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HYPERCOULOMETRIC RESPONSE IN A d.c. ELECTRON CAPTURE DETECTOR

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SUMMARY

Hypercoulotmetric response has been observed in a d.c. electron capture detector operated under special conditions: Its responses, as measured in faradays peak area per mole of compound injected, were higher than 1 for many organic halides and nitro compounds. Hexachloroethane, for instance, showed response values up to 40. Although the cause of this phenomenon has not been determined, it may have implications for certain studies in electron capture detection.

INTRODUCTION

The term "coulometric" response has been used by Lovelock *et al.*¹ to describe the response of an electron capture detector (ECD) under conditions which involve ideally the capture of one electron per one molecule of gas chromatographic (GC) solute. For obvious reasons, this coulometric response is considered a natural limit for the efficiency of the electron capture process. Consequently, calculations of "maximum theoretical" detector sensitivity are based on this limit (*e.g.*, ref. 2), as are "absolute determinations" of electron-absorbing species (*e.g.*, ref. 3).

While the assumption of a coulometric limit is entirely reasonable and, in fact, borne out by some experiments¹, it is not generally applicable to all types of compound or all types of ECDs. There are (at least) two reasons for this.

First, as Lovelock *et al.* have pointed out in their pioneering paper¹, coulometric response presumes the absence of strongly electron-absorbing products arising from the initial electron capture reaction. For many of the more complex, polyhalogenated compounds typically determined by electron capture, this is not the case⁴. If prominent products are formed, ECD response reflects only in part the electron capture properties of the original solute; and response, originating from a series of compounds, may be beyond its coulometric limit.

Secondly, the true ratio of absorbed electrons to solute molecules entering the detector may not be correctly described by the ratio of peak area in faradays to moles of injected compound. The latter ratio, however, represents the measurement actually taken (denoted in this paper by "*e/m*").

Some of the reasons for such a discrepancy are trivial; others are less obvious.

Most should lead to e/m values being lower than the relevant processes in the detector cell would suggest. These reasons could include, in the GC system, thermal or catalytic decomposition of solute molecules; and, in the ECD cell, collection of negative molecular species, formation of positive solute ions, interference from contaminants, non-optimized conditions, etc.

Reasons for high e/m values are fewer and could include, in a d.c. system, contact potentials and space charges⁵. In general, however, d.c. systems are considered somewhat less sensitive than pulsed ones².

One of the reasons why a d.c. system could be expected to show low e/m values is illustrated in Fig. 1. The heavy curve represents the response of a typical chlorinated hydrocarbon and the light one the standing or baseline current as recorded in one of the experiments. Obviously, maximum e/m values would be measured at a voltage corresponding to the maximum in the response curve. If one were to assume, however, that changes in electron concentration due to a reaction with the solute are attenuated to the same degree as the baseline current itself (a quite reasonable assumption), then the "true" electron capture reaction would be indicated by the dashed line. Note

