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Electron Absorption Detectors and Technique for Use in Quantitative and Qualitative Analysis by Gas Chromatography

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▶ The electron absorption detector is by far the most sensitive detection device available for use in gas chromatography; furthermore, its selectivity permits the realization of extreme sensitivities in the face of a high level of extraneous material. These desirable properties have encouraged its widespread use in such otherwise intractable problems as pesticide trace analysis. It is not commonly realized, however, that the simpler and frequently used versions of this device are readily capable of generating erroneous and even totally false responses. This paper describes the basis of operation of electron absorption detectors and the nature and cause of the erroneous and anomalous responses it may generate. An alternative method of analysis by electron absorption is the pulse sampling technique; this retains the sensitivity and selectivity of the simple low potential ion chamber method, but is substantially free of errors and anomalous responses. The basis of this improved method is described and an account is given of the technique for its use in quantitative and qualitative analysis.

DETECTION OF components emerging in the effluent stream of a gas chromatography column by electron absorption was first reported in 1958 (*8*). At that time there was a need for a simple sensitive detector which would extend the range of gas chromatographic measurement beyond that possible with the relatively insensitive thermal conductivity and gas density balance detectors. Several methods were tried, based on the fact that the conductivity of gases in an ionization chamber is exquisitely sensitive to small changes in gas composition. When the chamber was filled with nitrogen and ionized by radiation from an internal radioactive source, the conductivity at low applied potentials was observed to change greatly when minute traces of other compounds were present in the vapor phase. Although the method was undoubtedly highly sensitive, the response to vapor concentration was very nonlinear and the response factors to different compounds varied greatly and in an unpredictable manner. For quantitative measurement the electron absorption method was soon displaced by more stable ionization processes such as those used in the argon and flame ionization detectors. The possibilty of electron absorption in the qualitative analysis of unknown components emerging in a gas chromatography effluent was nevertheless a potential application of this highly selective detection method. A preliminary study of the application of the method for this purpose was reported in 1960 (*11*). At that time also, conventional methods of gas chromatographic analysis could not be applied where a minute trace of a wanted component was present in a great excess of extraneous material moving on the column with a similar retention time. In one particular application—namely, the analysis of pesticide traces in materials of biological origin—the need was so great that in spite of its many disadvantages the electron absorption method using a simple ion chamber was pressed into use (*2*). The success of this application was partly attributable to the sensitivity and selectivity of the electron absorption method but mostly due to the painstaking care taken by Goodwin and his colleagues to ensure that some of the anomalous responses of the simple electron absorption detector were avoided. The importance of pesticide trace analysis and the fact that at low levels it is almost impossible to achieve analysis by any other method has led to its widespread use and commercial exploitation. The pace of these developments and the deceptive simplicity of a detector which is no more than a simple ion chamber operated at a low applied potential has given rise to a feeling of confidence in the method which is false and unjustified by the necessary experimental evidence.

The extraordinary sensitivity of the electron absorption detector which enables the analysis of even picagram samples is in itself a hazard to accurate measurement since the fate of such small samples in a chromatographic system is far from certain. In addition the simple, direct current, ion chamber form of electron absorption detector is hardly suitable for quantitative analysis. Small changes in operating conditions can cause its response to vapor concentration to be profoundly nonlinear. Also its capacity to function simultaneously in several different modes of detection renders its use even in qualitative analysis of doubtful

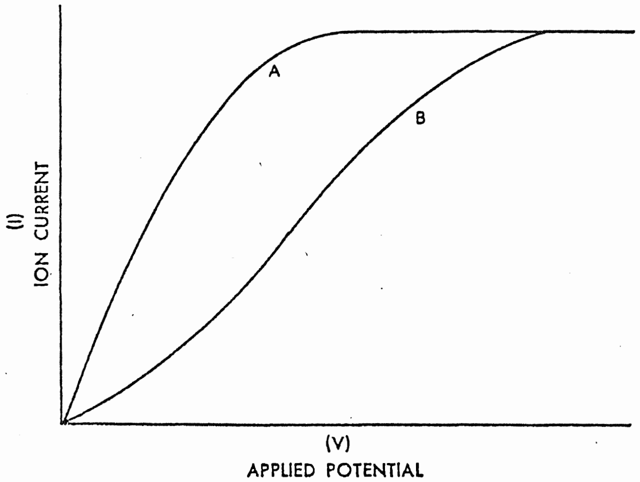

Figure 1. Relationship between current and applied potential with a simple ion chamber when filled with pure nitrogen, *A*, and with nitrogen containing a trace of a strongly electron absorbing vapor, *B*

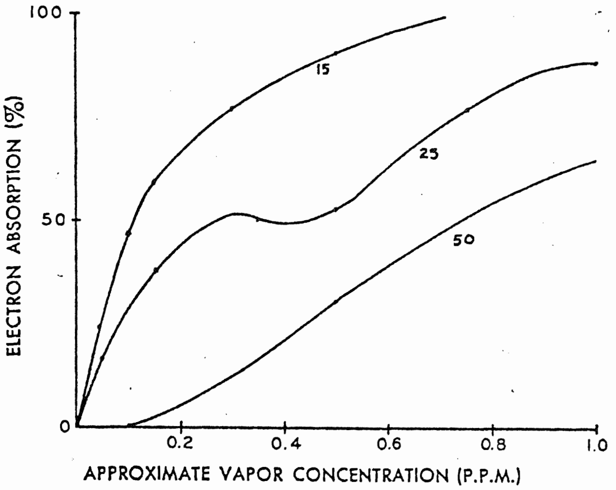

Figure 2. Response of a plane parallel geometry electron absorption detector, of the type shown in Figure 5, with varying vapor concentration

Carrier gas, nitrogen; test vapor, chloroform. The parameter is the potential applied to the detector in volts

reliability. No other detector in use in gas chromatography is so prone to erroneous and even totally false responses.

