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EVIDENCE FOR SURFACE EFFECTS IN AN ELECTRON-CAPTURE DETECTOR

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SUMMARY

We have found surface effects in a conventional electron-capture detector that are significantly reduced in an experimental, more inert version of this detector, both by Varian. These surface effects generate unique patterns of solute response for both pesticides–herbicides, and derivatized cytosine strong electrophores. They also cause a minimum followed by a more pronounced maximum in the response factor with increasing solute concentration, demonstrated with lindane. Certain speculations are presented to account for these observations.

INTRODUCTION

As reported in our preceding paper[1] we seemed to encounter surface effects causing variations in gas chromatography–electron-capture detection (GC–ECD) response with changes in such equipment for a series of electrophore-derivatized amino acids and peptides. One aspect of this data was the high structural specificity of these variations. This could affect not only the sensitivity, but also the precision and accuracy of this type of analysis. Thus, we decided to pursue the specificity of these surface effects in more detail.

It is clear from the literature that surface effects in GC can be quite specific, particularly toward certain functional groups such as hydroxyl[2–4], amino[4,5], and carboxyl[2]. Also, "labile" structures such as endrin[6,7], and *p,p'*-DDT[8,9] can undergo specific losses. Apparently it is not uncommon for such losses to take place without accompanying changes in peak shape[2], consistent with our prior observations[1].

In this paper we analyze two mixtures of strongly-electrophoric compounds where each mixture involves more similar structures than the peptides we investigated before. Several pesticides (pesticides–herbicides) comprise the first mixture, including endrin and *p,p'*-DDT so that our results can be related to some of the work just cited. Three pentafluorophenylsulfonyl-dimethyl-cytosines differing only in substitution at their 5-carbon by hydrogen, methyl or fluoro are analyzed as the second mixture.

In order to vary the surface effects in our GC–ECD system, we changed pri-

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marily the detector. This is because we suspected that the surface effects in our previous studies, involving changes in equipment throughout the GC–ECD, arose primarily in the conventional detectors that we used. Such detectors expose the solutes to hot ceramic and steel surfaces prior to the ^{63}Ni foil region.

EXPERIMENTAL

Cytosine, 5-fluorocytosine and 5-methylcytosine were acquired from Sigma (St. Louis, MO, U.S.A.), derivatized as described[10], and prepared as a mixture (156, 107 and 243 pg/μl, respectively) in isooctane. The pesticide (pesticide–herbicide) mixture containing 2,4-D methyl ester, 2,4,5-T methyl ester, lindane, aldrin, endrin, *p,p'*-DDT and methoxychlor (400, 400, 20, 40, 160, and 240 pg/μl, respectively) was purchased from Supelco (Bellefonte, PA, U.S.A.). Isooctane was obtained from Burdick & Jackson Labs. (Muskegon, MI, U.S.A.).

A Varian Model 3700 gas chromatograph was fitted with a Model 1095 on-column injector and a constant current, variable frequency ^{63}Ni electron-capture detector operated at 360°C unless another temperature is indicated. Six conventional Varian electron-capture detectors were used, each having a 350-μl volume for the ^{63}Ni foil region, and also two, experimental Varian detectors[11], one having a conventional 350-μl foil volume, and the other having a 100-μl foil volume due to a stainless steel insert present in the foil region. Ultra high purity helium and nitrogen (Matheson, Gloucester, MA, U.S.A.) were used as carrier and make-up gases respectively. They were filtered with 13X molecular sieves, activated charcoal and an Oxyclear disposable purifier (Labclear, Oakland, CA, U.S.A.) and their respective flow-rates were 5 and 20 cm^3 min^{-1}, measured at room temperature and uncorrected. A fused-silica capillary column 15 m × 0.25 mm I.D., DB-1701 (J & W Scientific, Rancho Cordova, CA, U.S.A.) was used at 200°C unless indicated otherwise. Injections of the solutes in isooctane were made into the gas chromatograph with a 5-μl syringe (Varian Assoc., Sunnyvale, CA, U.S.A.) fitted with a fused-silica needle. Chromatograms were recorded and peak areas integrated with a SP 4270 integrator (Spectra-Physics, San Jose, CA, U.S.A.).

Procedure

One electron-capture detector after another was installed onto a given GC instrument for the analyses reported in this paper, unless indicated otherwise. After installation, each detector was baked out at 420°C for approximately 1 h until a stable base frequency was obtained. The detector temperature was next lowered to the actual working temperature (360°C). The detector was allowed to "equilibrate" overnight.

