EFFECTS OF CONTAMINATION ON ION MOBILITY DETECTION AFTER GAS CHROMATOGRAPHY

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SUMMARY

The ion mobility detector is a device that can be used for the selective, ultra-trace detection of organic compounds after capillary gas chromatography. It is the only gas chromatographic detector which does not require heteroatomic compounds for selective response, yet concern is often expressed over its quantitative capabilities. Being a secondary ionization device, competitive charge transfer reactions from unseparated compounds or detector gas contamination may decrease the accuracy of measurement. This paper investigates the effects of both electronegative and electropositive contaminants on the detector's response. In general, it was found that contamination of the detector did affect response but no more severely than in conventional detectors such as the electron-capture detector or the flame ionization detector.

INTRODUCTION

The use of ion mobility spectrometry for the selective detection of trace compounds after capillary gas chromatography (GC) has been recently demonstrated[1]. In selected examples this ion mobility detector has been shown to be both sensitive and selective for naphthalene in gasoline[1], terpenes in orange oil extracts[2], and 2,4-dichlorophenoxyacetic acid in soil extracts[3].

One criticism often voiced regarding the use of GC detectors, such as the ion mobility detector, which employ secondary ionization sources is that response characteristics can be drastically altered by background contamination of the system. In certain cases, low levels of column bleed, co-eluting components in the sample mixture and/or impurities present in detector gases can compete with the specific compound of interest for the available concentration of reactant ions. As discussed by Baim and Hill[3], special precautions, including concentrating or diluting samples and comparing the resulting responses to those predicted from calibration plots, can indicate whether co-eluting components are hampering quantification using the ion mobility detector. These procedures are, however, not as useful for addressing possible sources of contamination or interference not contained within the sample itself.

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In an effort to quantify the effect of background contamination on ion mobility detector response, calibration graphs were produced, using both the positive and negative operating modes, in the presence of various known concentrations of organic compounds continuously bled into the detector. To compare the performance of the ion mobility detector with those of flame ionization and electron-capture detectors, analogous calibration graphs using these commercially available systems were also produced.

EXPERIMENTAL

The ion mobility detector and gas chromatograph used in this study were the same as those described by Baim and Hill[3]. Low levels of two potentially interfering compounds, hexane and carbon tetrachloride, were individually bled into each of the three detectors using a sampling apparatus similar to that described by Baim and Hill[1] for the continuous introduction of organic compounds. Hexane is representative of compounds detected with the positive ion mode of the ion mobility detector while carbon tetrachloride is a strongly electron capturing compound which would normally be detected using the negative ion operating mode. The interfering compound under study was placed in a glass sample holder connected to the branch of a 1/4-inch tee fitting and the holder was immersed in a temperature controlled water bath. A low flow-rate of helium, on the order of 5–10 ml min^{-1}, was maintained through the tee and into a heated and insulated noncoated fused-silica transfer line connected, using a second tee, to make up gas fitting of the detector in use. The amount of the compound entering the detector was varied by controlling the temperature of the water bath. All calibration compounds were introduced via a 30 m × 0.25 mm I.D. DB-5 fused-silica capillary column (J & W Scientific) which was installed in the gas chromatograph in the usual manner. Operating conditions of the gas chromatograph and the three detectors as used in this study are summarized in Table I.

Two calibration compounds, naphthalene and hexachloroethane, were used to produce a total of 17 individual calibration graphs with the three detectors. Naphthalene was chosen as a compound typical of those selectively detected using the positive mode of the ion mobility detector. The detector was tuned to monitor the naphthalene product ion with a drift time of 8.50 min and five samples ranging from 20 pg to 2 ng were injected to establish the plot. Each point represents an average of three injections. Calibration graphs were produced under non-doped conditions and with two levels of hexane doping and two levels of carbon tetrachloride doping acting as background contamination. For comparison, naphthalene calibration graphs were obtained using the flame ionization detector under non-doped and doped conditions. Hexachloroethane was chosen for use in the negative mode of the ion mobility detector. The detector was tuned to monitor the chloride ion with a drift time of 6.64 min under the conditions employed in these experiments. Calibration graphs were produced without background contaminants and with two levels each of hexane doping and carbon tetrachloride doping as described above. Calibration graphs were also obtained using the electron-capture detector under both non-doped and doped conditions for comparison with the negative mode of the ion mobility detector.