This communication describes the physical basis of electron absorption measurement; it lists and explains, where possible, the many anomalous responses which so far have been observed with the simple direct current detector. An account is given of the basis and operation of the pulse sampling method of electron absorption analysis (*11*, *14*, *15*) by which these false responses can be avoided or reduced. The description of the pulse sampling method is limited, for the detailed theory of its operation is still under investigation and forms the subject of a future communication. The practical performance is however, sufficiently established and its advantages insufficiently recognized to justify its discussion in this paper. The technique of quantitative and qualitative analysis by electron absorption is also discussed.

PHYSICAL BASIS OF ELECTRON ABSORPTION MEASUREMENTS

The free electron is a fundamental particle not only in the discipline of physics, but also in that of chemistry; it may be regarded, for example, as the simplest of free radicals or as an unattached valence bond. Because of this duality of function the process of electron absorption is analogous physically to light absorption where a flux of electrons, de Broglie wavelength between 70 and 7 A., are absorbed specifically by certain molecules much in the same way as are photons. Alternatively, it is possible to consider the reaction between a dilute solution of free electrons and reactive molecules both suspended in an inert gas. Whichever of these models is considered the basic reaction of electron absorption are:

$$\bar{e} + AB \rightarrow \overline{AB}$$

$$\bar{e} + AB \rightarrow A^{\cdot} + B^{-}$$

In the first reaction where a molecular negative ion is formed, the energy of electron capture (the electron affinity of the molecule) is liberated either as radiation or shared with other molecules on subsequent collisions. With this type of reaction the cross section for electron absorption decreases with an increase in temperature or electron energy; the effect of temperature is large and may exceed tenfold over the range of temperatures commonly used in gas chromatography. In the second class of reaction the molecule dissociates after electron absorption to give a free radical and an atomic or molecular negative ion. In this reaction the energy required to dissociate the molecule is frequently greater than that released by the formation of the negative ion; an increase in temperature or of electron energy may increase the probability of electron absorption. Resonance processes are also observed where a large increase in absorption cross section occurs over a sharply defined range of electron energies. The general phenomenon of electron absorption can be crudely observed in a simple ion chamber traversed by a flux of ionizing radiation such as that from a radioactive source. The chamber is connected to a source of low potential and to some means of measuring current flow. A stream of inert gas which does not itself absorb electrons is passed through the chamber; nitrogen, hydrogen and the noble gases are inert in this sense. The potential is adjusted to a value just sufficient to collect all of the electrons liberated from the gas by the ionizing radiation; if now an electron absorbing vapor is introduced into the gas stream the flow of ion current is observed to decrease. The decrease in current is due to the fact that the negative molecular ions formed by electron absorption are more easily recombined with the positive ions in the chamber than are free electrons. Also, because the mobility of the negative ions is much less than that of the free electrons they are collected less rapidly by the applied field and have more time to encounter and recombine with positive ions. If the potential is sufficiently increased, a point is reached where the introduction of absorbing vapor no longer causes a decrease in current; at this high potential the free electrons are so rapidly removed from the chamber after their production that there is little opportunity for them to encounter an absorbing molecule; and in addition the few negative molecular ions which are formed may also be carried to the anode. Figure 1 shows the relationship between current flow and applied potential when the chamber is filled with a pure inert gas such as nitrogen and also when a trace of strongly absorbing vapor is present. Under ideal conditions, which are seldom realized, the relationship between vapor concentration and the observed decrease in current is similar to that of Beer's Law for light absorption. The number of electrons reaching the anode per second, N, in the presence of a vapor concentration, c, is:

$$N = N_0 \exp^{-KcX}$$

where N_0 is the number of electrons reaching the anode per second in the

Table I. False Responses of D. C. Ion Chamber Electron Absorption Detector When Used with Various Carrier Gases and Test Samples

Unwanted mode of detection	Carrier gas	Extent and nature of error or false response with test samples		
		[a]	[b]	[c]
Cross section	Helium Hydrogen	Very slight reduction	Signal reduced	Negative response
	Nitrogen Argon Argon–methane	None	Signal reduced	Slight negative response
Metastable atom processes ("argon" detection)	Helium Argon	Slight reduction	Signal greatly reduced	Large negative response
	Nitrogen Argon–methane	None	None	None
Electron mobility effects	Argon Helium	Slight reduction	Signal increased	Large false response
	Nitrogen	None	Signal increased	False response
	Argon–methane	None	None	None

[a] Low concentration of a stong electron absorber. [b] High concentration of a weakly absorbing compound or a low concentration of strong absorber mixed with a high concentration of nonabsorber. [c] High concentration of a nonabsorber.

pure carrier gas, K is the electron absorption coefficient of the vapor, and X is a proportionality constant.

Most of the electron absorption detectors presently in use in gas chromatography employ the simple scheme just described and observe the presence of electron absorbing vapor in terms of the decrease in current flow within the chamber. In the classical physical studies of electron absorption in the gas phase—an outstanding review of these is given by Loeb (*6*)—it was long ago realized that such a naive method was totally unsuited to accurate measurement. The sources of error are complex but can be considered individually as follows.

