NON-LINEAR RESPONSES OF THE ELECTRON-CAPTURE DETECTOR TO ALKYL MONOCHLORIDES

E. P. GRIMSRUD and D. A. MILLER

Department of Chemistry, Montana State University, Bozeman, Mont. 59717 (U.S.A.)

(First received October 30th, 1979; revised manuscript received December 7th, 1979)

SUMMARY

Calibration curves for the response of a constant-current electron-capture detector with a ^{63}Ni ionization cell to methyl and ethyl chloride are reported to be non-linear. The molar response to low-concentration samples is shown to be very much greater than to high-concentration samples. Oxygen contamination of the carrier gas is investigated as a likely cause of the low-concentration, increased responses, but this possibility is not supported by the experiments reported here. Other possible causes are discussed. Superior calibration curves for alkyl mono-chlorides are obtained by the use of intentionally oxygen-doped carrier gas.

INTRODUCTION

One of the most significant improvements made in the pulsed electron-capture detector (ECD) for gas chromatography (GC) occurred with the introduction of the constant-current or frequency-modulated mode of signal processing[1]. While possessing the high sensitivity and specificity characteristic of all ECD configurations, this mode of operation greatly extended the linear dynamic range of response of the pulsed ECD from two to four or five orders of magnitude change in the sample concentration. This wide range of linear response has been demonstrated for many electron-attaching molecules (ref. 2, for example). Some exceptions to linearity have been observed for the cases where the sample molecule attaches electrons so rapidly that its concentration within the cell is altered by the electron-capture process itself. Lovelock and Watson[3] recently described and explained this anomaly of the constant-current ECD for the case of CCl_3F. For most molecules, however, for which the electron attachment rates are not ultra fast, linear responses have come to be expected when using the constant-current ECD.

In this paper the responses of a constant-current ECD to simple alkyl chlorides are described, and are shown to be non-linear under all of the conditions examined here. While the ECD is used most frequently for polychlorinated molecules, to which it responds extremely sensitively, the ECD is also used for the analysis of many other classes of compounds, such as mono- and dichlorinated hydrocarbons, to which it may respond three to five orders of magnitude less sensitively. The analysis of methyl

chloride in air, for example, has been performed using the ECD[4-6], undoubtedly because of its lack of response to potentially interfering hydrocarbons. For these compounds linear responses might have been expected since their electron attachment rates are relatively slow. The intention of this article is to characterize and discuss the non-linear responses observed for alkyl chlorides so that improved accuracies in the analysis of these compounds by the ECD might result.

This study is also motivated by a recently discovered application of the ECD —the use of oxygen doping of the carrier gas for obtaining improved responses to alkyl chlorides[7-9]. In addition to providing greater sensitivity, another potential application of oxygen doping is the use of "response enhancement" values which might facilitate the identification of unknown sample components. A response enhancement value for a given compound is the ratio of its ECD responses with and without oxygen added to the carrier gas. This application of the ECD, however, requires that the normal response, as well as the oxygen-caused responses, be well understood.

EXPERIMENTAL

All halocarbons studied were reagent-grade obtained from commercial suppliers. Standards of methyl and ethyl chloride were prepared by the successive dilution of the pure compound into nitrogen gas using airtight glass flasks and carboys. Standards for 1,4-dichlorobutane and tetrachloroethylene were prepared by dilution into hexane.

The gas chromatograph used for most of these studies is a Varian 3700 Aerograph with constant-current, pulse-modulated operation of a ^{63}Ni detector. A 10 ft. × 1/8 in. stainless-steel column packed with 10% SF-96 on Chromosorb W was used at oven temperatures of 30 to 60°. The GC flow-rate was 30 ml/min. The detector temperature was 300°. Gaseous samples were introduced to the gas chromatograph using a 2-ml volume sample loop (Carle 8030). Liquid samples were introduced with a 10-μl syringe and the normal injection port.