For the pesticide mixture, the following GC conditions were used: injector, 30°C to 250°C at a setting of 180°C min^{-1}; and oven, 85°C to 250°C at a setting of 60°C min^{-1} after a 1 min initial hold. Chromatographic conditions for the derivatized nucleobases were: injector, 30°C to 260°C at a setting of 180°C min^{-1}; and oven, 130°C to 260°C at a setting of 65°C min^{-1} after a 1 min initial hold. The base frequency of each detector was measured with the column oven at 200°C.

Triplicate or more injections of 1 μl each were made for all data points.

RESULTS AND DISCUSSION

In our previous GC–ECD work with some electrophore-labeled amino acids and peptides[1], we reported responses relative to that of lindane. This normalization was intended to monitor any differences especially in the injector and detector with changes in the GC–ECD equipment. Mostly a direct injection technique was used.

Here we employ only on-column injection, mostly change only the detector, and report absolute response factors for two other groups of compounds, a pesticide (pesticide–herbicide) mixture, and three derivatized cytosines. In the former mixture, lindane is maintained as one of the solutes.

The high precision possible with on-column injection[12] can minimize the need to monitor this step. However, some normalization of the ECD sensitivity is still needed for the several constant current, variable frequency detectors that we use. The following theory[13] is applicable:

$$\Delta f = \frac{k_1 f_0}{K_D} [AB]$$

where Δf is the response of the detector to the electron-capturing solute, AB; k_1 is a forward bimolecular rate constant for electron capture; K_D is a pseudo-first-order rate constant for the removal of electrons by processes other than capture by AB; and f_0, the base frequency, is the response of the detector in the absence of AB. Thus, the response of a constant-current variable-frequency electron-capture detector is linearly related to its base frequency within the approximations guiding this theory.

The linearity of Δf with f_0 has been confirmed for a conventional Varian electron-capture detector, using lindane as the test solute, where f_0 was changed by varying the reference current[14]. Other aspects of the detector were kept constant, apparently including the rate of production of electrons, assumed to be constant by the above theory.

However, varying f_0 by changing the detector, as we do here, probably changes the rate of electron production. This is because the higher f_0 values that we observe most likely arise from a decreased ^{63}Ni foil activity, inherent or acquired (*e.g.* due to contamination, or to migration of the ^{63}Ni into the nickel alloy backing material), that, in turn, causes fewer primary electrons to be released into the cavity of the detector. Thus, the above theory can only be used as a guide in this study.

Pesticides

The structures of the pesticides that we analyzed are shown in Fig. 1. They are seen to not only have analogous structures overall, but especially so when considered as certain pairs (*e.g.* methoxychlor and *p,p'*-DDT).

The GC–ECD response factors for these compounds using six different detectors are shown in Fig. 2. We varied these detectors by substituting one after another onto a given gas chromatograph fitted with the same on-column injector and column. All of the detectors that we tested were in routine use on other gas chromatographs in our laboratory, and were baked out and conditioned on the given gas chromatograph until a stable base frequency was obtained prior to these analyses. The response data were obtained from an average of at least five injections, with a relative standard

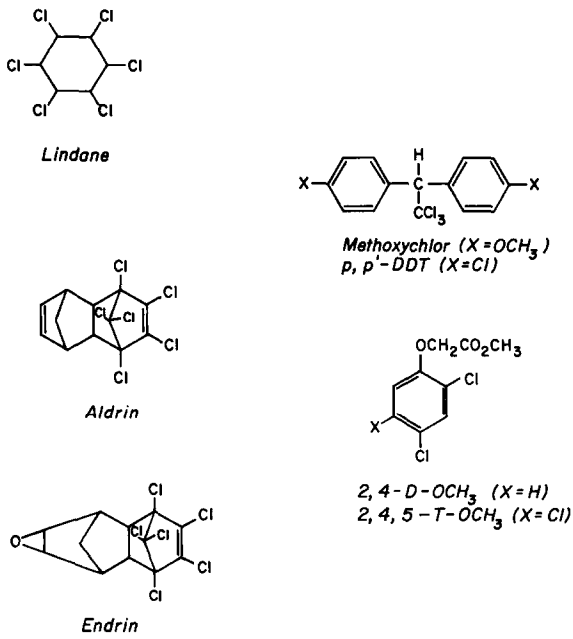

Fig. 1. Structures of pesticides (pesticides-herbicides).