Other Modes of Detection. A simple ion chamber operated at low potentials does not function uniquely as an electron absorption detector, but it can also function in additional detection modes: as an ionization cross section detector (*9, 12*); as a detector employing metastable atom ionization processes (*8*); and as an electron mobility detector (*9*). The extent to which these other detection processes predominate depends upon the composition of the gas in the chamber, the intensity of the radiation source, the applied potential, and the geometry of the detector. Table I lists the type of error or false result given by these other modes of detection under three practical conditions and with various carrier gases. The practical conditions considered are these: first, where a pure strongly absorbing substance is present at high dilution, the usual condition for detector calibration; second, where there is a high concentration of a weak absorber, or a low concentration of a strong absorber accompanied by a high concentration of a nonelectron absorbing component—for example, a vegetable lipid component moving with the same retention time as a trace of electron absorbing pesticide; and third, a high concentration of a nonabsorbing compound. The table indicates both the danger of assuming that the calibration conditions for a single pure component are applicable to practical analyses and the occurrence in complex mixtures of not only inaccurate but even totally false results.

Errors Inherent in D. C. Ion Chamber Measurements. The current flow in an ion chamber where the applied potential is low and the ion density is high is strongly affected by the development of space charges. Thus in a typical electron absorption detector filled with inert carrier gas, the positive ion concentration may be several thousand times greater than the free electron concentration. The existence of this positive ion excess is due simply to the fact that the free electrons are collected at the anode very soon after their liberation, whereas the positive ions with their low drift velocity move only slowly to the cathode and accumulate there as a space charge cloud. The cloud of positive ions near the cathode sets up a potential in opposition to that applied to the chamber and may hinder the collection of free electrons. The introduction of a polyatomic vapor into the chamber changes the electron mobility and as a result the extent of the space charge cloud and the observed current flow; in addition, the probability of electron absorption depends upon the time the electrons spend in the chamber and upon their energy. Together these effects can cause a variation with vapor concentration in the probability of electron absorption and in turn produce a nonlinear response of the detector to varying vapor concentration. Furthermore, where comparatively high applied potentials are used, the positive ion cloud is compressed near the cathode, and electron absorption in other regions of the chamber can give rise to a negative ion space charge near the anode, because the physical separation of the oppositely charged ion leaves little opportunity for their encounter and recombination. Figure 2 shows the response of an electron capture detector to varying concentrations of chloroform, a strong absorber, when the applied potential is at the various values indicated against each curve on the diagram. At only one applied potential does the response approximate the ideal Beer's Law type of response. As the potential is raised discontinuities appear in the response curves due presumably to the separation of the negative and positive ion clouds. These effects are more serious than the diagram would indicate, for the change in applied potential could be duplicated at a constant potential by a change in the concentration of some nonabsorbing component or by a change of temperature. It would appear that consistent results might be obtained at a low applied potential; this is illusory, however, because the use of low potentials brings other problems in its train which are equally serious and will shortly be

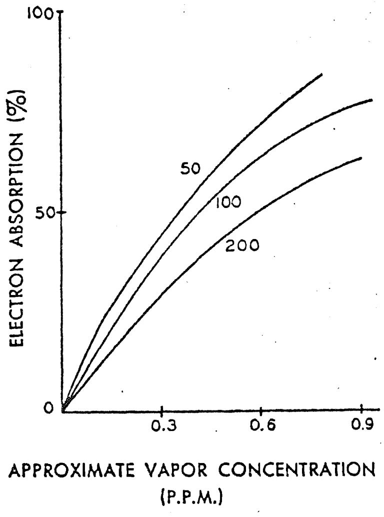

Figure 3. Response of an electron absorption detector with an asymmetric electrode configuration to varying vapor concentration

Carrier gas, nitrogen; test vapor, chloroform. Parameter is potential applied to the detector in volts

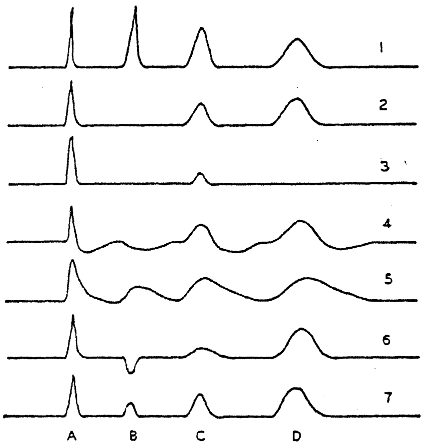

Figure 4. Anomalous responses which may occur with an electron absorption detector when it is operated as a d.c. ion chamber

Anomalies are illustrated in the form of a series of imaginary chromatograms:

1. Chromatogram which truly represents the quantities of the four components: *A* and *D* are peaks of electron absorbers, *B* is a larger amount of a nonabsorber; *C* is a mixture of absorbing and nonabsorbing compounds unresolved by the column
2. Response from a correctly operating electron absorption detector
3. Electron absorption detector exhibiting severe space charge effects. Note the disappearance of peak *D*
4. Detector with a contact potential enhancing the applied potential
5. Detector with a contact potential opposing the applied potential. Note the increased tailing and the false peak at *B*
6. Detector which is responding as an argon or as a cross-section detector in addition to its function by electron absorption. Note the reversed peak, *B* and the reduction of peak *C*
7. Detector which is responding as an electron mobility device as well as in its function by electron absorption. Note the false peak at *B*

discussed. Space charge problems are less serious when a detector with a highly asymmetric electrode configuration is used. Thus the response of a detector with a small or remote anode is relatively independent of applied potential since the field is weak in the vicinity of the cathode and the separation of positive and negative ions cannot easily occur. This is illustrated in Figure 3 in which is shown the response of a detector with a small coaxial anode remote from the cathode. There is, however, no essential difference between the operation of a symmetrical ion chamber at low applied potentials and that of an asymmetric detector at higher potentials; in both the field at the cathode is weak and such a condition is not consistent with accurate measurement.