RESULTS AND DISCUSSION

In Fig. 1 are shown the ECD responses measured as peak heights in units of kHz (ref. 2) to methyl and ethyl chloride in the small sample concentration range where the sample size is increased to about 500 times the detection limit. It is seen in each case that only a narrow range of approximate linearity exists prior to the onset of curvature and diminished molar response. For more strongly electron capturing molecules, the instrument used here has been shown in our laboratory and elsewhere[2] to provide linear responses up to peak heights correspondnig to pulse frequencies of 100 kHz. For the molecules examined here the range of initial linearity extends only to considerably less than 1 kHz of frequency increase above the baseline frequency of 2 kHz. In Fig. 2 the responses to larger sample sizes of methyl and ethyl chloride are shown. It is seen that a wide, linear plateau of response is observed after the region of curvature. The sensitivity of response in this region is very much less than in the small sample region, especially for the case of ethyl chloride.

We have recently demonstrated that the response of the ECD to mono-
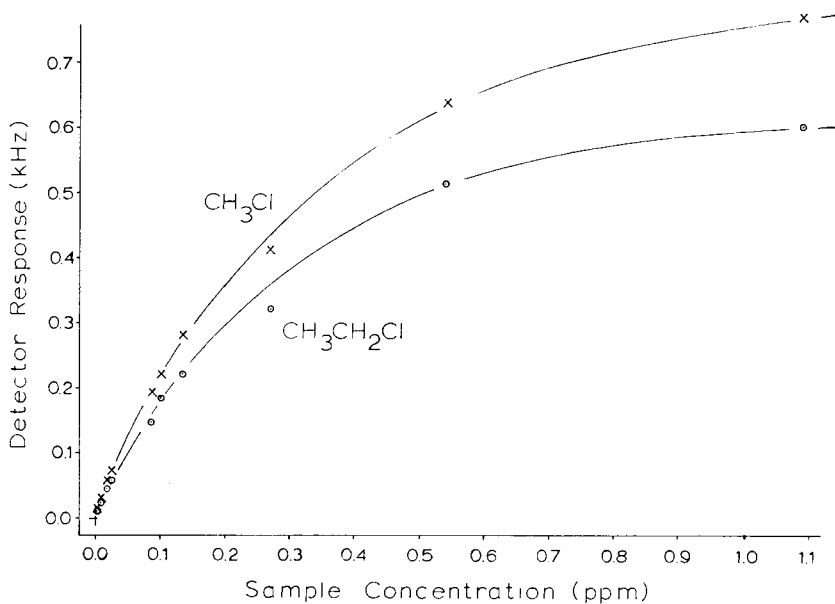
Fig. 1. ECD response to standards in the low-concentration range. Units of sample concentration are molar ratio (ppm) of gaseous sample in nitrogen. Detector temperature 300°.
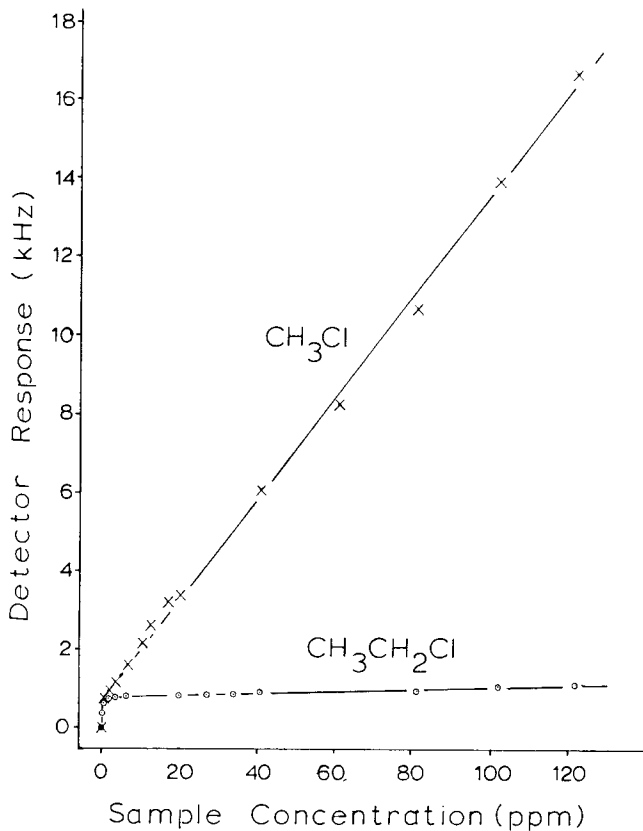