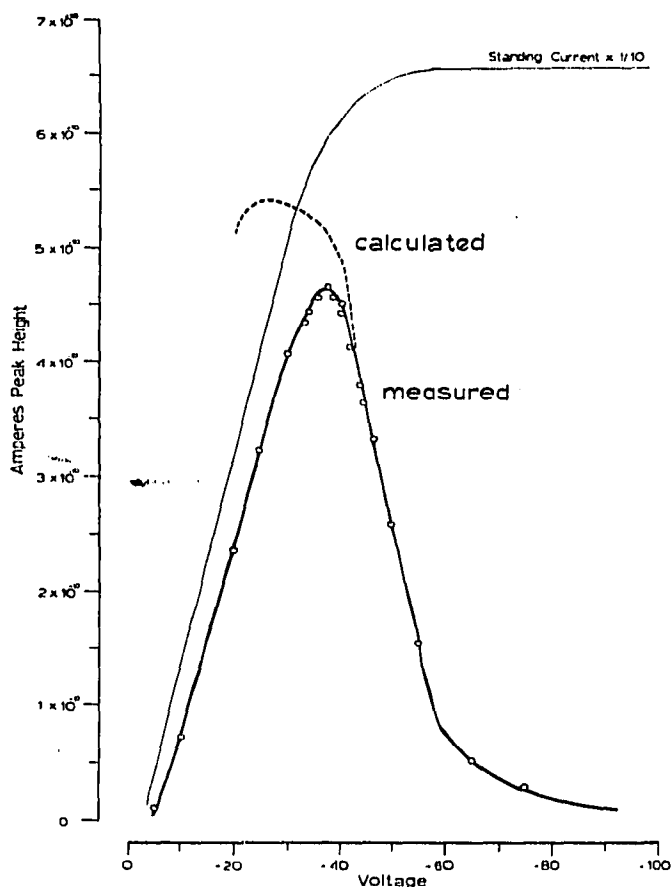


Fig. 1. Measured response of a typical chlorinated compound, with calculated "true" response (see text).

that at 0 V, the extent of electron capture reaction would be pronounced (comparable to that in a pulsed system), but the response is negligible.

This and other effects contribute to the expectation that e/m values measured in a d.c. system should not even approach the coulometric limit. A value beyond this limit, *i.e.* "hypercoulometric" response ($e/m \gg 1$), has never been reported in any ECD system, despite the fact that experiments of this sort were undoubtedly carried out in various places. In our own work, we occasionally found e/m values up to 2 with extremely pure, pulsed systems; but the effect was small and readily explained by the added contribution of electron capture products.

To find responses clearly beyond the coulometric limit would be quite notable (or disturbing) for any ECD system, pulsed or d.c., since much reasoning in the ECD literature is based, implicitly or explicitly, on the existence of such a limit. It should again be stressed, however, that the e/m ratio as used in this paper is a quantity solely determined by experiment and not a description of processes occurring in the electron capture cell. Mechanisms are a different matter altogether.

In this study, we chose to utilize a clean d.c. system at hand, *i.e.*, one assembled for an earlier study on electron capture products⁴. The first of its detectors was quite sensitive under the elevated pressure inherent in the system, and all measurements were done on it. A few, minor details were changed to improve response, but none of the various parameters was truly optimized with the exception of the detector voltage.

EXPERIMENTAL

The "Detector 1" in the previously described system⁴ was operated in d.c. mode for the measurements. The upper electrode served as the polarizing one in the usual manner, but the GC effluents were introduced from the bottom (sensing region) rather than from the top (ionizing region) of the Tracor ⁶³Ni ECD. Its temperature was 295° and the flow-rate of the nitrogen carrier varied between 50 and 60 ml/min as measured at atmospheric pressure by a bubble flowmeter. The second GC column, which separated the effluents from ECD-1, differed slightly from the original one. We now used a 1.5 m × 6 mm O.D. × 4 mm I.D., coiled Pyrex tube packed with 9% OV-101 on 40-60 mesh Chromosorb W AW, resulting in a somewhat higher pressure in ECD-1.

In order to minimize possible errors, several of the test solutions were prepared independently by cooperative graduate students. Three different electrometers (Tracor, Bendix Mark I and Bendix Mark III models) and two different recorders (Linear Products and Shimadzu dual-channel 1-mV models) were used.

Peak areas were converted to faradays (ampere·seconds/96,500) and divided by the moles of compound injected to give e/m ratios.

RESULTS AND DISCUSSION

Table I summarizes the e/m ratios obtained for a variety of compounds injected in different amounts. A few compounds (with asterisks) showed obvious decomposition in the GC system and the values reported for them should be considered low. All compounds were of the highest purity commercially available, but none was specially

TABLE I
 "e/m" RATIOS (FARADAYS/MOLE)

Some of the *e/m* values listed below may be low due to premature solute decomposition. They were determined at different column temperatures (*i.e.*, bleed) and should therefore not be used for quantitative comparison of different solute structures.