Contact Potentials. The temporary absorption of a trace of an eluted component upon one of the electrode surfaces of the detector can in certain circumstances give rise to a contact potential which may either enhance or oppose the potential applied to the chamber. Such potentials are usually on the order of a few volts. The effects of contact potential errors on the response of electron absorption detectors are illustrated together with those of other anomalous effects in Figure 4. Where the contact potential opposes the applied potential the chromatogram peak has an erroneously large area and frequently shows severe tailing; where the potential enhances that applied to the detector there is a diminished response and the peak may show a drift below the base line at the tailing edge (*1*). As might be expected this effect is most pronounced with weak fields which otherwise would be the preferred conditions of operation. Where the contact potential opposes the applied potential there is always the possibility of a false response from a compound which generates the potential at the electrode surface but which does not absorb electrons. Contact potential effects can be reduced by the frequent cleaning of the detector but its onset is insidious and again inconsistent with accurate measurement.

Electron energy changes. In carrier gases such as the noble gases and to a lesser extent in nitrogen the electron energy even at moderate applied potentials is considerably above that of thermal equilibrium with the gas molecules, because the energy the electrons gain from the applied field is not easily lost during their elastic collisions with the gas molecules. The addition of a polyatomic vapor, however, reduces the electron energy by nonelastic collisions. Certain compounds especially those containing halogen atoms have cross sections for electron absorption which vary sharply with electron energy. The cross section for electron absorption of chlorobenzene, for instance, is observed to change over a twentyfold range when between 0 and 5% by volume of methane is added to an argon carrier stream. This process is a potent source of error when more than one component is present in the carrier stream presented to the detector.

There is no simple compromise by which all of these and possibly other sources of error can be avoided with the direct current method of electron absorption detection. There are however, alternative methods in which electron absorption is uniquely measured and other detection modes disregarded; these more sophisticated methods are also for the most part free from the anomalous effects of space charge limitation, contact potentials, and unpredictable changes in electron energy. In one of these the electrons and negative ions are separated by an alternating electrical field (*17*). The pulse sampling method has been described (*10*) and is well established; its freedom from the many drawbacks of the d.c. method have not, however, previously been discussed or explained. The discussion that follows is an attempt to correct this omission.

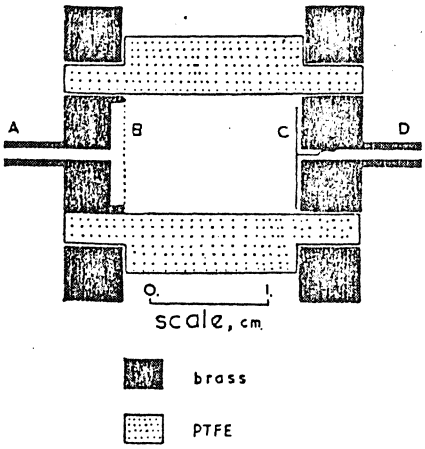

Figure 5. Detector for use with the pulse sampling technique

- *A* Inlet for carrier gas and anode
- *B.* Diffuser made of 100 mesh metal gauze
- *C.* Tritium source of ionizing radiation
- *D.* Gas outlet and cathode

The Pulse Sampling Technique. This method employs a simple plane parallel ionization chamber of the type illustrated in Figure 5. The ionization source consists of a sheet of stainless steel coated with a layer of titanium containing occluded tritium in sufficient quantity to provide an ion current of between 3 and 10 nanoamperes. The ion source is attached to the cathode and is 1 cm. distant from the chamber anode. At atmospheric pressure the low energy radiation from the tritium source is unable to penetrate a depth of carrier gas deeper than 2 mm. and the entire plasma of positive ions and electrons resides in a disk-shaped space extending 2 mm. from the cathode. A detector in this form cannot function as a cross section ionization detector since the presence of a vapor with a higher ionization cross section than that of the carrier gas will only modify the range of the radiation and not the total number of ions generated in unit time. The carrier gas used with this detector is argon containing a sufficient quantity of some nonelectron absorbing gas or vapor to reduce by nonelectric collisions the energy of the free electrons to that of thermal equilibrium with the carrier gas. The most suitable polyatomic gas for this purpose is methane at a concentration of between 5 and 10%, the exact concentration is not critical. Other gases and vapors such as CO_2, water vapor, and hydrogen can be used but methane appears to be the most convenient for this purpose. The presence of the quenching gas

