ELECTRON-CAPTURE DETECTOR

THEORY AND PRACTICE. II

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SUMMARY

In Part I a simple numerical model of the electron-capture detector (ECD) was described that could account with fair accuracy for the performance of the detector in the constant-current and constant-frequency methods of operation.

In this paper, the model is extended to include the effects of electron loss by recombination and by reaction with trace amounts of contaminants in the carrier gas. These refinements appear to improve the predictions of the model to an accuracy of 5% or better. The practical problem of coulometric analysis with the ECD as its own standard is discussed.

The environmental problem posed by the presence of atmospheric halocarbons demands an analytical accuracy of 3% or better. The theoretical considerations and practical experiments here reported were made within the context of this need for improved accuracy. To meet it and also to validate the model of the ECD, an exponential dilution chamber was constructed and used to prepare in one step accurate standards with a parts per trillion (10^{12}) by volume concentration in air.

INTRODUCTION

Many compounds and classes of compound that react vigorously with free electrons are either toxic or represent some real or imagined hazard in the natural environment. Until recently, for most purposes it was sufficient to use this reaction in the electron-capture detector (ECD) to register the presence of materials such as pesticide residues in foodstuffs or explosive vapours escaping from a package that otherwise seemed innocent. Although competent analysts could and did make accurate measurements with the ECD, there was a greater need for sensitivity than for accuracy or precision. The performance expected of the ECD was greatly increased in 1975, however, when we were made aware of a new environmental problem, namely that of the accumulation in the atmosphere of chemically stable halocarbons, especially the chlorofluorocarbons. The potential of these substances to deplete the concentrations of stratospheric ozone was first recognized about 4 years ago[1,2] and has been well reviewed[3]. What is less well known is that the severity of this hazard depends on, among other things, whether or not there are natural processes in the

lower atmosphere that can scavenge the halocarbons from the air. Hence there is reason to believe that such a process capable of removing $CFCl_3$ from the air at 6% per year would decrease by three-fold the expected depletion of stratospheric ozone. To reveal the presence or otherwise of such a small sink for halocarbons requires the accurate analysis of their atmospheric concentrations over long periods of time. An analytical precision of 1% and an absolute accuracy of 3% are needed in the solution of this important environmental problem.

These requirements could be met by using currently available commercial gas chromatographs equipped with ECDs if standard dilutions of halocarbons were either available or easy to prepare. In most laboratories familiar with the analysis of chlorofluorocarbons, replicate analyses of a stored air sample can be made with a precision of 1% or less. In two inter-calibration exercises, the same air sample was analysed blind by 16 laboratories. Rasmussen[4], who conducted this test, found that the standard error of the mean was between 11 and 18% for fluorocarbons 11 and 12 and some reported measurements differed by more than 100% from the mean. The great difference between the precision and the accuracy of the analysis of fluorocarbons suggests that the inaccuracy is attributable to deficiencies in the standards used rather than to the method of analysis. This is not a surprising conclusion to anyone who has attempted to prepare a dilution of a halocarbon at the parts per 10^{10} by volume level. To do so with an accuracy of 1% in a typical laboratory environment rich in the vapours of halocarbons is a formidable problem. The importance of this analytical problem justified the unusual step of assuming that the ECD itself, although of unknown absolute accuracy, was sufficiently consistent to serve as a secondary standard. That is to say, if the operating conditions of the chromatograph and detector were accurately known and recorded at each analysis and a value was chosen and kept for the rate constant of the reaction between electrons and the compound, then an estimate could be made that is precise but of unknown absolute accuracy. This procedure has been used as a basis for estimates of the global burden of the halocarbons from a series of measurements in the Northern and Southern Hemispheres over the past 7 years[5–7]. Experience over this long period has shown that although this procedure does not provide an absolute value of the atmospheric burden, it does give consistent results from which the rate of increase can be calculated accurately. It also had the purpose of linking past historic measurements to the time when accurate standards became available.

During the past 4 years, other observers[8–11] have calibrated their instruments with prepared standards and reported their analyses of the aerial concentration of the fluorocarbons. It is probable that some of these measurements are accurate to the extent needed but the scatter among them still remains large and makes it difficult to decide which are correct.

This paper is concerned with the attainment of accurate analysis with the ECD and discusses this problem in the light of developments of the model[12] of the ECD. It also reports some preliminary experiments with a large-scale exponential dilution chamber designed for the preparation of accurate standards at the parts per 10^{10} by volume level. These standards have been used to compare the predictions of the model of ECD operation with the observations of known aerial concentrations.

THEORETICAL

The kinetics of the reaction within an ECD were first described by Wentworth *et al.*[13] and were used to produce a practical working model of its function[12]. Briefly, this model considered the detector as a well stirred reactor of volume V ml into which electrons were continuously introduced by ionization with a radioactive source at a rate A sec$^{-1} \cdot$ ml^{-1}. Detectable molecules were introduced at a rate B sec$^{-1} \cdot$ ml^{-1} in a stream of carrier gas flowing at a rate U ml $\cdot$ sec^{-1}.

The key assumption of this model was that electrons and molecules combine in a simple irreversible second-order reaction:

$$e^- + AB \xrightarrow{K_1} [AB]^{*-} \tag{1}$$

The rate of the reaction is determined by the simple second-order unidirectional rate constant (K_1) and the product is an excited negative molecular ion $(AB)^{*-}$.

The fate of this negative molecular ion after its formation is of the greatest interest in the investigation of ion–molecule reactions and in the design of ion drift devices and the plasma chromatograph. In contrast, in the modelling of the ECD the subsequent reactions of the negative molecular ions are significant only if the dissociation products include either free electrons or fragments that are highly reactive towards free electrons. Fortunately, in the analytical use of the ECD, compounds that attach electrons rarely have negative ions that behave in this way.