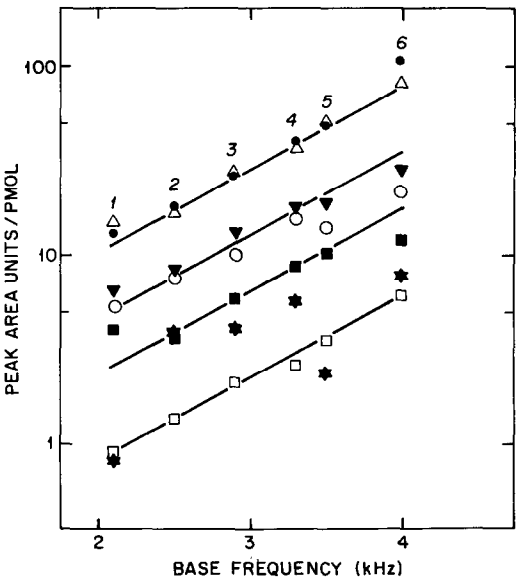

Fig. 2. Response factor *vs.* base frequency for the GC analysis of a pesticide mixture with a 350-μl Varian experimental electron capture detector 3, and five Varian conventional electron-capture detectors 1, 3, 4, 5, 6. Key: ●, lindane; △, aldrin; ▼, endrin; ○, *p,p'*-DDT ✱, methoxychlor; ■, 2,4,5-T-OCH_3; □, 2,4-D-OCH_3.

deviation (S.D./$\bar{x}$ expressed as a percent) within each set of injections ranging from 0.7 to 6.6%. Thus, error bars are not shown because essentially all of the data points lie within the symbols. No change in peak shape and no extraneous peaks or baseline disturbances were seen throughout this work.

Quasi-log linearity

In general agreement with the above theory, the response factors of these compounds increase with the base frequency. However, instead of a simple linearity, we see in Fig. 2 that a quasi semi-log linearity is obtained. As discussed above, this is probably due to the expected variation in rate of electron production in these detectors, causing a departure from the theory. Consistent with the theory, however, the semi-log slope in this figure corresponds to progressively increasing slopes as the sensitivity of the compounds is higher when the data is plotted against a linear response factor axis. This latter behavior is consistent with $\Delta f/(AB)$ increasing with k_1.

Response factor lines

The lines to which we have fitted the data in Fig. 2 are based on two, somewhat arbitrary, considerations. First of all, we drew the lines through the response points of detector 2, since this detector is a Varian 350-μl experimental electron-capture detector fabricated to be highly inert[11]. Thus, we relied on this detector to provide an arbitrary reference set of response values that are assumed to be least perturbed by "surface effects" in the detector. (This aspect is investigated experimentally later.) Such effects are considered here as changes in the response of a solute due to its interaction, or interaction of its degradation or electron capture products, with surface or surface-derived materials in the detector.

Secondly, we kept the response factor lines parallel while fitting them simultaneously to the responses of the more "well-behaved" compounds (best-fit of the points to the line): lindane, aldrin, endrin and 2,4,-D-CH_3. In three cases, a single line is drawn to simultaneously represent the behavior of two different solutes: lindane and aldrin share a line, as do endrin and *p,p'*-DDT, and also 2,4,5-T-CH_3 and methoxychlor. This is done to help visualize the data. Thus, four lines account for the variations in response factor for seven pesticides, where the four lines are anchored on the response factors of the more inert detector, 2, and have a common slope.

Methoxychlor and p,p'-DDT response

Aside from the high degree of semi-log linearity for four of these solutes, lindane, aldrin, endrin and 2,4-D-OCH_3, the markedly adverse behavior of methoxychlor is prominent as a major feature of this plot. For all of the conventional detectors (all except 2) the response factor for this solute is below its semi-log response factor line, with particularly low values (about 4-fold below the line) for detectors 1 and 5. Clearly methoxychlor (or its ECD products) is the most susceptible to surface effects here of the pesticides that we examined.

The behavior of *p,p'*-DDT somewhat mirrors that of methoxychlor, which is consistent with the structural similarity of these compounds. Nevertheless, their behavior is quite different on detector 1, where only methoxychlor drops significantly in response. Thus, even this very close solute pair can be discriminated by surface effects in an electron-capture detector.