The ionization detector was used to determine the mass flow-rates of all background contaminant doping levels used in these studies. The flame ionization detector

TABLE I

OPERATING CONDITIONS FOR THE STUDY OF BACKGROUND CONTAMINATION

Chromatograph	
Column	30 m fused-silica, DB-5 coated
Carrier gas flow-rate	1.5 ml min^{-1} (helium)
Split ratio	50:1
Injection port temperature	250°C
Column temperature	150°C (isothermal)
Ion mobility detector	
Drift tube length	7.5 cm
Temperature	150°C
Ambient pressure	700 torr
Nitrogen drift gas flow-rate	400 ml min^{-1}
Nitrogen make-up gas flow-rate	200 ml min^{-1} (doped with 0.5% oxygen in the negative mode)
Electric field gradient	positive mode: +230 V cm^{-1}
	negative mode: −230 V cm^{-1}
Chart speed	0.5 cm min^{-1}
Flame ionization detector	
Temperature	250°C
Hydrogen flow-rate	30 ml min^{-1}
Air flow-rate	350 ml min^{-1}
Helium make-up gas flow-rate	30 ml min^{-1}
Bias voltage	−300 V
Chart speed	0.5 cm min^{-1}
Electron-capture detector	
Temperature	350°C
Operating mode	pulsed, constant current
Saturation current	2.5 × 10^{-9} A
Nitrogen flow-rate	50 ml min^{-1}
Chart speed	0.5 cm min^{-1}

was chosen because it responds to both doping compounds and, under clean operating conditions with no organic impurities present, it exhibits essentially no background current. Once a doping level was established, a fused-silica transfer line was temporarily conneted to the flame ionization detector. The increase in background current resulted from the continuous bleeding of either hexane or carbon tetrachloride into the detector. After removal of the transfer line, injections of the pure compound were made into the GC column and peak heights were matched to the background current level observed during the continuous bleed.

The mass flow-rate of a compound continuously bled into the detector may be calculated by a two-step procedure. First, the weight of the compound required to produce a peak with a maximum current equal to the background current during a continuous bleed is determined via GC injections. Second, the weight obtained is multiplied by 45% (based on Gaussian distribution considerations) to yield the mass flow-rate, in grams per second, through the detector at the peak maximum. All mass flow-rates quoted for the following calibration graphs were determined using this procedure.

RESULTS AND DISCUSSION

Effect on the positive mode of the ion mobility detector

Fig. 1 illustrates three calibration graphs obtained using the positive selective product ion mode of the ion mobility detector. Plot a, produced under non-doped conditions, is a standard calibration graph for naphthalene. Only a portion of the full operating range of the detector was examined, from 20 pg to 2 ng. Upon continuously bleeding hexane into the make-up gas of the detector, responses for identical injections of naphthalene decreased compared to those obtained in the non-doped mode. The doping levels used, determined by convenient water bath temperatures for the sampling apparatus, are representative of what would be encountered from the co-elution of a large interfering GC peak. Plot b was produced with a background level of 0.3 μg sec^{-1} hexane entering the detector and shows a decrease in response of approximately 50%. Increasing the rate of hexane bleed to 0.5 μg sec^{-1} resulted in a further response reduction to a level approximately one-third of that obtained under non-doped conditions. In each case, the peak-to-peak noise level of the detector remained constant at $1 \cdot 10^{-14}$ A and the detector baseline remained stable. Although often not as important to successful use of a detector as the peak-to-peak noise level, a randomly drifting base line can easily lead to quantitative errors in measuring peaks as well as require constant adjustment of the electrometer suppression current to keep the chromatogram on scale.