The usual method of observing changes in the electron population of the detector is to apply brief sampling pulses of amplitude about 30–50 V and 1 μsec in duration. The charge collected at the anode is then integrated and averaged to give a d.c. signal that is either observed directly or used to vary the frequency of the pulses so as to maintain a constant current. In the latter instance the frequency then provides the signal. Both of these procedures require that the sample pulse collects almost all of the free electrons in the ion chamber. Until recently there was little doubt that this condition was met. Seigel and McKeown[14] have suggested that the cloud of positive ions and free electrons in the ECD is so dense that interactions between them prevent the independent motion of the free electrons when a field is applied. In other words, the ion cloud is a plasma and moves not by simple but by ambipolar diffusion. Reasonable though this proposal may be, it is easy to demonstrate by direct experiment that, even with densely ionizing tritium sources generating an electron concentration of $10^{11} \cdot$ ml^{-1}, their collection is not impeded in any way to effect the function of the detector. This is illustrated in Fig. 1, which shows the arrival of an electron pulse at the anode. The detector was a plane parallel version bearing a tritium ionizing source and an electrode separation of 1 cm, the carrier gas being argon–10% methane. The horizontal time scale was 1 μsec$\cdot$cm^{-1} and the vertical scale 20 μA$\cdot$cm^{-1}. The electrons arrived at the anode in 300 nsec travelling with an average velocity of 30 km$\cdot$sec^{-1}. The field was 30 V$\cdot$cm^{-1} applied for 1 μsec only, which is typical for the ECD. The electron drift velocity so observed is closely similar to that of free unimpeded electrons in argon–methane. It may be correct to assume that ion clouds within an ECD approximate to plasma conditions but, as with the fate of the negative ions formed, this does not significantly effect the practical theory of its operation.
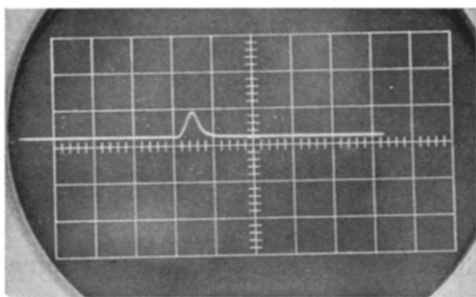
Fig. 1. Current flow from the detector anode during the application of a sampling pulse 30 V in amplitude and 1 μsec in duration. Vertical scale, 20 μA per centimetre; horizontal scale, 1 μsec per centimetre (each "box" is 1 cm square).

In addition to the primary reaction between electrons and molecules, the other reactions and processes that determine the detector function are as follows:

$$e^- + \oplus \xrightarrow{K_2} \text{Products} \tag{2}$$

$$AB + \oplus \xrightarrow{K_3} \text{Products} \tag{3}$$

$$AB \xrightarrow{U/V} \text{Ventilation} \tag{4}$$

$$e^- + X \xrightarrow{K_4} \text{Products} \tag{5}$$

In the model introduced in 1974, the effects of contamination of the carrier gas by electron-absorbing substances and of column bleed were not considered; this is now included as reaction 5, where electrons are taken to be attached to an unspecified electron absorber (X) at a rate K_4 sec^{-1}. It is further assumed that the concentration of X varies reciprocally with the flow-rate of carrier gas, which is in accord with experience. The model then becomes

$$\frac{1}{[e^-]} \cdot \frac{d[e^-]}{dt} = A - (K_1 c + K_2 + K_4[X]) \tag{6}$$

$$\frac{1}{[c]} \cdot \frac{dc}{dt} = B - \left(K_1[e^-] + K_3 + \frac{U}{V} \right) \tag{7}$$

The numerical solutions of these two equations are illustrated in Figs. 2, 6 and 7.

When sampling pulses are applied at a fixed frequency, the ECD responds linearly to variations in sample size so long as the electron concentration is not reduced by more than 10%. This property makes it easier to investigate the effects of changes in operating conditions than is possible with the more commonly used constant-current, variable-frequency method of operation. Consequently, most measurements reported in this paper were made at a fixed operating frequency of 4 kHz.

Fig. 2 shows the variation of ionization efficiency with carrier gas flow-rate for a strong electron absorber ($K_1 = 1.2 \cdot 10^{-7}$ ml·mole^{-1}·sec^{-1}). The curve falling from 1.0 on the ordinate, unity ionization efficiency, illustrates the proportion of sample molecules ionized. The curve beneath, falling from 0.9 at zero flow-rate, il-
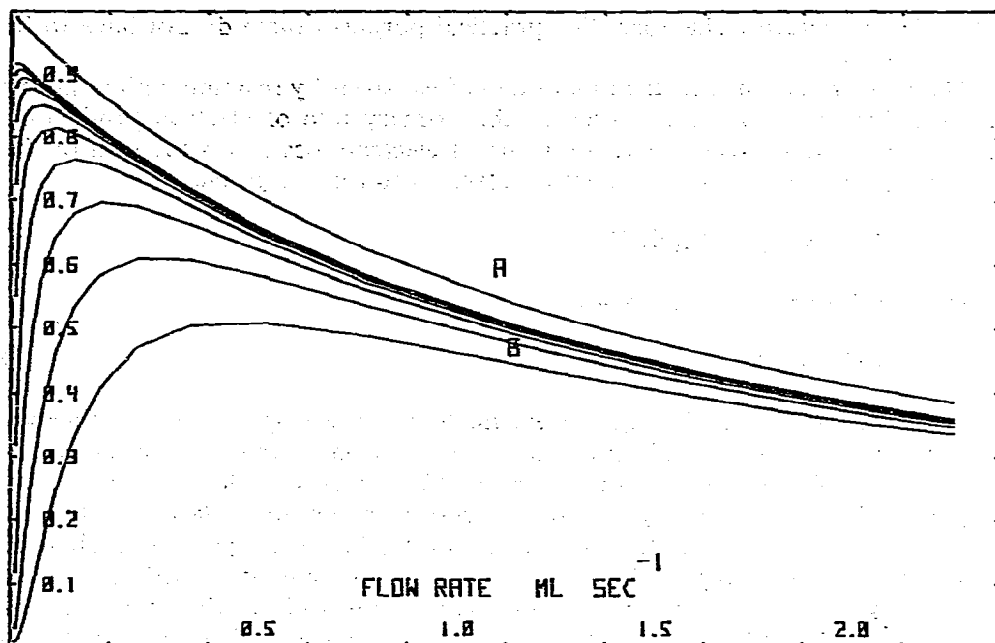
Fig. 2. Ionization efficiency, ordinate, of a typical ^{63}Ni detector at different flow-rates with CCl_3F as the test substance. Curve A: proportion of sample molecules ionized. The family of curves B represent the proportion of electrons removed by reaction with the test substance. The effects of various levels of contaminant are illustrated parametrically starting with a loss rate of 3160 sec^{-1} for the lowest curve and decreasing through division by 3.16 for each step upwards. Here and in Figs. 6 and 7 the calculations are for a detector with the characteristics of No. 1 listed in Table II. The carrier gas is taken to be argon–10% methane; recombination rate, 800 sec^{-1}.