Compound	Amount injected			
	1 ng	100 pg	10 pg	1 pg
Tetrachloroethylene	—	0.7	3.6	6.5
1,1,2,2-Tetrachloroethane	—	1.3	2.2	—
1,1,2,2-Tetrabromoethane	—	4	12	14
Hexachloroethane	—	—	16	25
Hexabromoethane	—	4.7	17	26
Octachloropropane	—	7.5	12	14
3-Chloro-1,2-propanediol	0.04	—	—	—
1,4-Dibromobutane	—	0.1	—	—
1,2,3,4-Tetrabromobutane	—	—	12	13
Di(pentachloroethyl) ether	—	9.5	22	24
Diethylfumarate	0.003	—	—	—
Octachlorocyclopentene	—	2.5	4	—
Chlorocyclohexane	0.025	—	—	—
Bromocyclohexane	0.04	—	—	—
α -Hexachlorocyclohexane	—	—	5	7
β -Hexachlorocyclohexane	—	2.5	6.2	7.6
γ -Hexachlorocyclohexane (Lindane)	—	—	13	17
δ -Hexachlorocyclohexane	—	3.6	14	21
Nitrobenzene	0.02	—	—	—
<i>m</i> -Dinitrobenzene	—	0.7	0.8	—
<i>o</i> -Dinitrobenzene	—	0.7	0.8	—
2,4,6-Trinitrotoluene	—	—	5.8	5.9
<i>p</i> -Chloronitrobenzene	—	1	1.6	2
<i>m</i> -Chloronitrobenzene	—	1.5	2.8	3
<i>o</i> -Chloronitrobenzene	—	1.6	3.5	3.8
<i>o</i> -Bromonitrobenzene	—	1.5	5.5	8.5
<i>o</i> -Iodonitrobenzene	—	4	8	8
<i>o</i> -Fluoronitrobenzene	—	0.5	0.8	—
<i>o</i> -Nitroaniline	0.09	0.13	—	—
4-Chloro-2-nitroaniline	—	2.2	3.6	4
2,6-Dichloro-4-nitroaniline (Dichloran)	—	4	5	4.7
2,5-Dichloroaniline	0.03	0.04	—	—
2,3,5,6-Tetrachloronitrobenzene (Tecnazene)	—	3	19	32
Pentachloronitrobenzene (Quintozene)	—	4.2	13	25
<i>o</i> -Chlorophenol	0.01	—	—	—
<i>p</i> -Bromophenol	0.02	—	—	—
Chlorobenzene	0.03	—	—	—
Bromobenzene	0.06	0.07	—	—
Benzyl chloride	0.08	0.15	—	—
Hexachlorobenzene	—	—	7	11
Hexabromobenzene	—	8	9	14
Decachlorobiphenyl*	—	4.3	7.4	—
Tetraethyllead	—	0.5	—	—
<i>p,p'</i> -DDT**	—	3.4	3	—
Heptachlor	—	—	11	15
Aldrin	—	—	14	17
Heptachlor Epoxide	—	—	16	17
Dieldrin	—	7.4	13	15
Methyl Parathion	—	—	1.5	2.3

* Excessive column bleed.

** Extensive decomposition evident from chromatogram.

purified, and by-products showed up occasionally. Again, this would cause a low e/m value to be reported. The fact that the system was not truly optimized (pressure, flow, temperature, GC column bleed, etc.) would also imply that the listed values are lower than they might have emerged from a more extensive and thorough study.

Despite these lowering effects, most compounds listed have e/m ratios far in excess of the coulometric limit. This includes almost all substances commonly known for strong ECD response. It should be noted in this context that we deliberately included in the list a variety of substances with only moderate ECD response in order to have a basis for (approximate) comparisons.

The largest e/m ratio ever measured in these experiments was 40, derived from 20 fg of hexachloroethane. It points out the fact that e/m ratios increase markedly as the amounts injected decrease. The effect appears stronger with halogenated compounds than with nitrocompounds, corresponding to a commensurate deviation from linearity in the calibration curve.