Similar effects were observed when carbon tetrachloride was continuously bled into the detector. Fig. 2 shows a series of three naphthalene calibration graphs obtained under these conditions. Plot a, produced with no carbon tetrachloride doping,
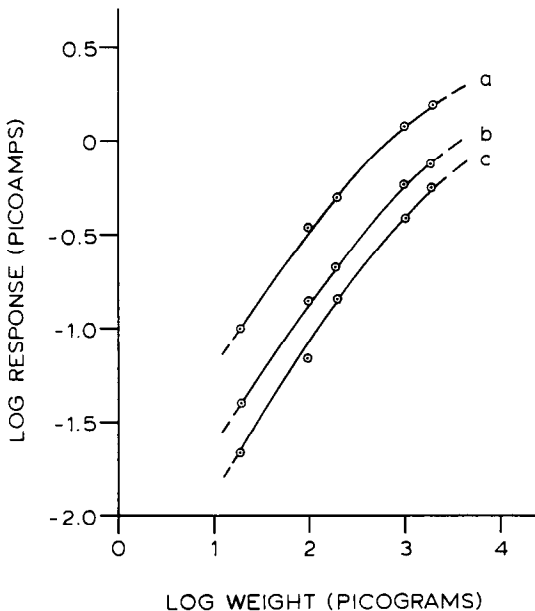

Fig. 1. Naphthalene calibration graphs using the ion mobility detector with hexane doping. The three plots correspond to (a) no doping, (b) 0.3 μg sec^{-1} hexane doping, (c) 0.5 μg sec^{-1} hexane doping.

is produced here from data shown in Fig. 1. Plot b was obtained with carbon tetrachloride continuously bleeding into the detector at a rate of 0.1 μg sec^{-1}. As occurred with hexane doping, response decreased. A further reduction was seen upon increasing the doping rate to 0.2 μg sec^{-1} as in plot c. Detector noise levels remained constant at $1 \cdot 10^{-14}$ A and the baseline remained stable in each case. Slightly greater variations in slopes of the plots with changes in the amount of naphthalene injected may be seen in Fig. 2 under carbon tetrachloride doping conditions than under hexane doping conditions as in Fig. 1. It is possible that the strongly electron capturing carbon tetrachloride is more able to interfere with production of the positive reactant ions necessary for response in this operating mode of the ion mobility detector. An appreciable depletion of reactant ion concentration can lead to detector saturation and a reduced response for the compound of interest. The effect, however, appears to be minor.
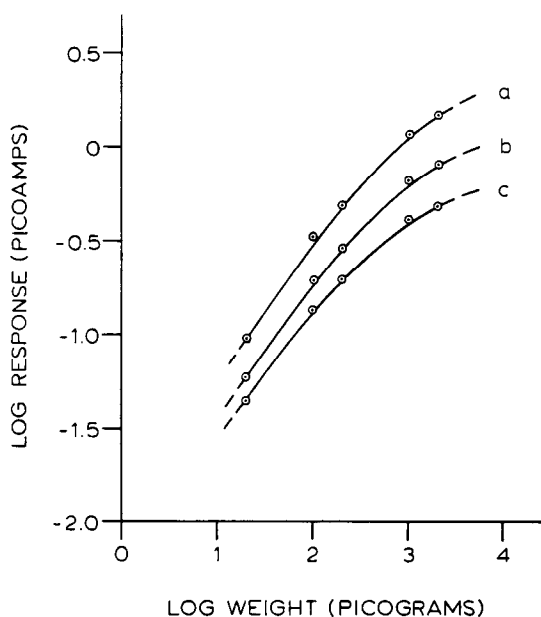

Fig. 2. Naphthalene calibration graphs using the ion mobility detector with carbon tetrachloride doping. The three plots correspond to (a) no doping, (b) 0.1 μg sec^{-1} carbon tetrachloride doping, (c) 0.2 μg sec^{-1} carbon tetrachloride doping.