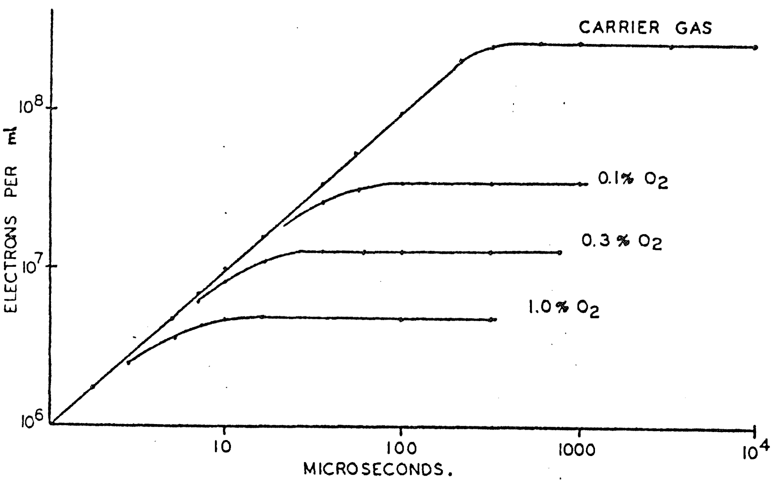

Figure 6. Growth of the electron concentration in plasma of the detector shown in Figure 5 immediately after total removal of electrons by a sampling pulse. Effect of various concentrations of oxygen in argon–methane carrier gas is also shown

serves not only to maintain the electron energy at a constant thermal level but also to remove the argon metastables as fast as they are formed by deactivating collisions. The detector cannot therefore function either as an argon detector, or as an electron mobility detector; the electron energy, and hence the cross section for absorption, cannot be changed by the presence of other gases or vapors, for it is already so low that no further reduction take place. Using such a detector and carrier gas, electron absorption could be observed with greater certainty in the d. c. mode of operation. However, the undesirable effects of space charge limitation and of contact potentials would be much greater than they would with nitrogen as a carrier gas, because in the argon–methane mixture the electron drift velocity in a field is higher than in any other gas and lower applied potentials would be needed to observe electron absorption. Furthermore, the shape of the detector in Figure 5 is conducive to the separation of the positive and negative ion space charges and a reasonable linear dynamic range would be critically dependent upon the applied potential.

Instead of a steady d.c. potential to collect the electrons, brief pulses of potential, at relatively infrequent intervals, may be used. A pulse of potential 50 volts in amplitude and 0.5 μsecond in duration applied to the anode is sufficient to collect all of the electrons present in the plasma adjacent to the cathode. The loss of electrons by recombination and diffusion to the detector surfaces is slow in the argon–methane mixture so that intervals as long as 100 microseconds can be permitted between sampling pulses without the loss of more than 5% of the electrons set free by the radiation source. Figure 6 shows the rate of increase of the electron concentration in the plasma immediately after the application of a pulse; the effect of adding various amounts of oxygen, a weak electron absorber, on the plasma electron concentration is also shown.

The pulse sampling procedure has conspicuous advantages. For most of the time no field is applied to the detector, and the free electrons are certainly in thermal equilibrium with the gas molecules; also the electrons do not drift out of the plasma so that negative ion formation occurs in the region where the positive ions are also present and where recombination can most efficiently take place. Too, the sampling pulse is so brief that no significant movement of the negative ions can occur; consequently, the accuracy of the measurements are not impaired by space charge effects or by the collection of negative ions at the anode. Also, a pulse amplitude of 30 volts is sufficient for the complete collection of the electrons. In practice an amplitude of 50 volts is used so that a contact potential of even 20 volts does not prevent the complete collection of the free electron. Indeed, with the pulse sampling method contact potential effects are rarely if ever encountered. Finally, the ultimate sensitivity of any method of analysis by electron absorption depends upon three principal factors: the cross section for absorption of the test molecular species, the electron concentration in the carrier gas, and the time allowed for encounter between absorbing molecules and electrons. With the pulse method alone the time for encounter can be extended to the point where the natural recombination between electrons and positive ions limits any further increase in sensitivity. With those compounds whose cross section for absorption increases greatly with small increases in electron energy, improved sensitivity may be possible in d.c. systems using pure argon as a carrier gas (*5*). A high price in reliability is paid for this improved sensitivity and with many other compound classes the sensitivity is less than when thermal electrons are used.

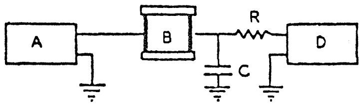

Figure 7. Circuit diagram for the pulse sampling method

- *A.* Pulse generator providing negative pulses
- *B.* Detector
- *D.* Electrometer
- *R.* 10 to 100 megohms
- *C.* 100 pF

Figure 7 shows the response of the detector to various concentrations of chloroform when operated with intervals between sampling pulses ranging from 5 to 200 μseconds; the carrier gas was argon with 5% of methane, and the pulse duration and amplitude were 0.5 μsecond and 50 volts, respectively. The sensitivity increases directly with the time interval during which the electrons are permitted to react with the vapor, and at any chosen interval the response is substantially linear with vapor concentration up to absorption of 50% of the electrons present in the chamber. Electron absorption detectors are for many purposes inconveniently sensitive and the ability to reduce the detector sensitivity by using short sampling periods is a further advantage of the pusle sampling method.