lustrates the ionization efficiency of the ECD as observed from its signal. The difference between these two curves is a consequence of the loss of electrons by recombination with positive ions during the interval between sampling pulses. This means that in practice the detector never gives a signal that is truly coulometric and there will always be some small proportion of the signal electrons lost by recombination.

In argon–methane or argon–hydrogen carrier gas, recombination reduces the expected signal by about 10% at a pulse period of 250 μsec. With shorter intervals between sampling pulses, the loss is less but so is the sensitivity of the ECD. With nitrogen as a carrier gas the recombination rate is considerably greater ($K_2 = 3000$) and the loss of signal is closer to 30%.

With the long coulometric detector previously described[12], the same arguments apply and with this detector a strong electron adsorber gives a signal that is 90–97% of coulometric with argon-based carrier gases and 70% of coulometric with nitrogen, both operating at a pulse period of 250 μsec.

The effect of column bleed or of other leaks of an electron-adsorbing impurity into the carrier is illustrated by the lower family of curves in Fig. 2. Each represents the effect of a different "bleed rate" (K_3) represented by a value of from 1 to 3000. This value is the product of the rate constant of the adsorbing impurity and its con-

centration in the detector chamber. For practical purposes these do not have to be known separately.

The recombination rate, the rate of loss of electrons by reaction with impurity and the other detector properties such as the primary rate of electron production can now be measured directly. The total rate of electron loss (K) is the sum of the loss rate by recombination and by electron reaction to form negative ions:

$$K = K_2 + (K_1[c] + K_4[X])/U \tag{8}$$

In the absence of sample this becomes

$$K = K_2 + K_4[X]/U \tag{9}$$

The observations illustrated in Fig. 3 were made by observing the pulse frequency at which the current was $1/e$ (37%) of the d.c. saturation current at a series of different carrier gas flow-rates. The direct observations were then fitted to eqn. 9 by plotting the observed rate (K) against the reciprocal of the flow-rate $(1/U)$. By this means, the recombination rate, K_2, and the bleed rate, K_4, were separately evaluated.

There is virtually no probability of electron loss by ventilation with the carrier gas and the rate of loss of electrons by diffusion to the walls is small at the intervals between pulses commonly used (less than 1 msec). In any event, these two small loss
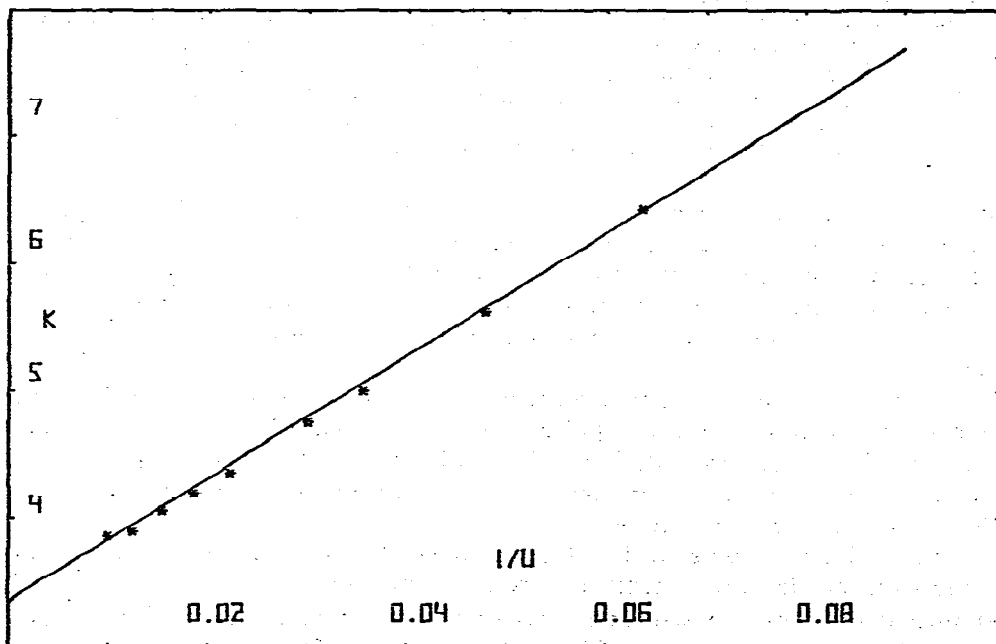

Fig. 3. Experimental measurement of the recombination rate (K_2) and the rate of reaction with contaminants (K_4) in a working detector. The ordinate is the observed frequency (kHz) when the detector current is 36.8% of the d.c. saturation current. The abscissa is the reciprocal flow-rate (sec·ml^{-1}). The intercept at the ordinate indicates a recombination rate of 3240 sec^{-1} and the slope a "bleed rate" of 42 sec^{-1}. Carrier gas, nitrogen; detector, No. 1 in Table II.

rates appear as a slight increase in the observed recombination rate, which is the quantity sought.