Fig. 2. ECD response to standards throughout wide range of concentration.

chlorinated aliphatic hydrocarbons can be greatly increased by the intentional addition of oxygen to the carrier gas[7-9]. For this reason it was initially suspected that the effects shown in Figs. 1 and 2 may be due to traces of oxygen frequently present in sources of nitrogen carrier gas. Considering this possibility for the moment, at very small sample sizes, reaction 1

$$O_2^- + RCl \rightarrow Cl^- + \text{neutrals} \tag{1}$$

may provide the fastest means of sample ionization, as long as the sample size is small. If reaction 1 occurs, the negative charge is then irreversibly held by Cl^-, rather than O_2^- which would rapidly release the electron. The steady-state electron density of the ECD plasma would be thereby reduced, causing a response. This mechanism is discussed in detail in previous studies of oxygen's effects[9,10]. At higher sample sizes, the steady-state O_2^- negative ion concentration may be depleted by reaction 1, and the slower electron-capture reaction 2,

$$e^- + RCl \rightarrow Cl^- + \text{neutrals} \tag{2}$$

must provide any further increase in response as the sample size is increased. The observation that the slope of the high-concentration plateau for methyl chloride in Fig. 2 is significantly larger than that for ethyl chloride would be taken to indicate that its electron capture rate is greater. A portion of the difference in these slopes, however, will also be attributed to a dilution effect of the solute in the carrier gas where the larger compound's retention time and longitudinal spreading within the column is greater.

  We have conducted several experiments designed to test whether or not the initial portion of the calibration curves are being determined by the trace presence of oxygen. We have added oxygen scrubbers to the carrier system which are reported to remove trace oxygen to less than 1 ppm. The normal carrier gas was ultra high purity nitrogen guaranteed to contain less than 10 ppm oxygen. The addition of the oxygen scrubber had only small effects (less than 10% reduction of responses) on the calibration curves of Figs. 1 and 2. Calibration curves were also obtained with oxygen intentionally added to the carrier gas. These are shown in Fig. 3 for methyl chloride with 30 ppm oxygen added to the carrier gas. It is seen in Fig. 3 that the addition of oxygen does amplify the initial portion of the calibration curves somewhat. However, if the initial responses for the case where no oxygen has been added are assumed to be proportional to trace oxygen, Fig. 3 would imply that the oxygen concentration of the undoped carrier is roughly 100 ppm, much higher than is expected of our carrier gas.

  It is always possible that the oxygen content of a carrier gas is much higher in the detector than in the purified carrier further upstream, due to leaks in the flow system. This is especially true if leaks occur at the column–detector interface where the system pressure is only slightly above atmospheric pressure. For this reason we performed another experiment by which it appears a very large fraction of any trace oxygen entering the detector can be removed. This is done by a procedure which was discovered accidentally while cleaning our detector with hydrogen as recommended by the instrument manufacturer. For a period of time of about one hour after flowing
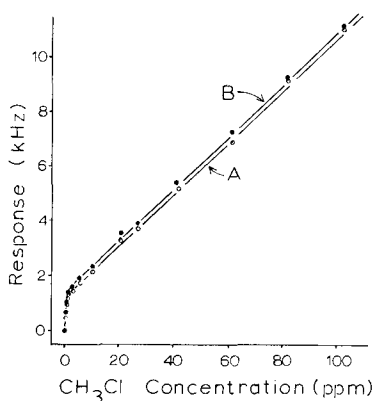
Fig. 3. ECD response to methyl chloride standards using (A) high purity nitrogen carrier gas and (B) nitrogen carrier gas doped with 30 ppm oxygen.

hydrogen gas at high temperature through the detector and the transfer line leading to it, the transfer line apparently becomes activated by the hydrogen and then has the capacity for removing oxygen in the carrier stream. Evidence for this effect is shown in Fig. 4, where chromatograms of the same standard containing ethyl chloride in utility-grade nitrogen are shown. In Fig. 4A a peak due to oxygen in this contaminated nitrogen source, as well as one due to added ethyl chloride, is observed. Following treatment of the detector with hydrogen at high temperature, a repeated analysis is shown in Fig. 4B. The peak due to oxygen is now absent. Upon repeated analyses, the oxygen peak begins to reappear in about one hour and increases steadily until the original peak height is reestablished. It appears that this effect is due to a surface reaction removing trace oxygen probably within the transfer line. That it is not due to a gas-phase reaction involving small amounts of hydrogen within the ECD cell itself, was indicated by our observation that the suppression of the oxygen peak is not caused by doping the carrier gas with small amounts of hydrogen.