High specificity of the surface effects

Every detector in the plot of Fig. 2 gives rise to a unique fingerprint of ECD response (vertical patterns of the points for each detector) with the response patterns of detectors 3 and 4 probably the most similar. This is in spite of a general similarity in structure for all of these compounds. Further, the patterns as a function of the detector are significantly different not only for the close structural pair, methoxychlor and *p,p'*-DDT, as just pointed out, but also for the close pair 2,4-D-OCH_3 and 2,4,5-T-OCH_3. Thus, the surface effects in these detectors are clearly remarkable both in terms of their overall specificity of solute fingerprinting for every detector, and in the ability of certain detectors to distinguish very close structural analogues. Further evidence for the high specificity of these surface effects is the relatively "good behavior" seen here with endrin, a compound that others have reported to be highly susceptible to such effects[6,7].

Possible enhanced response

We are confronted here with the possibility of surface effects in the electron-capture detector enhancing the response, since some of the data points lie above the lines. In this regard, it should be noted once again that all of the five individual values averaged to give each data point fall within the symbol used in essentially all cases. For example, even the small degree to which the data points for lindane and aldrin are separated from the line, and from each other, for detector 1 are well beyond the precision of this data. The two, potential enhancements that most stand out in this respect are the responses for 2,4,5-T-OCH_3 on detector 1, and lindane on detector 6, where the values are 1.5X and 1.3X, respectively, above the correlation line for each. However, given that the lines are somewhat arbitrary, as discussed above, any enhanced response is only a speculation.

Derivatized cytosines

We next turn to analogous data, presented in Fig. 3, for electrophore-labeled, permethylated cytosines. The structures of these compoounds are apparent in an accompanying paper[10]. Once again, we have anchored our log response factor *vs.* starting base frequency lines through the data of detector 2, the experimental electron-capture detector. However, none of the sets of points for the three compounds in Fig. 3 correlate as well to a straight line as the data for the more consistent pesticides of Fig. 2. Thus, we somewhat arbitrarily imposed the slope obtained from Fig. 2 on the data points in Fig. 3 for comparison purposes. As seen, this slope seems to fit the data at least to some degree.

Consistent with the previous data, each detector in Fig. 3 tends to have a unique solute-response fingerprint, and very analogous structures can be discriminated. Also, some higher values occur relative to the correlation lines that are drawn, confronting us once again with some data that may reflect an enhanced response.

ECD sites of the surface effects

Within the electron-capture detector, surface effects changing the response potentially might arise in either the pre-foil or the foil region. The former in a conventional Varian electron-capture detector comprises ceramic and Kovar steel surfaces, as opposed to the end of a bonded, fused silica capillary column in a Varian exper-

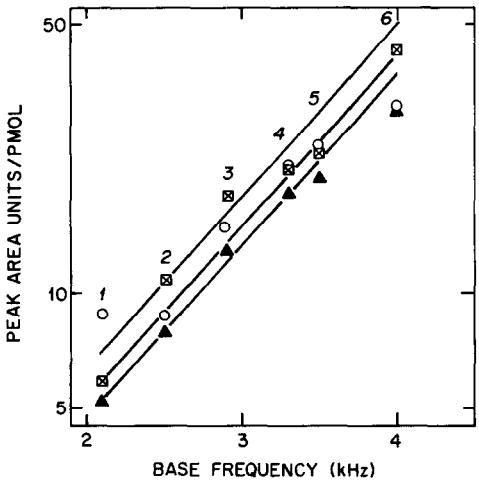

Fig. 3. A plot similar to that in Fig. 2 except for the analysis of pentafluorophenylsulfonyl-dimethylcytosines substituted at the 5 position by either H, CH_3 or F. Key: ⊠, 5-methylcytosine; ○, 5-fluorocytosine; ▲, cytosine.

imental electron-capture detector[11]. In the foil region, for both of these detector types, the surface of a platinum ribbon electroplated with ^{63}Ni is present along with some continuation of the ceramic and steel surfaces. All of these surfaces, of course, are subjected to the temperature of the detector.

We attempted to define whether the surface effects were in the prefoil or foil region by having Varian replace the ^{63}Ni foils, without any cleaning of the pre-foil region, in detector 1, giving 1′. We also had the foil replaced in detector 2 (here the detector was cleaned as well), giving 2′. Further, we obtained an experimental Varian electron-capture detector (detector 7) having a metal insert in the foil region that reduces the volume of this region from 350 to 100 μl[11].