Effect on the negative mode of the ion mobility detector

Three calibration graphs obtained using the chloride ion monitoring mode of the ion mobility detector under hexane doping conditions are shown in Fig. 3. The calibration compound used, hexachloroethane, was injected in amounts ranging from 20 picograms to 2 nanograms. Plot a represents a standard hexachloroethane calibration graph obtained under non-doped conditions. The chloride ion produced when hexachloroethane undergoes dissociative electron capture was monitored. Doping the ion mobility detector with low levels of hexane again resulted in a reduced detector response as was observed in the positive mode. Plots b and c correspond to hexane doping levels of 2 ng sec^{-1} and 3 ng sec^{-1}, respectively. The doping levels
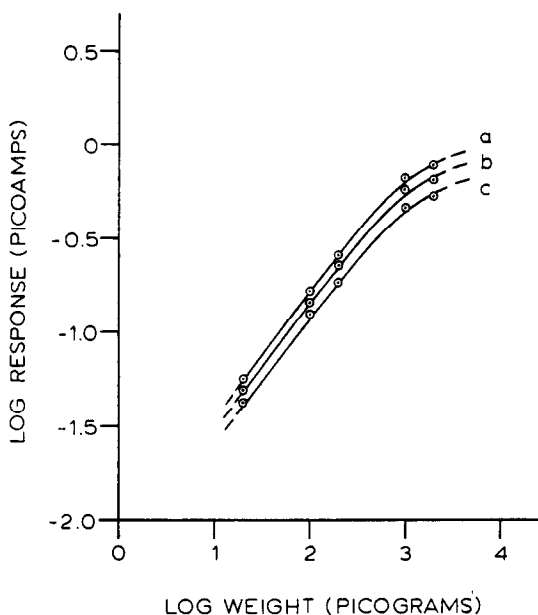
Fig. 3. Hexachloroethane calibration graphs using the ion mobility detector with hexane doping. The three plots correspond to (a) no doping, (b) 0.2 ng sec^{-1} hexane doping, (c) 3 ng sec^{-1} hexane doping.

used in the negative mode were considerably lower than those used in the positive mode. It was desired to approximately match background contaminant levels between the negative mode of the ion mobility detector and the electron-capture detector. The electron-capture detector was only able to operate with doping levels much lower than those used with the positive mode of the ion mobility detector. The ion mobility detector noise level and baseline were unchanged by hexane doping.

When the ion mobility detector is operated in the chloride ion monitoring mode, doping the detector with carbon tetrachloride represents a different situation. Carbon tetrachloride undergoes dissociative electron capture to form the chloride ion in the same manner as hexachloroethane. Therefore, both the background contaminant and the compound of interest respond in this configuration. Fig. 4 illustrates three calibration graphs for hexachloroethane obtained with carbon tetrachloride doping. Plot a is the non-doped calibration graph reproduced from Fig. 3. In plot b, the detector was doped with 0.6 ng sec^{-1} of carbon tetrachloride. At this doping level a minor reduction in response was observed. The peak-to-peak noise level of the detector remained constant but, as expected, the background current increased due to continuous production of chloride ions from the carbon tetrachloride. The increased height of the baseline, 0.6 pA, was easily lowered by use of the variable electrometer suppression current. Increasing the doping level to 0.8 ng sec^{-1}, as in plot c, resulted in responses being reduced by a factor of two-thirds as compared to the non-doped calibration plot. The detector background current increased by 0.8 pA over that observed on the non-doped calibration graph. Unlike in previous doping experiments, the addition of 0.8 ng sec^{-1} of carbon tetrachloride to the ion mobility detector operating in the chloride ion monitoring mode was sufficient to
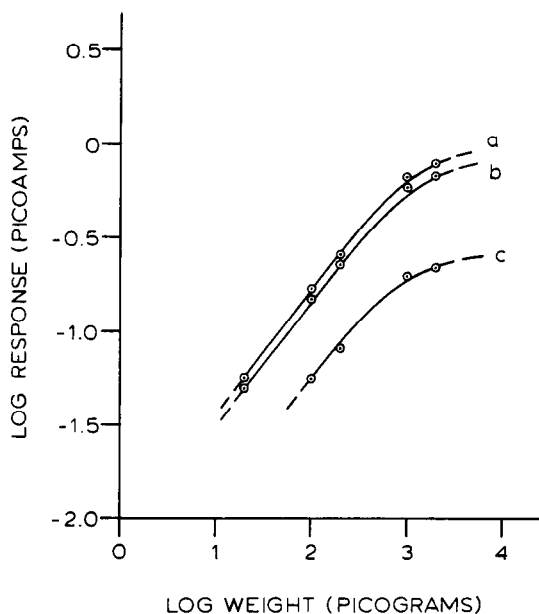
Fig. 4. Hexachloroethane calibration graphs using the ion mobility detector with carbon tetrachloride doping. The three plots correspond to (a) no doping, (b) 0.6 ng sec^{-1} carbon tetrachloride doping, (c) 0.8 ng sec^{-1} carbon tetrachloride doping.