The primary ionization rate changes only very slowly with the decay of the radioactive source and as a consequence of the deposition of carbonized material upon it. It is in any event easy to measure the saturation ion current directly by polarizing the detector with a potential of 30 V or more. The recombination rate should be constant provided that the gas used is pure enough for EC chromatography. Only the bleed rate (K_4) changes sufficiently to require frequent measurement. If we assume that the saturation current and the recombination rate are constant, the bleed rate can be read off from the change in baseline current in the absence of a signal. All or any of these operations could, of course, be made automatically by including the appropriate instructions in the chromatograph microprocessor programme.

The same possibilities of coulometry exist with the more commonly used constant-current, variable-frequency method of operation by observing the frequency change instead of the ion current. This is a more difficult operation and some of the problems involved will be discussed later.

EXPERIMENTAL

The experiments reported were made using a modified Hewlett-Packard 5830A chromatograph. The modifications consisted of the provision of an analogue-to-digital converter, a crystal-controlled pulse generator operating at a fixed frequency of 4 kHz and a unity gain electrometer amplifier to match the detector output to the analogue-to-digital converter. This modification was in addition to and did not replace the usual constant-current, variable-frequency mode of operation of the 5830A instrument. Provision was also made to mount experimental ECDs within the chromatograph oven. Samples in all experiments were introduced from a 5-ml sample loop maintained at 50°. The columns were either 3 m × 6 mm I.D. packed with 12% OV-101 on 101–120-mesh Chromosorb W or 1.5 m × 5 mm I.D. packed with 100–150-mesh Porasil D. The column temperature was maintained at 50°.

The halocarbons employed are listed in Table I. The standards used were prepared by dissolving in n-hexane all of the halocarbons listed to make a single solution, as follows: 240 ml of n-hexane, rendered free of halocarbons by refluxing for 5 h over sodium, were placed in a 250-ml standard volumetric flask. Each halocarbon solute was then drawn in turn into a calibrated 0.05- or 1.0-ml syringe and injected below the surface of the n-hexane. These dilutions were made in an environment kept between −1 and +1°. The n-hexane solution was then made up to 250 ml, stoppered and kept at 0°.

The concentration of each of the halocarbons in the solution was chosen so that at the ultimate dilution for analysis the peak areas on each differed by not more than 300%. All of the volumetric vessels, syringes and sample loops were calibrated by filling with water containing a trace amount of detergent at 20° and weighing.

The characteristics of the detectors used are listed in Table II. In all experiments the carrier gasses were delivered from their storage vessels through diffusion-resistant stainless-steel diaphragm pressure regulators and purified by passage over palladium catalyst at 300° and through a column of 13X molecular sieve at room temperature.

TABLE I

PROPERTIES OF HALOCARBONS EXAMINED

Values in parentheses are standard deviations.

Substance	Concentration at zero time (ppb)		Regression data			K_1 $(ml \cdot mole^{-1} \cdot sec^{-1} \cdot 10^7)$
	Released	Calculated	Area at zero time (nC)	Slope	Correlation coefficient (min^{-1})	
CF_3CFCl_2	20.58	—	14.14	0.0037 (0.0001)	1.000	0.032
CF_2BrCl	0.824	0.863 (0.0036)	9.40	—	—	1.18
$CFCl_3$	1.330	1.396 (0.0031)	15.57	0.0035 (0.0001)	0.997	1.26
$CF_2ClCFCl_2$	2.272	—	3.68	0.0036 (0.0001)	0.999	0.076
$CHCl_3$	31.76	—	32.74	0.0037 (0.0001)	0.997	0.045
CH_3CCl_3	2.741	2.52 (0.024)	11.80	(0.0036) (0.0002)	0.999	0.24
CCl_4	1.409	1.311 (0.0014)	23.06	0.0036 (0.0001)	0.998	2.60

TABLE II

CHARACTERISTICS OF DETECTORS USED

Detector No.	Chamber dimensions (cm)			Source	D.c. ion current (nA)
	Length	Diameter	Anode diameter		
1	1.5	1.25	0.3	^{63}Ni	12
2	1.25	1.25	0.1	^{63}Ni	10.5
3	5	0.5	0.03	^3H	42

Preparation of standard dilution

A sealed room $7.14 \cdot 10^7$ cm^3 in volume was used as an exponential dilution chamber. The room was constructed with polyethylene-lined plaster-board walls within a disused barn. The barn itself was sited in open country 1 mile from the nearest house or public road and in a rural region of South West England close to the open Atlantic. At this site, whenever a general westerly air stream from the ocean persisted the background concentration of detectable substances (halocarbons) was steady within the limits of precision of measurement, less than 0.5%, for example, for fluorocarbon 11 (F11).

Standard dilutions were made by introducing into this room a sealed glass tube containing a solution in *n*-hexane of the halocarbons to be standardized.The tube was broken on a metal sheet placed in front of a fan capable of circulating room air in 20 sec. After allowing 2 min for mixing, samples were taken at regular intervals and both stored in stainless-steel vessels at 2 atm pressure and analysed directly. The room was ventilated by blowing in air from upwind of the barn at the rate in range 10^5-10^7 cm$^3 \cdot min^{-1}$.