The analysis of the pesticide mixture was then repeated as before, except now, for practical reasons, we employed different on-column injectors and used DB-5 columns. This gave the data shown in Fig. 4. (As seen, we changed the detector temperature as well, data that we will discuss shortly.) The overall data for 2′, 1′c and 7b, having the same detector temperature (360°C) as in Fig. 2, does not accommodate very well to the slope of Fig. 2, perhaps because of the changes in the equipment in addition to the detector. While the responses for 1′c and 7b were quite low in this respect, those of 2′ were somewhat elevated except for 2,4-D-OCH_3, that fit (perhaps coincidentally) to the line for this compound in Fig. 2.

The degree to which the surface effects are considered to arise in the pre-foil *vs.* the foil region of the detector depends on how much one considers the solute fingerprints in Fig. 4 for detector 1′c to match that of 1 in Fig. 2, and that of 2′ and 7b to correspondingly match that of 2. Although this is a subjective interpretation potentially complicated by the other changes in the GC system, we conclude that the overall similarities are strong, indicating that the pre-foil region harbors at least most of these surface effects. In particular, for detectors 2′ and 2, one can at least partly overlap the data points simultaneously for endrin, *p,p′*-DDT, methoxychlor, 2,4,5-T-OCH_3 and 2,4-D-OCH_3, although this displaces the points for lindane and aldrin

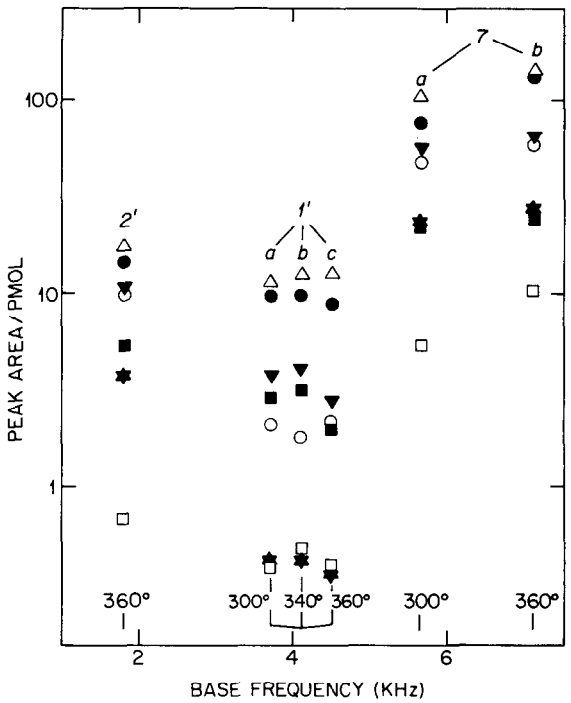

Fig. 4. Effect of changing the foil (detector 1 → 1'), changing the foil plus cleaning (detector 2 → 2'), and changing the detector temperature on the GC–ECD response factor fingerprints of the pesticide mixture analyzed in Fig. 1. Three detectors were used: 1', 2', and 7 as described in the text. Key as in Fig. 2.

upwards by 54 and 87% on the fingerprint of 2' relative to the values for 2. Since one also cannot perfectly overlap the fingerprints for 2' and 7b with that of 2, this still leaves open the possibility that the foil region has surface effects contributing to the response.

Stability of the response fingerprints

Previously we noted that the relative responses for representative derivatized peptides analyzed by GC with a conventional electron-capture detector gave the same values within ± 10% on two occasions one month apart[1]. In between, the GC–ECD system was used routinely to analyze a variety of other strong electrophores. A similar observation is made here. We re-installed detector 4 on the gas chromatograph used for the measurements reported in Fig. 2 after this detector had been in routine use on another gas chromatograph for 5 weeks. Although the base frequency changed and the absolute responses shifted, the relative responses were the same within ± 10% for all of the points, *i.e.*, essentially the same response fingerprint was obtained. This data, plus the similarity of the fingerprints for 1 and 1' cited above, and also the previous results with derivatized peptides, establishes that these response fingerprints are relatively stable under our experimental conditions.

Temperature

Changes in response factor with temperature for detector 7 (300, 360°C; pat-

terns 7a and 7b, respectively) and detector 1 (300, 340, 360°C; patterns 1'a, b, c, respectively) are shown in Fig. 4. For the latter data, changing the temperature has no significant effect on the base frequency, whereas this frequency increases for detector 7. This may reflect a difference in the contamination or aging of these two detectors perhaps related to the higher insertion of the polyimide-coated column into the latter detector.