raise the detector noise level to $1.2 \cdot 10^{-14}$ A. Although the response of 20 pg of hexachloroethane could still be observed, it was not twice the peak-to-peak noise level of the detector and was therefore not plotted.

Doping levels within the range of 0.6 to 0.8 ng sec^{-1} are equivalent to injecting quantities of carbon tetrachloride on the order of 1–2 ng into the GC column[4]. As may be observed on the non-doped hexachloroethane calibration graph, these quantities are near the point where detector saturation becomes a significant factor in determining response. Slight variations in doping levels within this range would be expected to greatly affect the availability of reactant ions for production of the hexachloroethane response.

Comparison with flame ionization and electron-capture detectors

When viewed in isolation, the reductions in response of the ion mobility detector caused by the presence of background contamination would appear to hamper quantitative use of the detector under less than ideal conditions. The key point to be addressed, however, is how these variations in response characteristics compare with those observed using other GC detectors, such as the flame ionization and the electron-capture detectors, under similar circumstances. For example, an attempt was made to obtain a naphthalene calibration graph using a flame ionization detector doped with low levels of hexane as a background contaminant. The flame ionization detector baseline could not be stabilized sufficiently for use when doping levels duplicating the ones employed with the positive mode of the ion mobility detector were introduced into the detector. Even reducing the hexane doping level below the 0.2 ng

sec^{-1} used in the negative mode of the ion mobility detector failed to adequately stabilize the detector at electrometer settings needed to observe a naphthalene response. In addition, the peak-to-peak noise level of the flame ionization detector under hexane doping conditions was nearly two orders of magnitude greater than that of the ion mobility detector. Using carbon tetrachloride as a background contaminant produced better results. Although the doping levels used in the positive mode of the ion mobility detector were still too high for use with the flame ionization detector, the latter was adequately stabilized for use at a carbon tetrachloride flow-rate of 0.1 μg sec^{-1}. A comparison of calibration graphs for naphthalene under non-doped and doped conditions is provided in Fig. 5. Plot a represents a standard flame ionization detector calibration graph for naphthalene with no background contamination. As with the ion mobility detector, only a range of 20 pg to 2 ng was examined. Doping the flame ionization detector with 0.1 μg sec^{-1} of carbon tetrachloride, as shown in plot b, resulted in a reduction in response of about 30%. More importantly, the noise level of the flame ionization detector increased from $6 \cdot 10^{-14}$ A with no doping to $8 \cdot 10^{-13}$ A under carbon tetrachloride doping. The increase in noise eliminated all responses for naphthalene injected in quantities less than 200 pg. In contrast, the ion mobility detector response to 20 pg of naphthalene was still clearly visible.
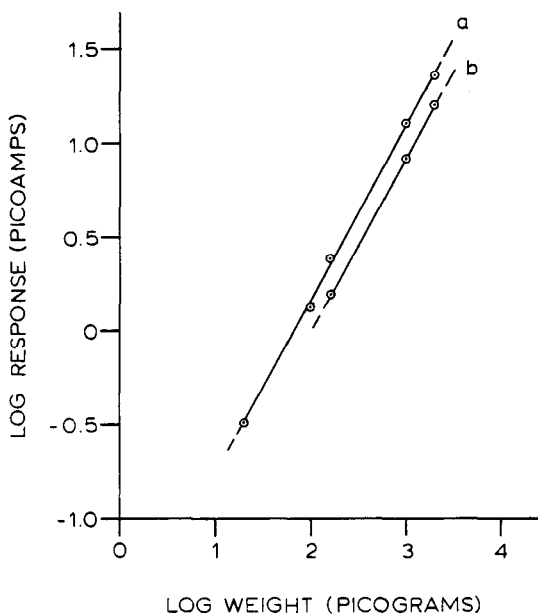

