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HYPERCOULOMETRY IN A PULSED CONVENTIONAL ELECTRON-CAPTURE DETECTOR*

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SUMMARY

Hypercoulometric response was observed in an electron-capture detector with conventional dimensions and geometry, and under typical pulsed conditions. This response is linked speculatively to the space charge mechanism.

INTRODUCTION

The possibility of using the electron-capture detector as a coulometric device has received much attention since the idea was first conceived¹. Under coulometric conditions, every analyte molecule captures an electron, and the detector response in faradays equals the analyte quantity in moles. When this happens, the method of analysis becomes absolute, and no calibration standards are necessary. Needless-to-say, such a system is highly attractive, especially in the field of atmospheric research, where it is often difficult to obtain and prepare high-purity standards of the various compounds of interest².

To achieve coulometry, traditional design has tended towards large detector volume and low flow-rates to maximize the probability of electron-capture^{1,3}. Recent studies by Grimsrud and co-workers^{4,5} favour the displaced coaxial geometry, a design having a large foil to anode area ratio (to minimize the fraction of positive ions collected on the anode during the pulse-free period).

Hypercoulometry, the phenomenon of apparent multiple electron-capture per analyte molecule, was first reported by Aue and Kapila⁶. Under d.c. conditions and a pressure of 5 atm, an e/m value (the ratio of peak area in faradays to moles of analyte injected) of 50 was observed for tecnazene (2,3,5,6-tetrachloronitrobenzene)⁷. The apparent capture of 50 electrons per molecule of tecnazene was difficult to rationalize with existing electron-capture theory⁸ even when electron-capturing products^{2,9,10} and "cyclic capture"¹¹ were taken into consideration. These and other phenomena eventually prompted the development of the "space charge" model in d.c. electron-capture detectors, in which detector response is thought to arise from

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the space charge effects of migratory anions¹². Thus, under this model, there is no inherent coulometric limit imposed on the detector's response. Such a model has recently been extended to the pulsed regime in a study using a large-volume, two-chambered electron-capture detector, in which both the "classical"⁸ and the "space charge"¹² mechanisms were observed to be operative¹³. How this relates to conventional, smaller volume electron-capture detectors, with which the vast majority of electron-capture work is done, is unknown, but it does raise several questions. Two obvious ones are: (i) if the space charge mechanism operates in one, though admittedly unconventional, electron-capture detector under pulsed conditions, would it also operate in smaller, conventional designs? (ii) Assuming that the space charge mechanism operates in the conventional design, would hypercoulometry not exist? This latter point is of significant practical importance: hypercoulometry is generally regarded to be associated with d.c. systems where space charge effects are prominent^{14,15}. In pulsed systems where the pulse durations are short and periods are long, *i.e.* conditions regarded as approaching steady-state, coulometry is considered a practical reality provided certain other conditions are met³⁻⁵. This study attempts to offer answers to these questions by examining hypercoulometry in the pulsed mode.

EXPERIMENTAL

Instrumentation

A Varian 6000 gas chromatograph was used. The Varian electron-capture detector has a displaced coaxial design and a volume of 0.3 ml. The radioactive source is a ⁶³Ni foil with a maximum activity of 8 mCi. The detector was disconnected from the variable-pulse frequency generator and the electrometer of the chromatograph. It was kept at 300°C for the analytes, lindane (γ -1,2,3,4,5,6-hexachlorocyclohexane) and carbon tetrachloride, and 200°C for sulphur hexafluoride.

For this study, the nickel foil was polarized by a constant-frequency pulse generator (Hewlett-Packard Model 8002A). For pulse heights higher than -10 V, the pulse generator's output was amplified by a laboratory-made circuit (Fig. 1). The pulse characteristics were monitored by an oscilloscope (Philips, Model PM 3110)

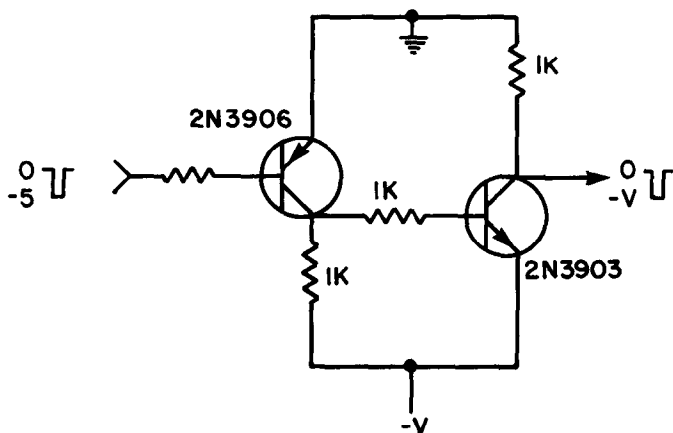


Fig. 1. Amplifying circuit.