The electrical connections for the pulse sampling method are simple (Figure 8). The pulse generator is expected to provide a pulse which is approximately rectangular in shape, although one in the shape of a Gaussian distribution would not be unacceptable. The amplitude of the pulse should be 50 volts and the width at half height not less than 0.5 μsecond and not greater than 1.0 μsecond; a ±10% change in either pulse width or amplitude has little effect upon the performance of the system. It is convenient to be able to adjust the period between pulses over the range 5 to 200 μseconds. Where such a facility is not available, a fixed pulse period between 10 and 50 μseconds will suffice. The source impedance of the pulse generator should not be greater than 3000 ohms and preferably between 50 and 500 ohms. With a higher source impedance, the pulse is easily distorted and reduced in amplitude by the capacitance of the connecting cable, the detector, and its housing. The electron pulses driven across the detector are readily integrated to provide a steady d.c. current by an appropriate resistance and capacitance. This is frequently supplied by the inherent input resistance and capacitance of the electrometer. The electrometer required is in no way different from that with the d.c. electron absorption system.

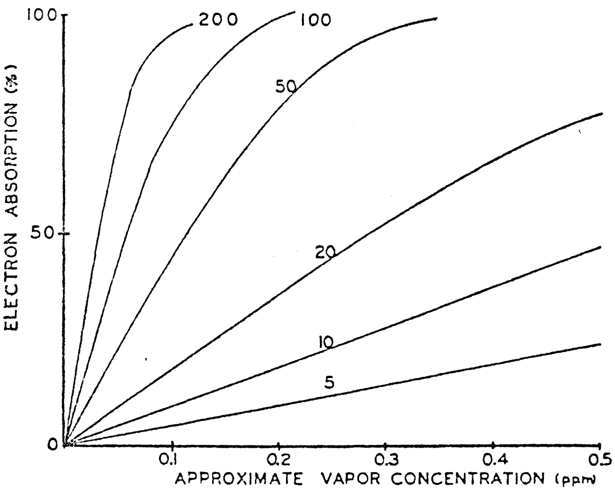

Figure 8. Response of the detector in Figure 5 to various concentrations of chloroform when operated by pulse sampling using argon with 5% of methane as the carrier gas

Period between pulses is the parameter in units μseconds

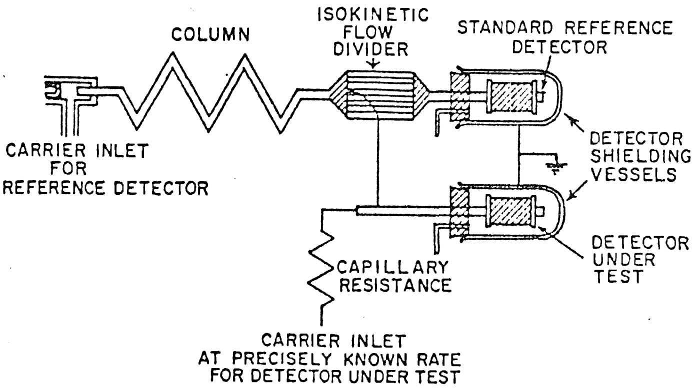

Figure 9. Apparatus assembly for electron absorption measurements and calibration of detectors

Calibration and Performance. The extraordinary sensitivity of electron absorption detectors makes the accurate estimate of their performance characteristics a formidable problem. In addition, for strongly absorbing compounds—e.g., carbon tetrachloride—the ionization efficiency with a typical detector approaches 100%, which implies that the response must be expressed in terms of rate of mass input rather than in concentration units; for weakly absorbing compounds the reverse is true. Calibration methods such as the logarithmic dilution procedure (*9*) which are accurate and reliable with less sensitive detectors cannot be used with vapor concentrations in the parts per billion range. The least trace of surface adsorption is sufficient to invalidate the measurements. Calibration by the injection of dilute liquid samples to a complete chromatograph is notoriously inaccurate with sensitive detectors, and in the case in which the smaller loads may be in the picagram region, it implies a naive trust in the present performance of gas chromatography measurements.

The results reported in this paper were obtained using the apparatus illustrated in Figure 9. The test substance, usually chloroform, was mixed with two internal standard substances, toluene and cyclooctatetraene, and diluted in a large excess of methyl acetate, which as a solvent has been found to be unusually free of electron absorbing contaminants. Known quantities of the mixture were applied to a 200-foot 0.03-inch diameter capillary column coated with a polyglycol stationary phase. The test samples were directly injected from a microsyringe into the column; the effluent from the column was divided by an isokinetic flow divider consisting of 20 1-foot lengths of 0.01-inch uncoated capillary tubes. The flow through 19 of these tubes was recombined and passed directly into a micro-cross section ionization detector (*12*), and the flow of the remaining single tube was diluted in a flow of argon-methane mixture of 105 ml. per minute and then passed to an electron absorption detector. The carrier gas for the column was helium containing 3% of methane. An accurate estimate of the quantity of sample leaving the column could be obtained from the peak area of the toluene appearing on the chromatogram from the cross-section detector. The peak area of the chloroform appearing on the chromatogram of the electron absorption detector was referred to that of the cyclooctatetraene whose quantity was maintained approximately constant. A third check was sometimes also possible from the cyclooctatetraene peak on the cross-section chromatogram. Using this procedure, consistent and reproducible calibrations were possible and were used to construct Figures 2 and 3. Losses by absorption especially with the smaller sample loads could have occurred, although the double internal standard procedure suggested that this was unlikely. Table II lists the performance characteristics of the electron absorption detector described in this paper. The detectivity quoted is an extrapolation based on the assumption that the response of the detector was linear with vapor concentration from the lowest observed value to the noise level of the detector.