Fig. 5. Naphthalene calibration graphs using the flame ionization detector with carbon tetrachloride doping. The two plots correspond to (a) no doping, (b) 0.1 μg sec^{-1} carbon tetrachloride doping.

The electron-capture detector suffered less reduction in performance than the flame ionization detector when subjected to low levels of background contamination produced by hexane. Fig. 6 illustrates two graphs obtained using hexachloroethane as the calibration compound. Unlike the previous calibration graphs, response is plotted in terms of arbitrary units (A.U.) instead of current. The electron-capture
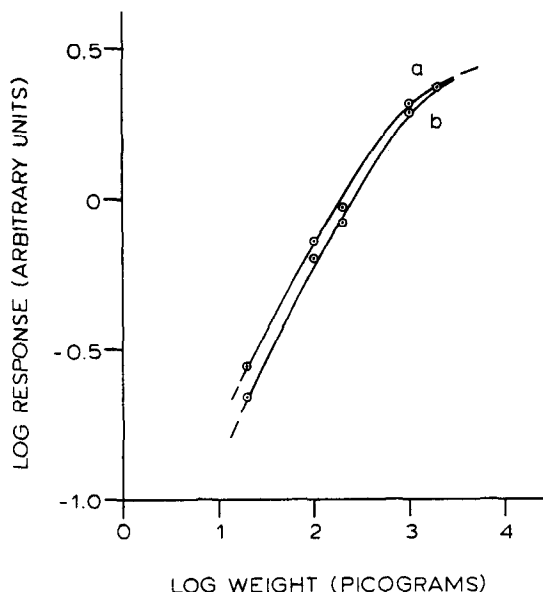
Fig. 6. Hexachloroethane calibration graphs using the electron-capture detector with hexane doping. The two plots correspond to (a) no doping, (b) 0.2 ng sec^{-1} hexane doping. (3 ng sec^{-1} hexane doping superimposes with plot b.)

detector was operated in the constant current mode which produces an output signal proportional to the pulsing frequency required to keep the detector current constant at a preselected value as compounds elute from the GC column. Plot a represents a hexachloroethane calibration graph produced under non-doped conditions. Doping the detector with 0.2 ng sec^{-1} as in the negative mode of the ion mobility detector caused only a slight reduction in response, shown in plot b. This behavior was expected due to the poor electron-capture behavior of saturated alkanes. Increasing the hexane doping level to 3 ng sec^{-1} produced no further reduction in response. The plot obtained superimposed with plot b and is therefore not shown in Fig. 6. The detector noise level increased from 0.06 A.U. under non-doped conditions to 0.15 A.U. with either level of hexane doping. Baseline stability decreased slightly upon introducing the background contaminant but did not hamper use of the detector. Increasing the hexane doping significantly over the levels reported here did not drastically lower response in the electron-capture detector but did increase the detector noise level and baseline wander to the point where it could not be used. At the lower hexane doping levels, however, the electron-capture detector was as stable as the ion mobility detector.

