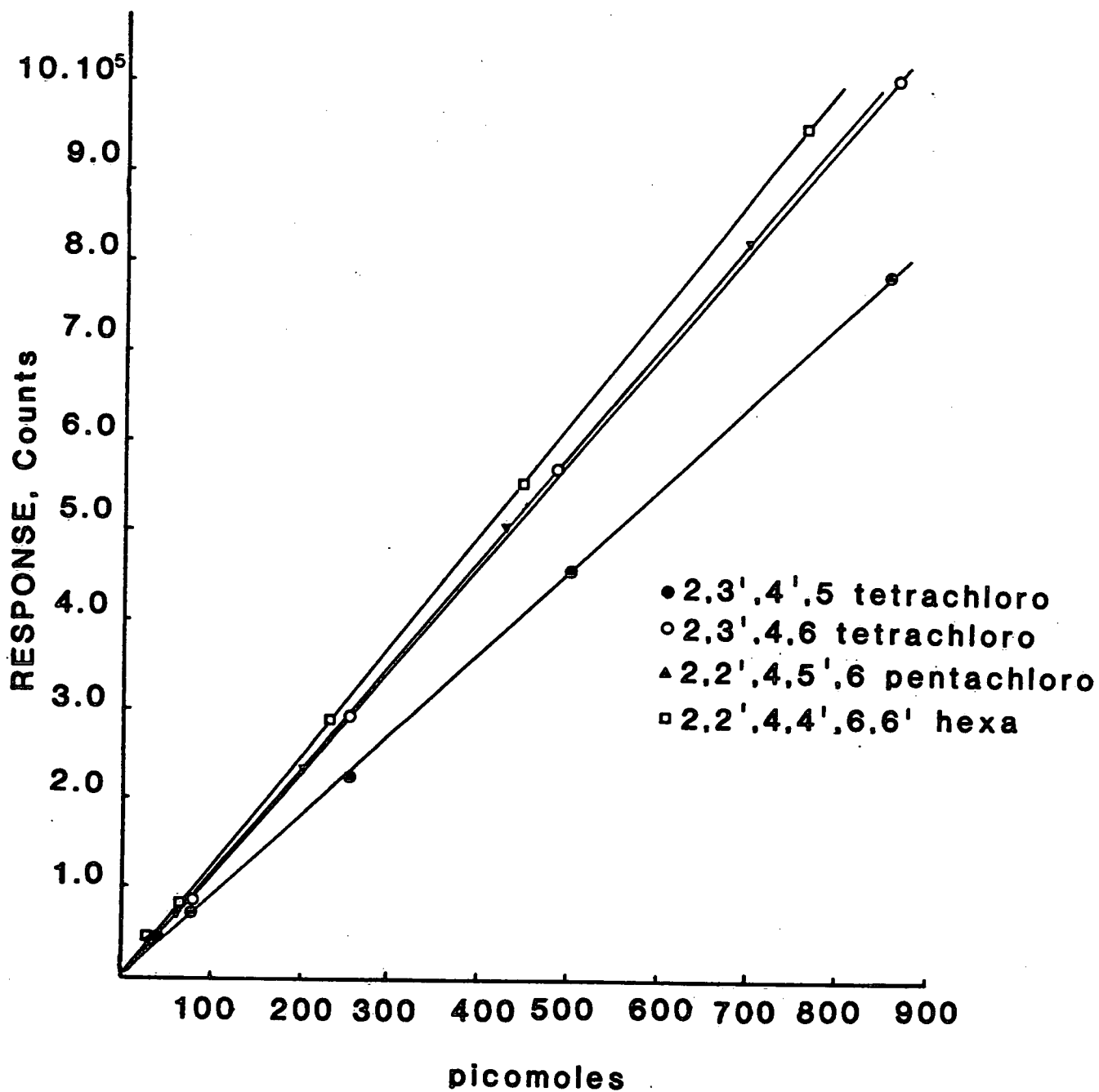
Fig.4

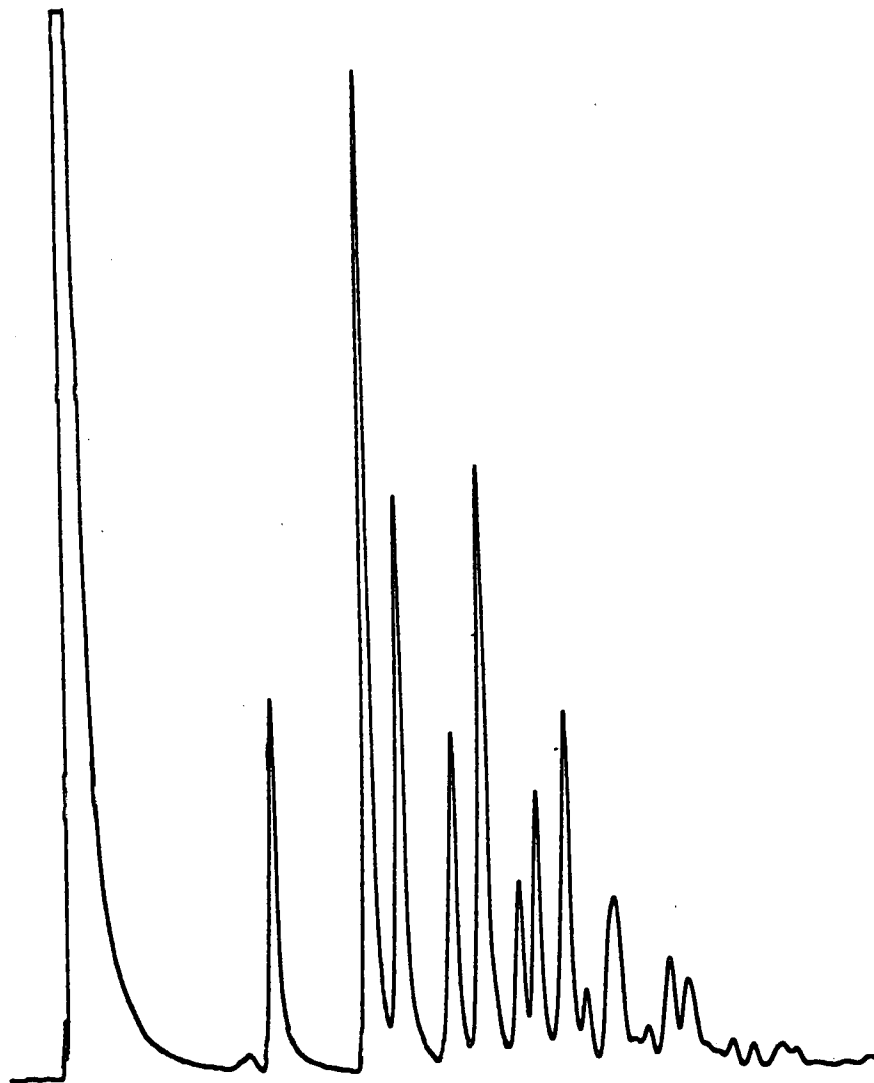# LINEARITY GRAPH FOR SELECTED PCB-CONGENERS

• 2,3',4',5 tetrachloro
○ 2,3',4,6 tetrachloro