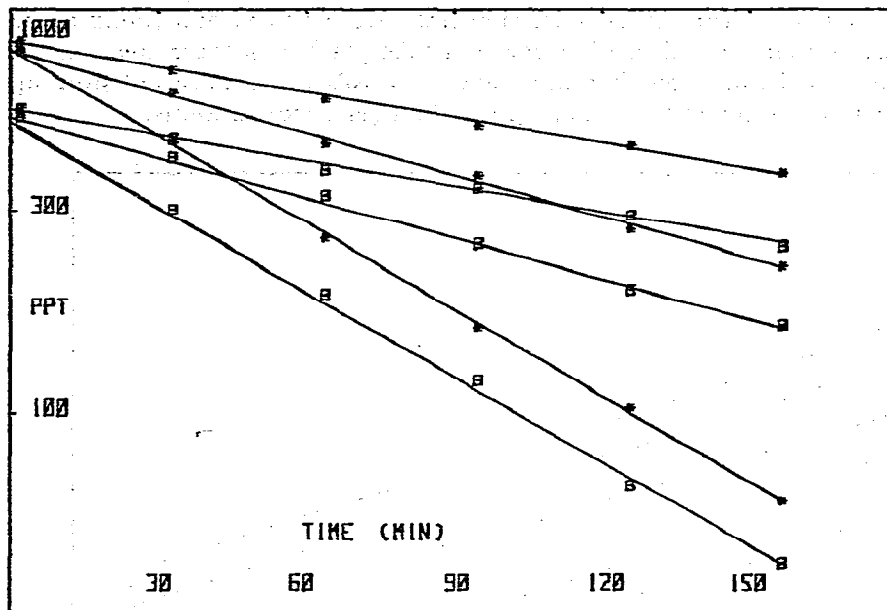Fig. 4 shows the decay of F11 and of bromochlorodifluoromethane (BCF)

Fig. 4. Decay by ventilation of CF_2BrCl and of CCl_3F simultaneously released in a test chamber $7.14 \cdot 10^7$ cm^3 in volume. Concentrations expected at zero time; CF_2BrCl 0.824 and CCl_3F 1.330 ppb. Three separate releases of the same amount of the two test substances but at different ventilation rates are shown. The zero-time intercept is seen to be independent of the ventilation rate.

in the chamber. From the regression line the precision of the measurement is available, together with the concentration at zero time. This can be compared with a concentration expected from the known volume of the room and the amount of halo-carbon introduced. In this method, which is a large-scale version of the well known exponential dilution procedure, it is unimportant if wall absorption or indeed any other loss process takes place in addition to loss by forced ventilation. The loss rates sum linearly so that the regression lines will always extrapolate to the same zero intercept; this is illustrated in the figure for three runs with the mixture of the two materials.

If adsorption or desorption effects are suspected, they can be confirmed or eliminated by comparing the slope of the test material with that of some inert substance, for example, SF_6, introduced simultaneously into the chamber. Its special value is that it makes possible a vast range of dilutions in a single error-free step. The initial mixture is typically a 0.3% solution of halocarbons, which can be prepared gravimetrically and accurately. The initial concentration after dilution in the chamber is close to 1 ppb (10^9) by volume and dilutes in a typical experiment to a few hundred parts per trillion (10^{12}) by volume.

Substances such as the fluorochlorocarbons have a background concentration in the air. With these the increment added to the test chamber is observed as the increase above this background and its subsequent decline towards it. In all experiments the background is observed before, during and after the test.

A simultaneous dilution experiment using all of the halocarbons listed in Table

I is illustrated in Fig. 5. The set of regression lines are expected and found to be parallel, suggesting that wall adsorption does not take place with these compounds. The large volume of the dilution chamber makes it possible to collect and store up to 100 l of air without significantly changing the chamber concentrations.
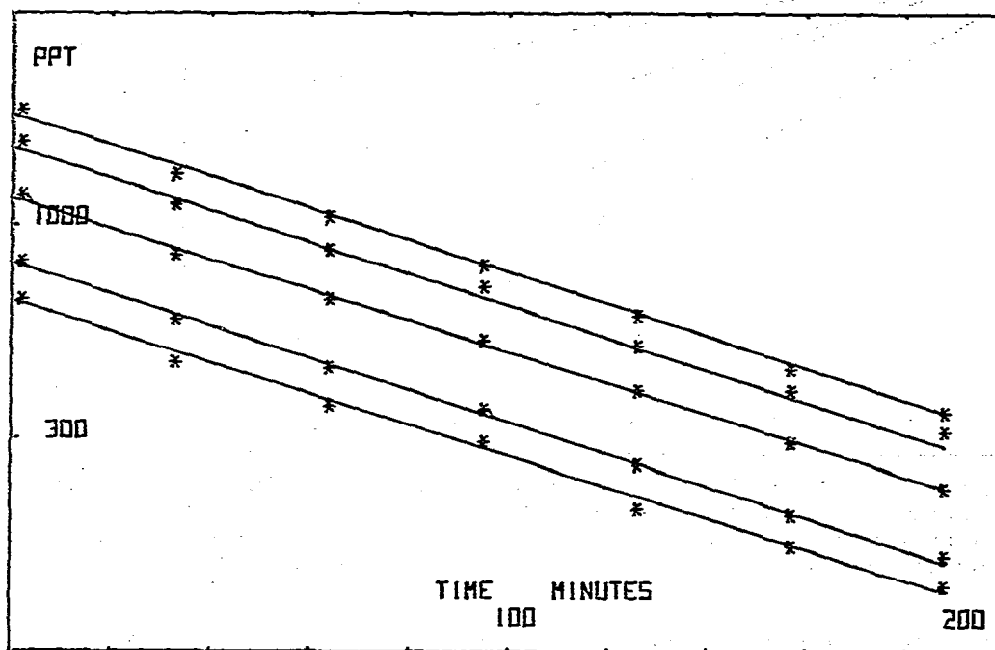

Fig. 5. Decay by ventilation of the aerial concentrations of $CHCl_3$, CCl_4, CCl_3F, CH_3CCl_3 and $CFCl_2CF_3$ after the release into the exponential dilution chamber of a solution containing a mixture of them. The lines corresponding to the list of substances above are in order downwards. The results of this experiment were used to calculate the rate constants listed in Table I.

Methods of measuring ionization efficiency

The possibility of using an ECD as a gas-phase coulometer has been described[15]. Briefly, with strongly electron-absorbing substances a substantial proportion becomes ionized and destroyed on passing through the detector. If two identical detectors are connected in series, it should in principle be possible to determine the portion ionized in either of them and hence the signal corresponding to complete ionization. The time integral of the number of electrons captured during a chromatogram peak is then equivalent, via Faraday's laws, to the number of molecules ionized.