When subjected to background contamination produced by carbon tetrachloride the electron-capture detector response is much more sensitive to doping levels. Fig. 7 shows calibration graphs obtained under these conditions. Plot a, produced with no carbon tetrachloride doping, is reproduced from Fig. 6. Doping the electron-capture detector with 0.6 ng sec^{-1} of carbon tetrachloride did not alter response. The curve produced superimposed over the non-doped plot and is not shown in Fig. 7. The detector noise level and baseline were unchanged. A comparison

with plots a and b of Fig. 4 shows that the electron-capture detector is more able to tolerate this level of contamination than the ion mobility detector. Increasing the doping level to 0.8 ng sec^{-1} produced a reduction in detector response as shown in plot b of Fig. 7. As occurred with the ion mobility detector, the peak-to-peak noise level of the electron-capture detector increased significantly from 0.06 A.U. under non-doped conditions to 0.32 A.U. under this higher level of carbon tetrachloride doping. Baseline wander was also increased. Quantities of hexachloroethane less than 100 pg could not be observed at all, and only those of 200 pg and up produced responses of at least twice the peak-to-peak noise level of the detector.
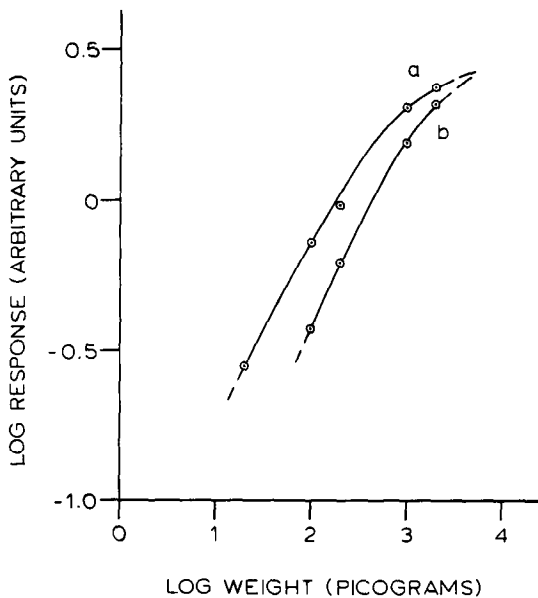

Fig. 7. Hexachloroethane calibration graphs using the electron-capture detector with carbon tetrachloride doping. The two plots correspond to (a) no doping, (b) 0.8 ng sec^{-1} carbon tetrachloride doping. (0.6 ng sec^{-1} carbon tetrachloride doping superimposes with plot a.)

In several of the above experiments an increase in detector noise was accompanied by large increases in baseline current. Specifically, doping the flame ionization detector with hexane or the electron-capture detector with carbon tetrachloride produced this effect. To insure that random fluctuations in contaminant flow, introduced via the make up gas fitting, did not produce the increased noise, these contaminants were also thoroughly mixed into the carrier gas on the high pressure (inlet) side of the GC column. Results comparable to those obtained in the above experiments were obtained in each case indicating that fluctuations in the concentration of the contaminants at the make up gas fitting did not account for the observed increase in detector noise. The observed noise is thus attributed to operation of the detectors under conditions of high background current produced by the added contaminants.

CONCLUSIONS

The general conclusion which may be drawn from the calibration graphs in Figs. 1–7 is that the ion mobility detector is no more affected by background contamination than either the flame ionization or electron-capture detectors. In terms of detector noise level and baseline stability, the ion mobility detector exceeded the performance of both the flame ionization detector and the electron-capture detector in nearly all cases. When operated in the positive mode, the ion mobility detector detected lower quantities of naphthalene than the flame ionization detector when both were subjected to carbon tetrachloride doping and was able to operate under hexane doping conditions where flame ionization could not. In the negative mode, the ion mobility detector and electron-capture detector suffered similar degradations in performance with the addition of background contamination. Only when carbon tetrachloride doping at 0.8 ng sec^{-1} was employed did either the electron-capture detector or the ion mobility detector response fall off appreciably.

ACKNOWLEDGEMENTS

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