This figure shows that unique solute fingerprints exist as readily at 300°C as they do at 360°C, and that these fingerprints are somewhat temperature-dependent, but without any consistent changes. However, one cannot reach any firm conclusions about the effect of temperature on these surface effects from this experiment, since the sensitivity of electrophoric compounds also tends to depend on the detector temperature. Nevertheless, if it is assumed that our compounds, having similar structures, capture electrons by a similar mechanism and therefore undergo a similar change in sensitivity with temperature, then the inconsistent effect of temperature on the response suggests a complex relationship between the behavior of these surface effects and temperature.

Response precision with the experimental electron-capture detector

Although the surface effects within each electron-capture detector are reproducible, they tend to degrade the precision of the response. Referring back to Fig. 2, the precision (S.D./$\bar{x}$ expressed as percent) for the experimental detector 2 ranged from 2.2 to 3.6% for the various pesticides, whereas this range extended to higher values (upper limits of 4.9 to 6.6%) for the analysis of these compounds on the conventional detectors. All of this data was obtained with the same injector and column. Consistent with its poorest behavior, methoxychlor generally gave the poorest precision. Also, the response data for the conventional detector, 1'c, in Fig. 4 similarly had a poorer precision (8–13%) than that obtained with the experimental detector, 2' (4–6%). Thus, the experimental 350-μl detector gives about two-fold improvement in within-run precision in our experiments involving the same injector and column.

Sample concentration

In Fig. 5 the solute-response fingerprint of the pesticide mixture is examined as a function of its concentration on two GC–ECD systems. The starting, highest concentration, "1", is that used previously for these compounds, and this concentration is diluted as shown for a GC system housing the experimental detector, 2', and a gas chromatograph fitted with a conventional detector, 8, not previously employed here.

Turning first of all to the data for 2', we see that no error bars for $\pm$S.D. are shown, as usual, for the response factors at concentration "1" since nearly all of the data points at this concentration fall within the symbols. The precision degrades, as seen, at the lower solute concentrations. The main point in regard to this data for 2', however, is that the solute-response fingerprint is somewhat concentration-dependent, at least for the response fingerprint at 0.005 dilution relative to the initial fingerprint. Also, we see that the change in the solute-response fingerprint for the 0.05 dilution of the sample on the conventional detector 8 seems to be greater than that seen with the experimental detector 2', consistent with the expected greater degree of surface effects in the former detector.

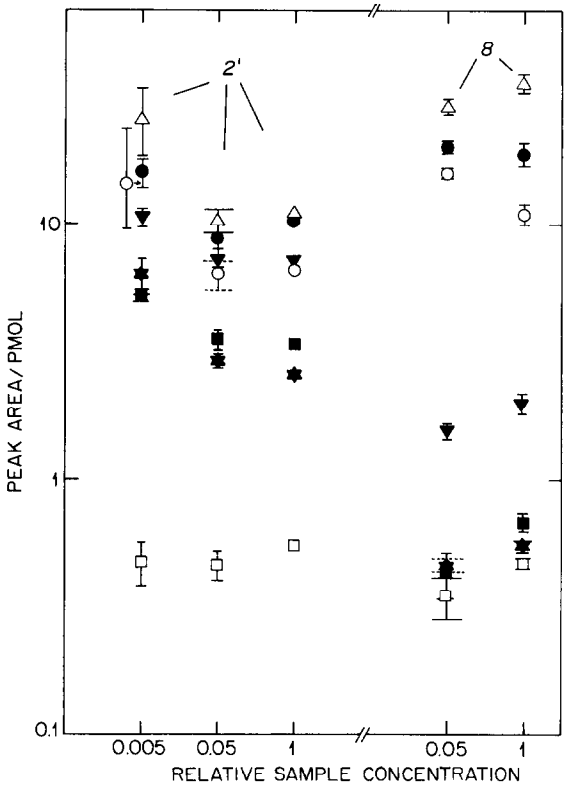

Fig. 5. Change in the GC–ECD response factor fingerprints with concentration of the pesticide mixture for detectors 2′ and 8. The error bars represent ±1 S.D. about the mean. Key as in Fig. 2.

As an aside, we note that the pesticide response fingerprint for detector 8 is the most unique of those encountered here. Whether this is related to this detector being the oldest in terms of its date of manufacture, or to some other aspect is not defined. The detector is also seen to give the lowest precision of those tested, requiring error bars for the data even at a solute concentration of "1".

Response factor maximum

Surface effects potentially can be saturated, giving a change at some point in solute response factor with concentration. We observed such a change here using lindane as the test solute. Four GC–ECD systems were employed in this experiment, two involving conventional detectors (5 and 6a, 6b), and two involving the experimental detectors 2′ and 7.