The use of a second identical detector to confirm the proportion ionized in the first is not easy to apply in practice and two alternative approaches are to be preferred and have been used in this work. The first of these, which can be used with any chromatograph operating in the fixed-frequency mode, is as follows. A series of equal sample loads of test material are chromatographed at different carrier gas flow-rates in the range 0.2–2 ml·sec^{-1}. It is preferable to keep the column flow constant and introduce the extra flow of carrier at a junction between the column and

the detector. The reciprocal of the peak area from each of these experiments is then plotted against the carrier gas flow-rate.

Under perfect conditions with a clean carrier gas, the plot of the reciprocal of peak areas against carrier gas flow-rate is linear, as illustrated in Fig. 6. The intercept on the ordinate gives the area corresponding to complete ionization. In practice, ion recombination in the detector raises the whole line to a parallel position above the ideal state. This means that the intercept on the ordinate now corresponds to less than 100% ionization. As we saw earlier, the departure from 100% ionization is about 10% with argon-based carrier gases and 30% with nitrogen.
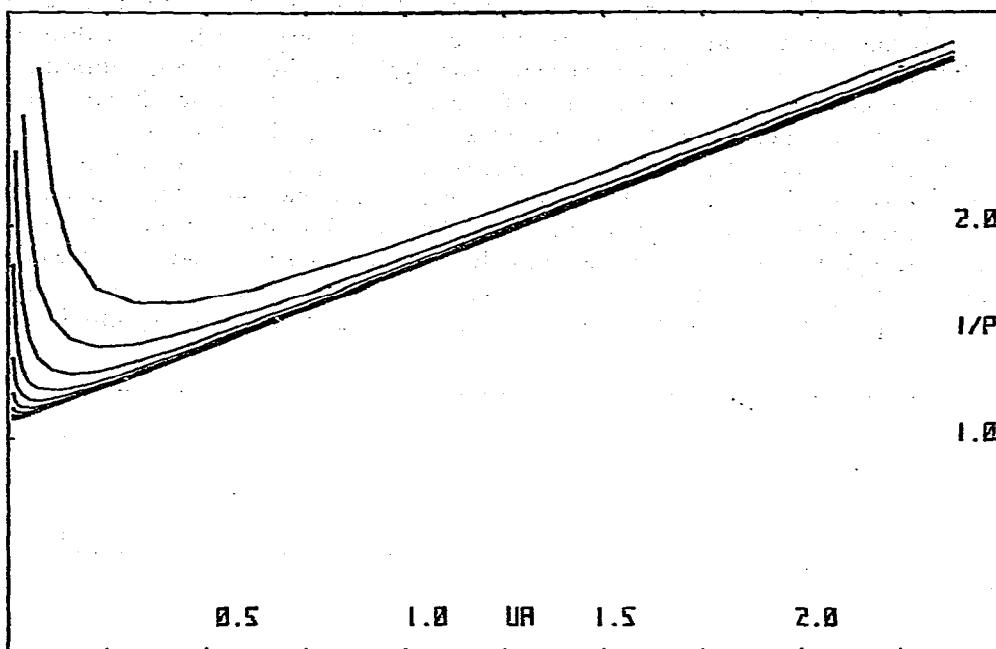

Fig. 6. Illustration from the model of an experimental approach to the measurement of the ionization efficiency of a single detector. The reciprocal of the peak area ($1/P$) in coulombs^{-1} of a constant concentration of test substance is measured over a range of flow-rates. When the loss of electrons by reaction with contaminants (K_4) is low the plot of reciprocal areas versus flow-rate is linear and the intercept at zero flow corresponds to complete ionization. The ionization efficiency at an operating flow-rate can then be read from the line.

The second method uses a detector specifically made to ionize almost all of the input of molecules[12]. The efficiency of this detector and the absence of electron-capturing reaction products has been demonstrated for the test compounds by connecting a second ECD at the output. With strong absorbers (F11 and CCl_4), the signal of the second detector is less than 1% of that of the first.

The effects of turbulence in the gas flow and of a non-uniform ionization along the length of this detector have been examined both experimentally and by modelling. Almost complete ionization readily takes place and is insensitive to moderate changes in the operating conditions.

Experiment and theory suggest that the signal represented by the change of electron current in this detector is directly related to the loss of electrons by their reaction with the sample and with contaminants and also by electron–positive ion recombination. It follows that the long coulometric detector will provide a signal where the electron loss closely approximates the sample molecules introduced. The loss of signal by the competitive reaction of recombination is the same as that for the simple ECD, namely 3–10% in argon-based carrier gas and 30% in nitrogen.