▲ 2,2',4,5',6 pentachloro
□ 2,2',4,4',6,6' hexa

Fig. 4

FAULT 10   22:01:49

FAULT
INJECT

A
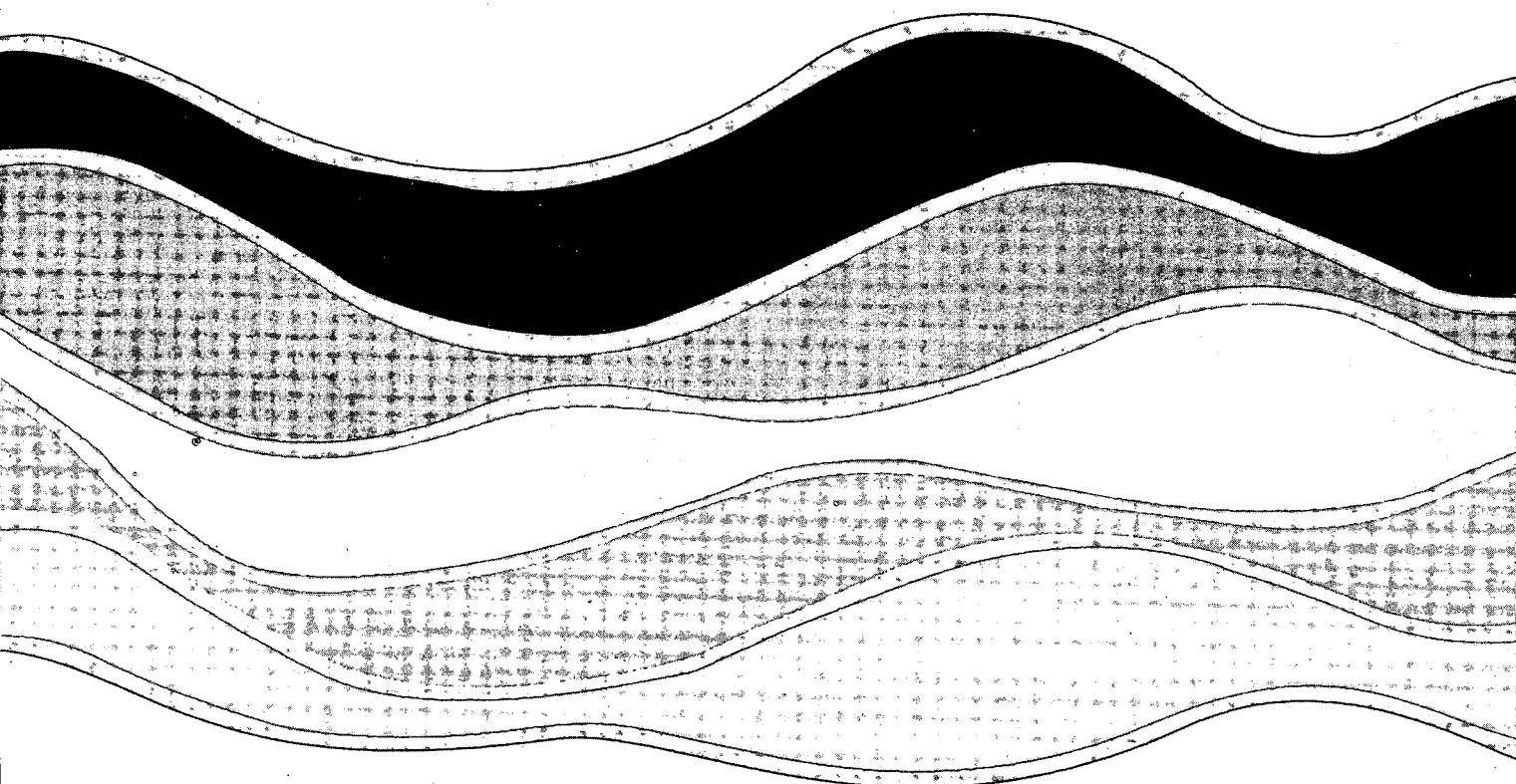
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