Very low amounts of solute mean, of course, a considerable excess of available

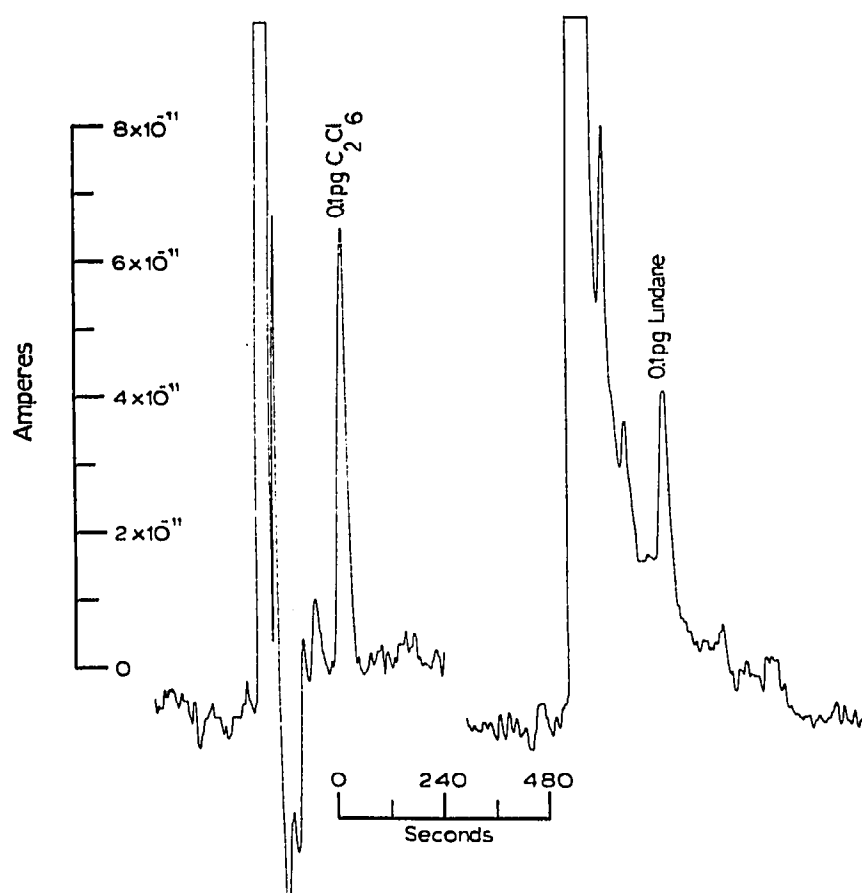


Fig. 2. Chromatograms of two test compounds at the 0.1-pg level. Column temperatures: C_2Cl_6 , 90° ; lindane, 190° .

electrons, and this may formally explain the effect. A valid explanation in mechanistic terms, however, is not available at present. If the system's response would reflect a coulometric limit—which it does not— e/m ratios measured at very low solute concentrations should level off around 1 or, considering the contribution of products, 2 or 3 at most.

This is not the case, and we have to conclude, therefore, that "hypercoulometric response" as defined is possible in an ECD system operated in d.c. mode. Though the reason or reasons for this behavior have not been elucidated, the fact needs to be taken into account in various contexts.

As one example, the "maximum theoretical" sensitivity should be better than can be calculated using the coulometric limit. Fig. 2 illustrates the general sensitivity we encountered, using simple electronics, and working with a non-optimized system under conditions of noticeable column bleed. The amounts of chlorinated test compounds injected are 0.1 μg each, and the minimum detectable limits are considerably lower (< 10 fg for hexachloroethane).

Yet, sensitivity *per se* is not the main issue. This extreme sensitivity is required only in a very few analytical cases, and it can, in fact, be inconsistent with good analytical practices in many others.

The real issue is, perhaps, that this demonstration of hypercoulometric response may lead to further research and a better understanding of ECD performance, as well as to a certain amount of caution in relating ECD response data to sample concentrations or detector processes. It is quite clear that, on one hand, even higher e/m values than 40 might be obtained and, on the other, that obtaining these values is based on a particular or even peculiar set of detector parameters. Under common ECD conditions, the effect would not have been noticed. Yet, the important fact is that it can occur.

ACKNOWLEDGEMENTS

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