and a counter (Fluke, Model 0372-C). The electron-capture detection (ECD) signal was processed by a picoammeter (Keithley, Model 417), the output of which was connected to a strip-chart recorder (Fisher Recordall, Series 5000) after a 2/3 signal attenuation.

Ultra high-purity nitrogen (Air Products), after purification by passing sequentially through a cartridge containing molecular sieve 5A and a heated oxygen scavenger (both from Supelco), was used as the carrier gas at 25 ml/min. The columns were borosilicate tubes, 1 m \times 2 mm I.D. packed with 6% OV-101 on Chromosorb W, 80–100 mesh for the studies of lindane and carbon tetrachloride, and with molecular sieve 13X, 60–80 mesh, for sulphur hexafluoride. The column temperatures were 170, 30 and 180°C, respectively.

Standards

The method of successive dilution was used. Lindane standards were obtained by dissolving the compound in iso-octane (Caledon, distilled-in-glass grade) and followed by multi-step dilutions. Gas standards of carbon tetrachloride and sulphur hexafluoride were prepared by a two-stage dilution method. A glass vessel with a known volume, fitted with a septum port and leak-tight stopcocks, was pumped down to a pressure of 0.1 torr while being heated with a hot-air gun. The required quantity of the pure compound or concentrated standard to be diluted was introduced via the septum port with a suitable syringe. The glass vessel was then filled with nitrogen to a pressure of 250 torr above atmospheric. An equilibration time of 30 min was allowed before any sampling was done. For the second dilution step, an appropriate volume of the first standard was withdrawn with a gas-tight syringe, and introduced into another similarly evacuated glass vessel. This procedure has been used for the preparation of accurate and precise gas standards (not necessarily for electron-capture work) in this laboratory for years. The main source of error lies in the volume dispensed by the syringe. The maximum error in the two-stage dilution used here was estimated to be no more than 5%, an acceptable margin for ultra-trace analysis and for this study as well.

RESULTS AND DISCUSSION

Hypercoulometric response in the pulsed mode is not unknown^{16–19}. In fact, its first observation dates back to the days when coulometry was first conceived¹⁶. Regarded primarily by most to be an anomaly and inconvenience for coulometry, it drew relatively little attention. Moreover, small effects were thought explainable by the presence of electron-capturing products^{2,9,10} and the mechanism of cyclic capture¹¹.

Recent advances, especially in the field of atmospheric pressure ionization mass spectrometry (APIMS), enable us to select test compounds that do not form electron-capturing products. Carbon tetrachloride and sulphur hexafluoride fall into this solute category. For the former, it has been shown that CCl₃, the major neutral product after the initial electron attachment to CCl₄ and the subsequent dissociation, does not undergo any further electron capture⁴. The latter compound, sulphur hexafluoride, captures an electron primarily in the associative mode to form the stable SF₆⁻ anion^{20,21}.

Electron-capturing products aside, one still has to consider the potential complication of cyclic capture¹¹ as a contributor to hypercoulometry. That this might take place was based on the argument that the residence time of a strong electron-capturing molecule in the electron-capture detector is much longer than its life-time against electron capture. Further, the neutralization rates between cations and anions were quoted to be 10^3 times higher than electron attachment rates. Thus a scenario could develop whereby an analyte molecule could capture an electron, "lose" it to the cations via neutralization and capture another electron. How this contributes to the overall reduction of electron concentration was not stated¹¹. Presumably, the fast neutralization of cations and anions results in a large population of analyte molecules which, in turn, results in an accelerated electron attachment and hence a bigger drop in electron concentration.