Response to Different Substances. Simple saturated ethanoid and ethinoid hydrocarbons, ethers, esters, alcohols, amines and thioethers do not absorb electrons appreciably. There are certain elements and structures which, if present in any of the above compounds, confer electron absorption upon the molecule. By analogy with light absorption these can be divided into two principal classes, simple and conjugate electrophores. Simple electrophores are exemplified by the halogen elements, with increasing effectiveness from fluorine to iodine, and also by the nitro group. Multiple substitution with simple electrophores may increase the molecular absorption by an amount which is much greater than expected of a simple additive effect; thus the absorption of electrons by carbon tetrachloride is at least ten thousand times greater than that of methyl chloride. The absorption conferred by a simple electrophore is also sensitive to the position of its substitution in a molecule, thus 3-chloro-

Table II. Performance Characteristics of Detector in Figure 5 When Used in Pulse Sampling Method

Carrier gas	Argon with 5% methane
Flow rate	100 ml./min.
Detector volume	0.8 ml.
Radiation source	200 mc. of tritium
D.c. saturation current	8.0 nanoamp.
Pulse characteristics	Amplitude, 50 volts, Duration, 0.5 μsec. Period, 50 Microsec
Test substance	Chloroform
Noise level	1.0 picaamp. at bandwidth of 0 to 1 cycle/sec.
Apparent ionization efficiency	4.3×10^{-3}
Minimum detectable concentration by volume	2×10^{-11}
Minimum detectable mass input for the stated conditions	3.3×10^{-13} g./sec.
Linear dynamic range	4000

Neither the test substance chosen nor the stated conditions indicate the sensitivity limit of the method for the most strongly absorbing substances. The sensitivity to carbon tetrachloride, for example, may be under optimum conditions as much as 100 or more times greater.

1-propene absorbs several hundred times more strongly than 2-chloro-1-propene. Examples of conjugate electrophores are ester, aldehyde, keto, nitrile, phenyl, linked by a suitable bridge—i.e., their direct conjunction as in diacetyl or in methyl pyruvate, or a double bond, a triple bond, an aromatic ring or in certain alicyclic structures such as are found among the steroids. Many of the more complex hydrocarbons such as cyclooctatetraene azulene and most polycyclic aromatic hydrocarbons are electron absorbers as are some inorganic compounds, including carbon disulfide, ozone, the oxides of nitrogen and probably many others. The values of the relative absorption coefficients of different compound classes are published in the following papers; halogenated compounds (*10*), polycyclic aromatic hydrocarbons (*15*), steroids (*13*).

Technique for Quantitative Analysis. The analysis of very small quantities by gas chromatography may be rendered inaccurate by the loss of a component during its passage through the chromatographic process. Effects such as those of reversible and irreversible absorption on the stationary phase support and other surfaces of the apparatus become more severe as the sample size is reduced. At high temperature, a trace of oxygen in the carrier gas may completely destroy a minor component. These effects may be particularly important in analysis by electron absorption because its selectivity and sensitivity make possible trace analyses which could not otherwise have been attempted. Although there is no simple solution to this problem, there are some general principles in the analysis of very small quantities by gas chromatography which can be applied in analyses contemplating the use of an electron absorption detector.

The detector should be operated at the lowest sensitivity consistent with the analytical needs. Sensitivity can be reduced by using a short repetition period between pulses (for instance 5 μseconds) and also by diluting the column effluent in a flow of carrier gas before it enters the detector.

Adsorption losses are related to the total active surface area presented to the sample. This area can be reduced by using the least volume of column packing consistent with the resolution needed. The various techniques for preventing adsorption tailing could also be applied to prevent losses. Electron absorption detectors using the pulse sampling technique will not for example be adversely affected by the use of water-saturated carrier gas provided that some dilution with dry carrier gas is made at the column outlet.

The direct application of the sample to the column is preferrable to the use of a flash vaporizer remote from the column and connected to it by a length of metal tubing. Similarly the shortest possible connecting link between the end of the column and the detector should be used.

Whenever possible a dual detection method employing a reliable quantitative detector as well as the electron absorption detector should be used (Figure 9). Such a combination renders calibration, which is always necessary in electron absorption detection, easier and prevents the confusion of a large quantity of weakly absorbing contaminant with the sought after trace of strong absorber.

Many of the commonly used solvents contain traces of strong electron absorbing material which can readily be confused with the test substance. Some of these such as carbon tetrachloride (which is found in almost all commercial solvents) are easily recognized by their retention times. Others, including the phthalate esters, may appear as a complex series of absorbing components.

Technique for Qualitative Analysis. The cross section for electron absorption is a characteristic molecular property provided that the electron energy is specified. With the pulse sampling technique, the electron energy is thermal so that if the temperature of the detector is known the absorption cross section can be used for the characterization of a compound. It is not easy to provide absolute values of the molecular absorption cross sections; however, the cross sections relative to that of some standard reference substance can readily be determined. An apparatus assembly similar to that in Figure 9 is required. The column effluent is presented simultaneously to a detector whose response is substantially independent of molecular species such as a cross section detector and also to the electron absorption detector. The apparatus is calibrated by introducing to the column the test substance and also a small sample of a reference standard substance—e.g., chlorobenzene. The area of the chlorobenzene peak on the electron absorption chromatogram, assuming that it is chosen not to exceed the linear dynamic range of the detector, is divided by the peak area appearing on the quantitative detection channel; the same ratio is now determined for the peaks of the test substance. The second ratio divided by the first gives the electron absorption coefficient of the test substance relative to that of the standard substance. The relative absorption coefficient is directly related to the molecular cross section for electron absorption. Provided that the detector temperature is maintained constant, this measurement is independent of other changes in the chromatographic system. It must be emphasized that in this application the d.c. system, in which the electron energy is uncertain, cannot be applied. As yet it is not possible to measure the relative absorption coefficients with an accuracy better than ±17%; however observed electron absorption coefficients cover a range of 10^7 so that arithmetic precision is not a great handicap in the characterization of unknown electron absorbing substances. The technique will grow in values as information on this molecular property is accumulated. Some preliminary and less accurate values for various compounds are given in the following references (*10*, *13*, *15*).