Fixed-current, variable-frequency mode of operation

The convenience to the user of this method, with its very wide dynamic range, makes it popular for many semi-quantitative ECD analyses. Unfortunately, with compounds that strongly attach electrons the response is very non-linear with concentration and in a manner which, for accurate analysis, requires separate calibration for each compound and for each condition of operation. Fig. 7 illustrates the variation of response of this method with the magnitude of the signal for a weakly ($K_1 = 10^{-14}$) and for a strongly ($K_1 = 1.2 \cdot 10^7$) electron-attaching test substance. The ordinate of the diagram is $1/K_1$ (dF/dB) where F and B are the signal frequency and the rate of input of test substance, respectively. The two families of lines and curves illustrate the effect of different carrier gas flow-rates, and show that with weakly electron-absorbing compounds an excellent linear dynamic range is available with this method. With strongly electron-attaching compounds linearity of response is ap-
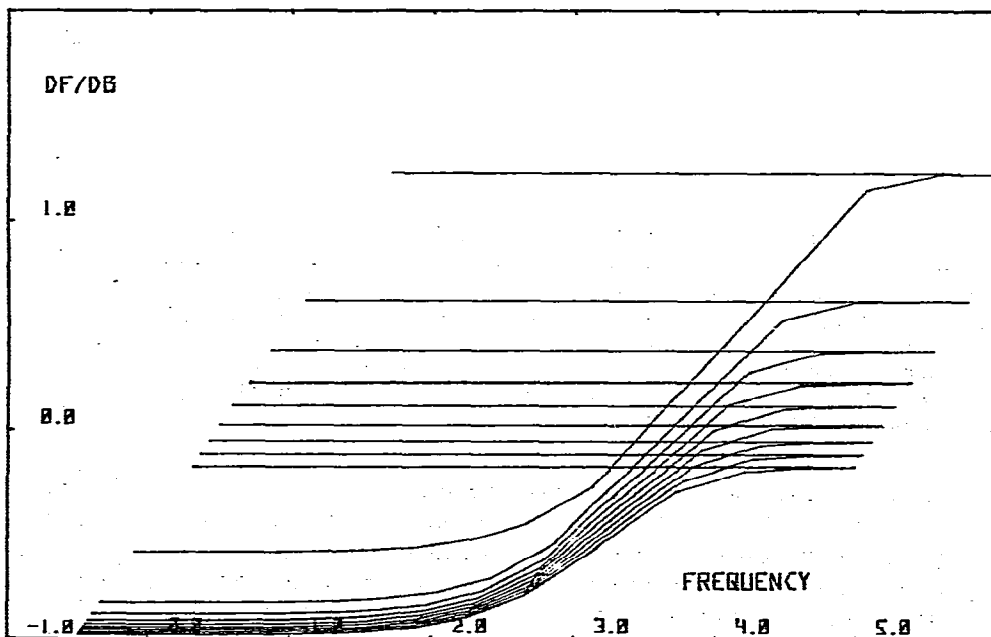

Fig. 7. Variation of the response of an ECD in the constant-current mode of operation with signal frequency for CCl_3F ($K_1 = 1.2 \cdot 10^{-7}$) and for a weakly electron-attaching substance ($K_1 = 10^{-14}$). The ordinate is $1/K_1$ ($= dF/dB$) and the abscissa the signal frequency (Hz) expressed logarithmically to base 10.

proached only at high flow-rates. For very small signals, up to a frequency of ca. 1 kHz, there is a limited fairly linear range of response to increasing sample size. Over this frequency range it is possible to calculate the concentration entering the detector provided that the operating conditions are known. These include the d.c. saturation current of the detector, the carrier gas flow-rate and the recombination and column bleed rates. Where the response changes rapidly with sample concentra- tion, above the frequency of 1 kHz, little can be done by simple means to achieve accurate analysis. It is possible to process the signal numerically so as continuously to correct the non-linearity. This can be done by applying eqns. 6 and 7 as a micro- processor sub-routine. It does require, however, the input at regular intervals of up- to-date information about the operating conditions of the detector and chromato- graph.

When using the constant-current method, it is helpful to employ argon con- taining 1% of hydrogen as the carrier gas. The electron drift velocity in this gas is nearly as fast as that in argon–methane, but it has the additional advantage that the catalytic scavenging of almost all impurities is very easily arranged. This is done by including before the column a 5-cm length of glass or stainless-steel tubing packed with 13X molecular sieve that has been coated with palladium. The tube is main- tained at 300° and is able to remove almost all commonly occurring contaminants, including oxygen, oxides of nitrogen and halocarbon solvent vapours. It lowers the minimum operating frequency and so extends the range of linear operation.

RESULTS AND DISCUSSION

The exponential dilution method was used to calibrate the chromatograph and to compare the concentrations predicted by coulometry with those released in ex- periments. It also served to check the linearity of the ECD over the range of con- centrations from 10^{-9} to 10^{-10} parts by volume, which is commonly encountered in atmospheric analyses. The results were also used to determine the experimental value of K_1, the rate constant of the forward reaction between electrons and test substances. The test substances and the above quantities are summarized in Table I.

The results confirm the validity of the coulometric calculations described earlier and suggest that with CCl_3F, for example, the error is less than 5%.

Under the experimental conditions used there was no sign of multiple ioniza- tion, but it will be necessary to prove coulometry with the ECD through the use of a wide range of conditions and detectors and with many different test substances.

In the course of the measurement of the atmospheric concentration of halo- carbons during the past 7 years, the detectors listed in Table II have been used. The concentrations calculated by coulometry for the same air sample were indistinguish- able. At least for these detectors and with some low-molecular-weight halocarbons the method is both consistent and accurate.

The multiple exponential dilution illustrated in Fig. 5 provided an opportunity to correlate the linearity of the response of the ECD with five substances simul- taneously. Over the 4-fold range of concentrations examined, the slopes of the lines did not differ by more than 4% and the multiple correlation coefficient of the whole test was 1.000.

Table I also lists the calculated values of the rate constants derived from the

experimental observations. It is recognised that the constant used here is the phenomenological forward rate constant and that the measurements are made under conditions that do not distinguish the effects of a back reaction through the dissociation of the negative ion or the production of electron-capturing reaction products. It is therefore interesting that these experimental values agree closely with those reported[16,17] for CCl_3F and CCl_4 using the electron swarm method.

Most experiments were made with the detector at 150° but, in order to confirm comparisons with earlier measurements, calibrations were made at detector temperatures from 50°-350°. The ionization efficiencies observed with a carrier gas flowrate of 0.7 ml·sec^{-1} and detector 1 are given in Table III.

TABLE III

IONIZATION EFFICIENCIES (%) OBSERVED WITH DETECTOR 1 AND A CARRIER GAS (ARGON WITH 1% HYDROGEN) FLOW-RATE OF 0.7 ml·sec^{-1}

Substance	Temperature (°C)						
	50	100	150	200	250	300	350
CF_3CFCl_2	2.1	2.7	3.4	4.1	4.7	5.5	6.3
CF_2ClBr	76	65	54	49	40	38	37
$CFCl_3$	77	65	55	45	44	39	39
$CF_2ClCFCl_2$	6.2	7.1	8.0	9.3	10.5	11.5	12.6
$CHCl_3$	3.0	4.3	5.1	5.8	6.4	6.3	6.4
CH_3CCl_3	11.8	19.1	21.3	22.3	25.3	26.1	27.6
CCl_4	90	85	81	77	75	62	55

It should be noted that the small change in ionization efficiency with temperature observed obscures a larger temperature coefficient of the rate constants. With 50% ionization or greater, the ionization efficiency is not very sensitive to changes in rate constant.