Reasonable as this model may seem, it does not agree well with known facts. To begin with, neutralization rates between cations and anions are not 10^3 times higher than electron attachment rates as quoted. (Cation-anion neutralization rate constants are much larger than reported electron attachment rate constants though.) In fact, the two rates have to be equal if one assumes steady-state conditions to be applicable (see, for example, these authors' own equation 7c in ref. 11). Further, since cation-anion neutralization rates and cation-electron recombination rates were quoted as comparable¹¹, it becomes difficult to see how capture would result in any significant decrease in electron concentration (*i.e.* any significant response), if the capture rates were much lower than cation-electron recombination rates. As well, the very assumption that cation-electron recombination rates be comparable to cation-anion neutralization rates also renders it impossible for this cyclic capture scenario to generate hypercoulometric response. Cyclic capture uses the cation-anion neutralization as an electron sink with the electron-capturer acting as the catalyst. For catalysis to work, the reactions involving the catalyst have to be faster than the original reaction. In the cyclic capture scenario, both reactions involving the catalyst, the electron-capturer and cation-anion neutralization, have comparable rates to cation-electron recombination. From a different perspective, any increase of analyte concentration from cation-anion neutralization must lead to a decrease of cation concentration which, in turn, results in a decrease of cation-electron recombination. Owing to the comparable reaction rates, any potential increase of electron-capturer concentration in this manner would result in a concomitant increase of electron concentration. Thus, although capture may be faster, less electrons are lost via recombination with cations; consequently, the net electron concentration is unchanged.

Experimental evidence discrediting cyclic capture has also surfaced recently. APIMS²¹ shows that cation-anion neutralization rates are comparable to cation-electron recombination rates (in fact, they may be slightly lower). Further, cation-anion neutralization is not a prerequisite for electron-capture response. No effect on detector response was observed when this neutralization reaction was precluded by disallowing the contact of cations and anions^{22,23}. Since cation-anion neutralization is the key to cyclic capture, this mechanism's proposed role in electron capture must be, if any at all, insignificant.

The experimental results of this present study are illustrated in Figs. 2, 3 and 4. They are plots of e/m values *versus* pulse periods for carbon tetrachloride, sulphur hexafluoride and lindane, respectively. The pulse parameters investigated were all

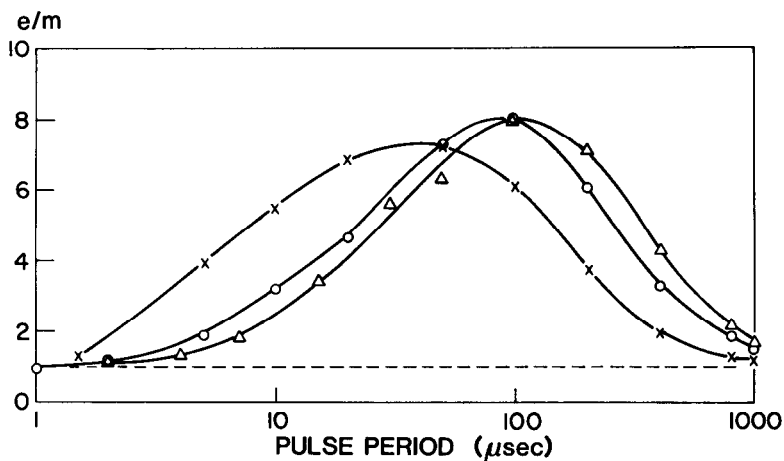


Fig. 2. e/m Profiles of carbon tetrachloride. 0.557 μg per injection. Pulse amplitudes: \times , -10 ; \circ , -20 ; Δ , -40 V. Pulse width: $0.5 \mu\text{sec}$.

typical of those used in most ECD work. All three solutes exhibited hypercoulometry, *i.e.* e/m ratios above unity. Not only that, hypercoulometric response was found from a pulse period of a few microseconds to almost a millisecond. As well, changing the pulse amplitude appeared to shift the e/m profiles, but had no apparently significant effect on the maximum peak e/m ratio for a given analyte. Increasing the pulse amplitude shifted the profiles towards longer pulse periods, in agreement with previous observations that the response maximum (or, the e/m maximum here) is a function of the "effective voltage" of the system, a combination of pulse amplitude, width and period¹³.