The chromatograms in Fig. 4 indicate that with the transfer line so activated, remaining traces of oxygen in the carrier gas should be further reduced to a small
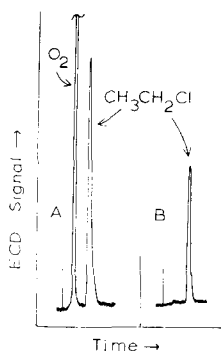

Fig. 4. Chromatograms of a standard containing 0.68 ppm ethyl chloride in nitrogen which is also contaminated with oxygen, (A) prior to hydrogen cleaning and (B) immediately following hydrogen cleaning of the detector.

fraction of the concentration present in the already purified carrier. Thus, analyses performed under this condition might be assumed to be uncommonly free of oxygen contamination. Calibration curves for ethyl chloride obtained before and after hydrogen activation of the detector transfer lines are shown in Fig. 5. It is seen that with this procedure the magnitude of the initial response region has been reduced, but only to about one-half of its original level. If oxygen had been the only cause of non-linearity, a much greater reduction of response might have been anticipated. It appears from this test, also, that something other than trace oxygen is a major cause of the high responses toward these compounds at low concentrations.
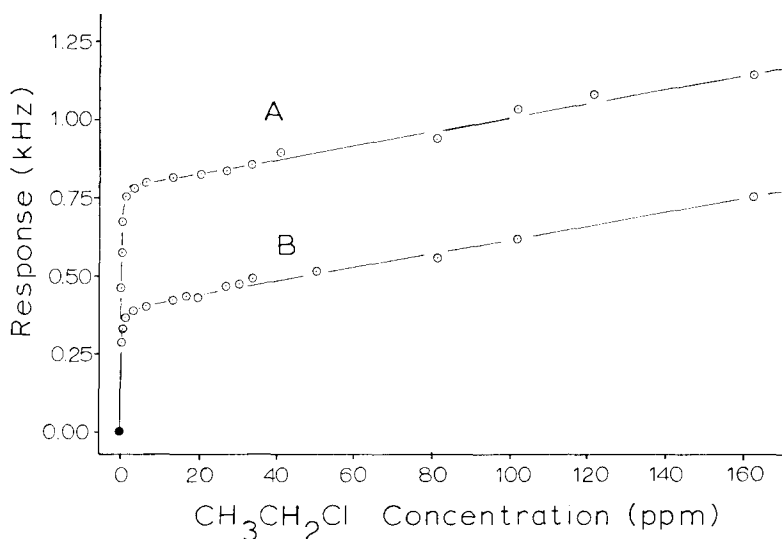

Fig. 5. ECD response to ethyl chloride standards (A) prior to hydrogen cleaning and (B) immediately following hydrogen cleaning of the detector.

At this time we can only speculate as to the basis of the unusual responses observed for monochloroalkanes (we have observed these effects for n-propyl and n-butyl chloride also). One possibility is that the carrier gas contains an impurity other than oxygen which causes this effect. Perhaps the partial removal of this unknown substance caused the decreased signals observed in Fig. 5 following treatment of the detector with hydrogen. The use of several different sources of carrier gas, however, has produced similar results. The possibility that column bleed provides this unknown impurity was not supported in an experiment where the peak areas of several small-concentration samples were found to be independent of changes in the temperature of the column. The responses of completely different instruments using various columns, carrier gases, detectors and signal processing methods were compared using a sample containing 1,4-dichlorobutane in hexane. These results are shown in Table I. Instrument A is the Varian 3700 used for all the experiments described above. Instrument B is another Varian 3700 with a similar ECD. This instrument is used daily for routine environmental analyses in another laboratory on our campus. Its response is also derived by the constant-current method. Its carrier

TABLE I

RESPONSES OF VARIOUS ^{63}Ni ECD GAS CHROMATOGRAPHS TO 1,4-DICHLORO-BUTANE AND TETRACHLOROETHYLENE

Responses are determined from peak heights and have been converted to the functions indicated. The function $(I_0-I)/I$ is explained in the text. Responses relative to that of the lowest concentration sample in each case are shown in parentheses. Instruments A, B and C are described in the text. Instrument C was used with nitrogen and argon–10% methane carrier gases.