The response data that we obtained are plotted in log form in Fig. 6 to illustrate the tendency of such a plot to mask such an effect, and as response factor in Fig. 7. A consistent maximum in this factor is seen for lindane with detector 5, 6a (270°C), 6b (340°C) and 7, whereas no clear maximum is discernible, as anticipated, with the experimental detector, 2′. Thus, this maximum seems to involve surface effects. The drop in response factor on the higher concentration side of lindane is the usual be-

havior of this detector at the upper limit of its "linear range", occurring as well with detector 2'.

Thus, the increase in response factor with increasing, intermediate concentrations of lindane may be due to saturating surface effects in the conventional detectors. In this case, these effects would predominantly act to lower the lindane response immediately prior to his region. Another possibility, however, is that some type of response enhancement is triggered by a higher concentration of this solute, *e.g.* degradation intermediates from lindane recombine to form products that capture electrons.

For either explanation, or possibly others as well, the definite maximum in response factor for the other experimental detector, 7, is unexpected. This detector is supposedly the same as 2' except that 7 has a metal insert in its foil region that reduces the volume of this region to 100 μl[11]. This suggests even more strongly than before that surface effects influencing the response can be present in this latter region of the detector. More detectors of both types need to be examined, however, to strengthen this conclusion.

Aside from differences in the base frequencies of these detectors that tend to change the upper limit of their linear range, and therefore the position of their maximum in response factor, the different positions of these maxima, ranging from 0.07

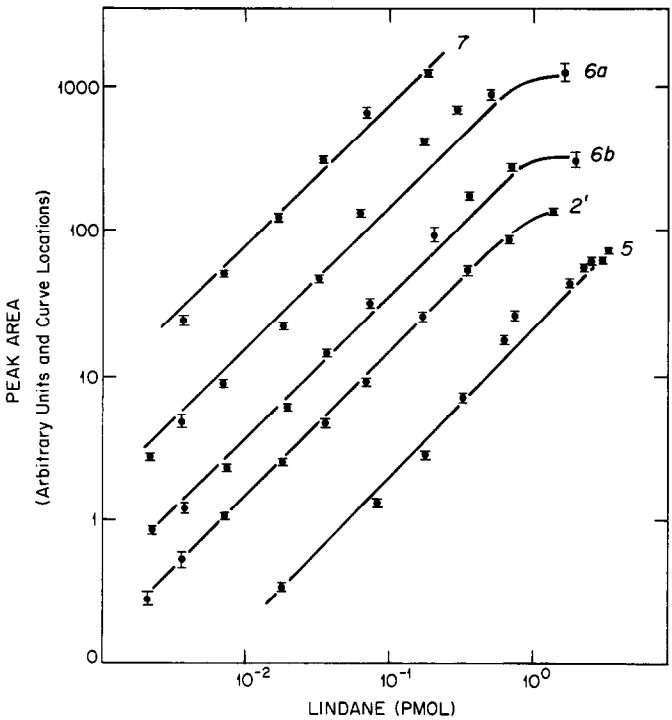

Fig. 6. GC–ECD response *vs.* concentration for lindane involving detectors 7, 6a, 2' and 5 at a detector temperature of 340°C, and 6b at 270°C. The amounts of lindane injected, proceeding from left to right, are 0.62, 1.03, 2.07, 5.24, 10.2, 20.7, 52.4, 102.4, and 207 pg, and the error bars represent ± 1 S.D. about the mean.

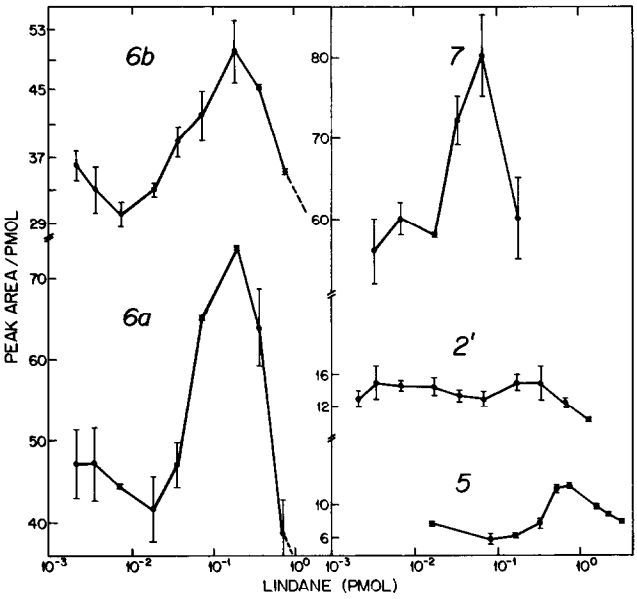

Fig. 7. The same data in Fig. 6 plotted as response factor. Those detectors (*e.g.* 7) having a higher base frequency are more sensitive, assuming, as is probably true, that the differences in base frequency arise essentially from variations in foil activity.

pmol (20 pg) of lindane for detector 7 to 0.7 pmol (200 pg) for 5, presumably reflect different extents of the surface effects for lindane.