Perhaps the most striking aspect of the results is the extent of conditions under which hypercoulometry occurs. As well, the magnitude of hypercoulometry is phe-

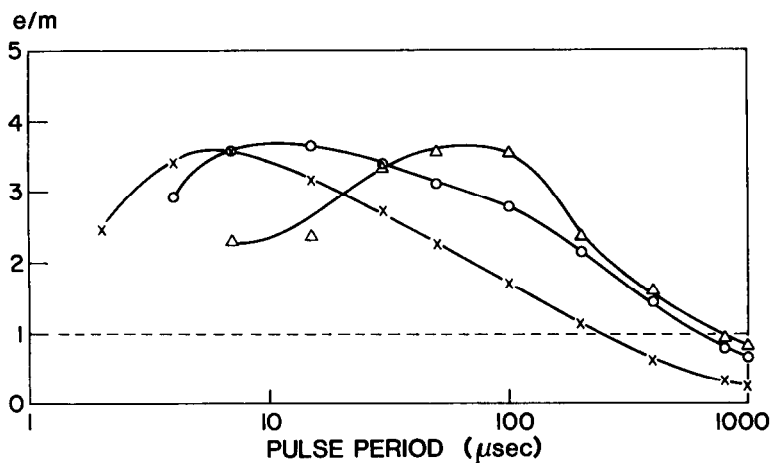


Fig. 3. e/m Profiles of sulphur hexafluoride. 0.626 μg per injection. Pulse amplitudes: \times , -10 ; \circ , -20 ; Δ , -40 V. Pulse width: $0.5 \mu\text{sec}$.

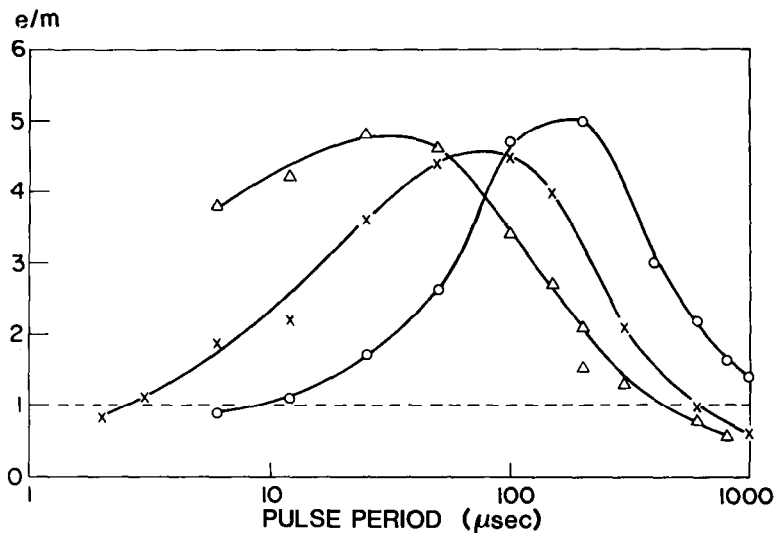


Fig. 4. e/m Profiles of lindane. 1.0 pg per injection. Pulse conditions: ○, -40 V amplitude and 0.5 μ sec width; △, -10 V amplitude and 0.5 μ sec width; ×, -10 V amplitude and 1 μ sec width.

nomenal. The potential error committed by assuming coulometric behaviour in the determination of carbon tetrachloride, a species said to exhibit coulometric response¹⁻³, with a pulse amplitude of -40 V, width of 0.5 μ sec and period of 100 μ sec, would be 800%. Similarly, errors of up to 350 and 500% could be made with sulphur hexafluoride and lindane. Evidently, no coulometric limit exists for these analytes, which include compounds that undergo associative and dissociative capture as well as compounds that do and do not form electron-capturing products. Based on these results, it may be reasonable to question whether the coulometric limit does indeed exist for any solute.

Analytical relevance aside, the present results have significant implications for the electron-capture mechanism. The experiments were carried out under typical pulsed conditions, with a detector of conventional dimensions and geometry, yet very unconventional results were obtained. Two of the analytes chosen, carbon tetrachloride and sulphur hexafluoride, do not form significant electron-capturing products. Even if such were present, they would not be expected to yield e/m values of 8 and 3.5. (Further, products are almost always poorer electron-captors than the parent compound.) With no contributions from electron-capturing products and cyclic capture, it is difficult to see how the classical mechanism could rationalize the occurrence of large-scale hypercoulometric response in the conventional ECD system over a wide range of typical pulsed conditions.

Earlier observations have turned up evidence that both the classical and space charge mechanisms may be operative in the pulsed mode¹³. It is tempting to assign the response seen in this study to the space charge mechanism, which allows hypercoulometric behaviour, despite the obvious difference in geometries and charge distribution between the detectors used in the two studies. However, this link is, at best, speculative at the moment and awaits further evidence.

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