Relative concentration*	Intrument							
	A, kHz		B, kHz		C (N_2), (I_0−I)/I		C (Ar–CH_4), (I_0−I)/I	
1,4-Dichlorobutane								
1	0.12	(1)	0.030	(1)	0.065	(1)	0.036	(1)
5	0.41	(3.4)	0.089	(3.0)	0.20	(3.1)	0.141	(3.8)
50	0.88	(7.1)	0.18	(6.0)	0.43	(6.6)	0.21	(5.8)
500	3.2	(23)	0.85	(28)	0.70	(10.8)	0.28	(7.8)
Tetrachloroethylene								
1	0.56	(1)			0.024	(1)		
2.5	1.20	(2.2)			0.055	(2.3)		
12.5	6.8	(12.2)			0.25	(10.2)		
25	14.8	(26)			0.51	(22)		
100	63.2	(105)			2.1	(90)		

* The concentrations of the smallest samples of 1,4-dichloroethylene and tetrachlorobutane in the 2 μl of hexane injected were $5.0 \cdot 10^{-10}$ g/μl and $1.3 \cdot 10^{-12}$ g/μl, respectively.

gas is nitrogen with a Varian oxygen trap. Its column is glass packed with a 6% QF-1 + 4% SE-30 stationary phase. Instrument C is a home-built gas chromatograph–ECD incorporating ^{63}Ni ionization detector of 1 ml volume. A 1/16 in. anode pin extends the length of its cylindrical geometry. This signal from this instrument was processed as the function $(I_0-I)/I$ where I_0 is the standing current obtained with 50 V pulses of 1.5 μsec duration and a period between pulses of 350 μsec, and I is the ECD current remaining at the point of maximum response to the sample. This function has been shown to provide the greatest range of linear response for the fixed frequency, pulsed ECD[11]. Instrument C contained a column packed with SF-96, and both nitrogen and argon–10% methane carrier gases were used with oxygen removing traps. It is seen in Table I that all instruments respond to 1,4-dichlorobutane, also, in a pronounced non-linear manner. Furthermore, instrument C responds non-linearly whether the carrier gas is nitrogen or argon–methane. To demonstrate that these instruments are, indeed, capable of responding linearly to more strongly electron-attaching compounds, the response of instruments A and C to tetrachloroethylene is also shown in Table I.

Another potential explanation for the responses observed of a completely different nature may be worthy of consideration. If the set of electrons within the ECD do not all have precisely the same energy, the possibility exists that the initially greater response to small samples of the alkyl chlorides is due to the faster electron attachment reactions of a fraction of the total electron population, which possesses greater than average energy. It has been shown[12] that the rates of electron attachments to 1,2-dichloroethane, for example, increases rapidly with small increases in the

electron energy above thermal energy. Electrons within the ECD have been produced initially at higher-than-thermal energies by ^{63}Ni β-radiation of the carrier gas. These electrons are generally thought to be thermalized rapidly by inelastic collisions in nitrogen or argon–methane carrier gas so that all electrons can be assumed to have the same energy determined simply by the temperature of the gas[13]. As this assumption has not yet been examined in great detail, however, it remains possible that small, but significant differences in the energies of the electrons exist, and that for some weakly electron attaching molecules some dependence of reactivity on these energy differences may be observable under conditions of the ECD. While this possibility has little precedence in the ECD literature, it is being investigated further in our laboratory.