Response factor minimum

In addition to a maximum in the response factor, we also observe a minimum in this response factor at a lower lindane concentration. This is also caused or promoted by surface effects since it arises only with the conventional detectors 5 and 6a,b in this experiment. The most interesting feature of this minimum is its upswing at the lowest concentrations of lindane. How can surface effects for a given solute enhance a response factor in this manner? One possibility, offered here only as a speculation, is that solute degradation intermediates from surface effects combine with a limiting, trace contaminant of the carrier gas such as oxygen or water, giving rise to secondary products that also capture electrons. An upswing in response factor then could be seen at a lower solute level due to a greater excess there of such contaminants relative to the solute intermediates. The persistence of trace oxygen and water in such a system as this, even after thorough attempts to eliminate them, is well-known[15]. Carrier gas doping with oxygen enhances the response of GC–ECD towards electrophores, especially weaker ones[16,17]. However, surface effects have not been implicated in these latter studies.

Referring back to the experimental detector 2' in Fig. 5, the highest response factors are seen for all of the compounds except perhaps 2,4-D-OCH_3 at the lowest relative concentration of 0.005. This latter concentration (*e.g.*, 0.1 pg of lindane injected) corresponds to a 6-fold lower value than the lowest concentration of lindane tested in Figs. 6 and 7. This upswing in response factor is also observed when ECD

2′ is used to analyze several O-pentafluorophenylsulfonyl phenols down to the 0.1-pg level[18]. This further raises the possibility, along with the data discussed earlier concerning the detector sites of the surface effects, that even detector 2′ is not fully inert. However, some surface effects might also arise in the last small part of the column that is heated to the temperature of the detector. In either case, the shift in the minimum to a lower solute concentration with detector 2′, along with the disappearance of the maximum in response factor at a higher solute concentration, could represent a shift in the limiting parameter for the minimum from the amount of carrier gas contamination to the magnitude of the surface effects.

Generality of these observations

Using conventional electron-capture detectors, we also see an initial minimum followed by a maximum in the response factor with increasing solute concentration for several O-pentafluorophenylsulfonyl phenols[18], and this overall pattern is present in the standard curves that we published previously for N,N-dipentafluorobenzoylpentafluoroaniline[19], and also apparently in the curves for several derivatized iodothyronines[20]. Further, a response factor curve reported by Bente[21] for lindane with a Hewlett-Packard GC–ECD system has the same pattern, with additional complexity present in a similar curve for aldrin. Thus, our observations seem to have a general relevance for the analysis of strong electrophores by GC–ECD.

CONCLUSIONS AND IMPLICATIONS

Some general conclusions or implications can be drawn from the results in this paper:

(1) Response factor patterns and curves for strong electrophores are useful for probing surface effects in electron-capture detectors.

(2) Some of the mechanisms proposed for strong electrophores in the prior GC–ECD literature to account for small differences (*e.g.* up to 5 fold) in response, or the effect of temperature on response, may need to be reconsidered now that a possible contribution from surface effects has been established. At the same time, this phenomenon may help to explain some of the anomalies in response in the GC–ECD literature, *e.g.* the unexpected, different increases in response for several pesticides at unusually high gas flow-rates in this electron-capture detector[22], or the common tendency of response values to vary somewhat with the GC–ECD equipment[1]. Perhaps these surface effects may also contribute to certain cases of presumed coulometric nonlinearity for strong electrophores[23].

(3) In addition to the need to make detectors as inert as possible, a second, future direction for electron-capture detectors should be considered. Given the degree of stability and high specificity observed here for surface effects, potentially such effects may be optimized to provide useful qualitative input, or perhaps even increased sensitivity, for the analysis of strong electrophores by GC–ECD. Nevertheless, this may be limited by the inherent tendency of surface effects to poison either on a temporary or permanent basis during the analysis of samples more contaminated than those done here. Also, as demonstrated here, the occurrence of surface effects tends to degrade the precision.

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