DISCUSSION

Analysis by gas phase electron absorption, commenced as a doubtful detection device in gas chromatography, is approaching the stage of an analytical technique in its own right, using the gas chromatograph column to provide a pure sample for measurement. It has already made possible the direct determination of electron affinities, once almost impossible (*18*). Substances which absorb electrons strongly are remarkable in falling with few exceptions into two classes; those which are important intermediates in the biological process of oxidative metabolism; and those which are highly toxic particularly to this biological process. The cross section for the absorption of thermal electrons may therefore be a molecular property of direct importance in a number of biological problems. Classical physical studies, notably those of Shulz (*16*) and of Bortner, Hurst, and their colleagues (*3*), have shown that the cross section for electron absorption varies with the electron energy with a degree of resolution approaching that of the variation of light absorption with photon energy. By appropriate sophistication such as the use of low pressure systems and electron beams of variable energy, the more advanced technique of electron absorption spectrometry is within sight. Less ambitious, but no less important, is the extension of the method in gas chromatography to classes of nonabsorbing compounds by the preparation of electron-absorbing derivatives pioneered by Landowne and Lipsky (*4*).

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Gas Liquid Chromatography

Temperature Changes during Passage of a Solute through a Theoretical Plate

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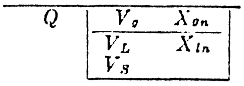
▶ This paper considers the change in temperature of a theoretical plate when a solute is absorbed and desorbed during its passage through it. An equation is derived that relates the temperature of the plate to the total flow of carrier gas. The effect of this temperature change on the column efficiency and peak symmetry is considered and by means of the derived equation conditions are predicted that will minimize or eliminate it. From the equation relating plate temperature to the total flow of carrier gas, theoretical curves are given which are substantiated by experiment.

During the passage of a solute through a theoretical plate adsorption and desorption of the solute in the liquid phase take place, accompanied by evolution and absorption of the heat of solution. This heat exchange between the solute-solvent system and its surroundings will result in a change in temperature of the contents of the theoretical plate. Ray (*7*) suggested that this temperature effect might form the basis of a detecting system and Klinkenberg considered it might affect peak symmetry (*6*). This phenomenon has been employed by Claxton as a detecting system for liquid solid chromatography (*1*). Recent work by Smith (*8*) has shown that under certain circumstances this temperature change can be particularly significant when large charges are placed on the column.

This paper describes a theoretical investigation of the temperature changes of the theoretical plate during the passage of a solute through it. An equation is given describing the change in temperature of the plate relative to its surroundings in terms of the various operating parameters. Two variables in the system are considered, the temperature and the total flow of gas through the plate. Experimental support to the theoretical equations is included and the significance of the heat effect on column performance and peak symmetry is discussed. Results are also considered with a view to modifying column design in order to reduce or eliminate the temperature changes, particularly with respect to preparative scale columns.

THEORY



Consider the *n*th theoretical plate of a chromatographic column and let the following designate its properties.

V_g = volume of gas in plate
V_L = volume of liquid in plate
V_S = volume of support in plate
S_S = specific heat of support in plate
S_L = specific heat of liquid phase in plate
ρ_S = density of support
ρ_L = density of liquid
X_{Ln} = concentration of solute in liquid phase in the *n*th plate
X_{gn} = concentration of solute in gas phase in the *n*th plate
θ = excess temperature of plate above its surroundings
Carrier gas flow rate = Q ml. per second

The following postulates will be made:

The gas flow rate through the plate is constant.

The temperature of the surroundings of the plate is constant.

The heat capacity of the gas in the plate is insignificant compared with the heat capacities of the liquid phase and support.

The concentrations of solute in the plate are at all times maintained at levels where the adsorption isotherm is linear and $KX_{gn} = X_{Ln}$.

It is required to derive an equation relating the excess temperature of the plate to its surroundings (θ) with a suitable operating variable. For convenience the variable chosen will be v, the volume of gas passed through the plate in terms of "plate volumes" (*5*).

$$\frac{Qt}{V_g + KV_L} = v$$

or

$$\delta t = \frac{V_g + KV_L}{Q}\,\delta v \qquad (1)$$

Consider the heat balance of the plate.

Heat capacity of plate × rise in temperature = heat evolved in plate − heat conducted from plate

Consider this balance during the passage of gas volume δv in time δt. Then

$$(V_L\rho_L S_L + V_S\rho_S S_S)\delta\theta = \text{heat evolved in plate} - \text{heat conducted from plate radially} \qquad (2)$$

As the solute is distributed over a total of $6\sqrt{n}$ plates (*5*), the temperature of the plates adjacent to the one under consideration may be considered the same and thus conduction of heat along the axis of the column may be considered negligible compared with heat conducted radially from the column.

Now, change in concentration in gas phase during passage of $\delta v = \frac{\delta X_{gn}}{\delta v}\,\delta v$

Thus, change in concentration in