We have recently described an improved analysis procedure for alkyl chlorides which results when relatively large amounts of oxygen are added to the carrier gas of a constant-current ECD. In Fig. 6 the calibration curve for methyl chloride is shown where the nitrogen carrier gas also contains 2000 ppm added oxygen. In comparing this with the calibration curve for CH_3Cl obtained under normal conditions shown in Fig. 1, the use of the oxygen-doped carrier is clearly recommended. Not only is the detector response to a given quantity of sample much greater with the oxygen-doped carrier, but also a linear calibration curve is obtained which passes through the origin and, as has been shown elsewhere[8], extends the full linear dynamic range (to 100 kHz) expected for this instrument.
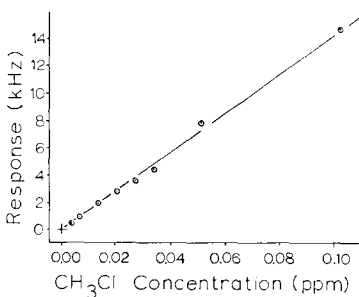

Fig. 6. ECD response to methyl chloride samples using nitrogen carrier gas doped with 2.0 parts per thousand oxygen. Detector temperature 300°.

In the use of oxygen-doping for the determination of response enhancements[7–9], however, caution is necessary because of the non-linearity of the normal response shown in Fig. 1. Our response enhancement measurements for methyl chloride will be reasonably constant only in the concentration range 0.0–0.1 ppm, where the calibration curve in Fig. 1 is reasonably constant. With higher concentrations of methyl chloride, the measured response enhancement caused by oxygen doping will increase continuously with increased sample size. In the use of response enhancement measurements for compound identification, therefore, it is recommended that the range of linear response of the instrument to each sample component be established under the normal oxygen-free carrier gas condition, and that response enhancement values then be used only for sample sizes within this range.

CONCLUSIONS

Regardless of the cause of the non-linearity of response of the ^{63}Ni ECDs to alkyl chlorides, which as been characterized here but not identified, it seems likely that this may constitute a common source of error wherever the ECD is used for the analysis of simple alkyl chlorides. Although we have altered our experimental conditions in many ways, we have as yet been unable to obtain linear responses to these compounds using the normal ECD carrier gases. If calibration curves are unwittingly prepared for alkyl monochlorides from the measured responses of a few high concentration standards (which is often the easiest procedure) and by forcing the calibration line to pass through zero response at zero sample concentration, very large errors in subsequent analyses of small sample sizes will result. In spite of the wide linear dynamic range commonly associated with the constant-current ECD, it remains necessary to carefully check the response of the instrument over the entire concentration range to be used for each type of compound analyzed. The basis of the non-linear calibration curves described here is under continued investigation in hopes that this GC detector might be more completely understood and controlled. The use of oxygen-doped carrier gas is strongly recommended in the analysis of alkyl monochlorides by the ECD as higher sensitivity and a linear calibration curve are thereby enjoyed.

ACKNOWLEDGEMENT

REFERENCES

1 R. J. Maggs, P. L. Joynes, A. J. Davies and J. E. Lovelock, *Anal. Chem.*, 43 (1971) 1966.
2 P. L. Patterson, *J. Chromatogr.*, 134 (1977) 25.
3 J. E. Lovelock and A. J. Watson, *J. Chromatogr.*, 158 (1978) 123.
4 J. E. Lovelock, *Nature (London)*, 256 (1975) 193.
5 R. A. Cox, R. G. Derwent, A. E. J. Eggleton and J. E. Lovelock, *Atmos. Environ.*, 10 (1976) 305.
6 H. B. Singh, L. Salas and A. Crawford, *Atmos. Environ.*, 11 (1977) 819.
7 E. P. Grimsrud and D. A. Miller, *Anal. Chem.*, 50 (1978) 1151.
8 E. P. Grimsrud and D. A. Miller, *Special Publication 519*, National Bureau of Standards, Washington, D.C., April, 1979.
9 D. A. Miller and E. P. Grimsrud, *Anal. Chem.*, 51 (1979) 851.
10 E. P. Grimsrud and R. G. Stebbins, *J. Chromatogr.*, 155 (1978) 19.
11 D. C. Fenimore, A. Zlatkis and W. E. Wentworth, *Anal. Chem.*, 40 (1968) 1594.
12 J. P. Johnson, L. G. Christophorou and J. G. Carter, *J. Chem. Phys.*, 67 (1977) 2196.
13 W. E. Wentworth, E. Chen and J. E. Lovelock, *J. Phys. Chem.*, 70 (1966) 445.