Accurate analysis applied to an environmental problem

Observations of the halocarbon content of the atmosphere began in 1970 and rapidly developed into a full-time investigation involving up to 3000 measurements yearly at fixed monitoring sites and also aboard ships and aircraft travelling between the hemispheres and into the stratosphere.

At the beginning of this long series, the chromatogram peak areas were converted into approximate concentrations by the use of the coulometric calculations described here and previously[12]. At that time this procedure was intended to be a temporary measure which would be discarded in favour of calibration with accurate standards when these became available. As we have seen, few standards were made and these often disagreed by factors as large as 2, so consequently there was little confidence in their accuracy.

At the same time it was noticed that in the Southern Hemisphere where the aerial concentrations of the halocarbons were low and changed only slowly. EC chromatography gave consistent analyses with peak areas varying within a range of 3% over a period of months. Over a period of a year or more an upward drift with time was noticed but this was at a rate close to that expected from the known releases

of the compounds into the atmosphere. Fig. 8 illustrates some of these observations taken aboard ship and at fixed sites in Southern Africa and Australia and also at a permanent monitoring site in Western Ireland. Halocarbons are released into the air almost entirely from North America and Western Europe. It is not surprising, therefore, that the observations from Western Ireland have a large scatter. Parcels of clean air from Polar or Atlantic regions alternate with halocarbon-loaded air from Europe or North America at this site. No such variability is seen with observations from the Southern Hemisphere.
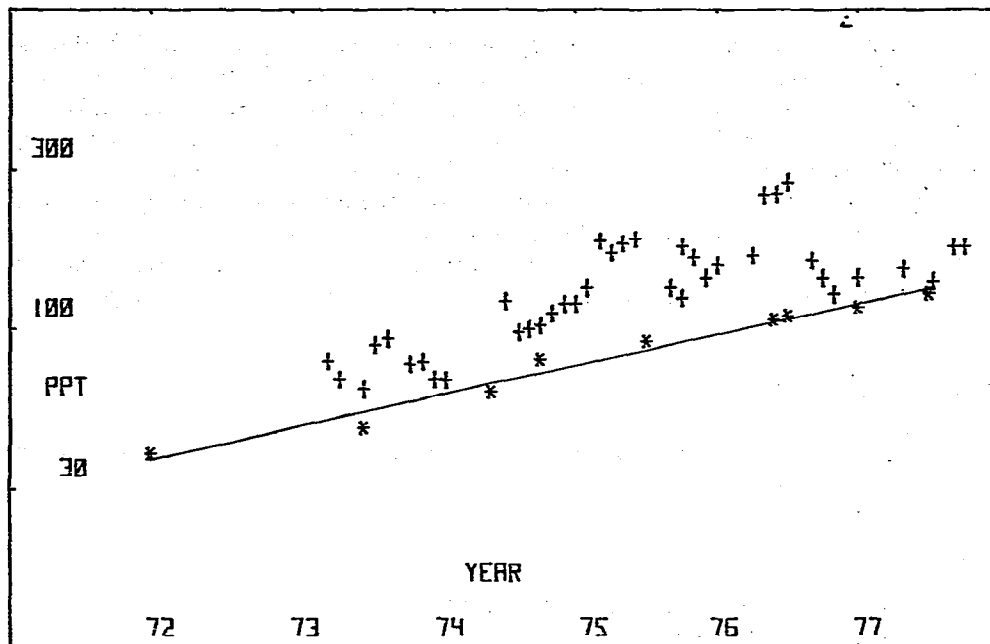

Fig. 8. Atmospheric concentration of CCl_3F in the Southern (*) and Northern Hemispheres (+) during the past 5 years. Each point is the mean of 30 or more observations over a period of a week in the Southern Hemisphere or a month in the Northern Hemisphere. All concentrations have been calculated using the detector as its own internal standard.

To some extent, the atmosphere itself constitutes a large-scale dilution chamber. The total amount of chlorofluorocarbons released was available from the chemical industry and the accuracy of their estimates was within 20%. The chemical fate of these compounds, although uncertain, was expected to involve slow reactions at rates certainly not exceeding 10% a year. Hence a very approximate estimate of the total global burdens could be compared with releases. This was done for those up to 1971 and found to agree with the observations remarkably well[5]. This fact, together with the consistency of the observations over the years, has given confidence that, at least for the volatile halocarbons of the air, the ECD is a reliable analytical device. We could not be sure that it was absolutely accurate but we were content at these early stages to accumulate information that could be revised whenever accurate standards became available.

In this long investigation, which is still continuing, many different detectors have been used, some with nickel and others with tritium radioactive sources. The d.c. ion currents have varied from 5 to 40 nA and very different detector geometries have been used. Whatever the detector, the chromatogram peak areas indicated the same aerial concentrations when they were corrected by applying the carrier gas flow-rate, ion current, recombination and bleed rates according to the procedures described here.

These experiences, together with those now available from the exponential dilution chamber, confirm that absolute analysis by the ECD can be accurate to within 5%.

This new confidence in the accuracy of analysis has helped to justify the establishment of a global network of monitoring stations[18] specifically for halocarbon measurements. Within a few years it may be possible to accumulate enough information from which the global distribution of the compounds can be calculated. Only then can we determine the site and magnitude of their atmospheric sinks.

In other analytical uses, such as pesticide residue analysis, the preparation of accurate standards does not seem to have been so difficult. Even so, some benefits can be derived from the use of the ECD as a rational device. Perhaps rate constants for electron reactions or coulometry will eventually replace the arbitrary and primitive use of the response factor.

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