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Electron Affinity Spectroscopy—A New Method for the Identification of Functional Groups in Chemical Compounds Separated by Gas Chromatography[1]

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RECEIVED MAY 14, 1959

A sensitive ionization method has been devised to determine the ability of certain organic vapors to capture free electrons. It was noted that electron affinity is determined principally by the predominant functional group present in the molecule, particularly when this includes some atom other than carbon or hydrogen. Different electron affinities were found for such compounds as esters, ethers, ketones, halides and alcohols. These specific differences provide a basis for the assignment of an unknown organic compound to a characteristic class. This method of spectroscopy offers a promising basis for automatic gas analysis and qualitative gas chromatography.

The growing importance of gas chromatography as an analytical method has recently stimulated the development of ionization methods for quantitative gas analysis. Two of these, the flame ionization detector[2] and the "argon" detector[3] possess sensitivities and a range of response far exceeding any previously existing methods of quantitative analysis.

An ideal automatic analytical method must possess not only the ability to separate and measure the quantity of the components of a mixture but also the means of identifying each component as it is separated. The first two of these requirements are satisfied by existing methods of gas chromatography; the third cannot be achieved automatically and requires the laborious method of collecting and identifying by conventional methods each component as it emerges from the chromatograph column. Since the separating ability of chromatograph columns is greatest when the quantity of the sample applied is small, the present trend is therefore toward the use of samples as small as one microgram or less. The collection and identification of separated components by conventional means when the total quantity of a mixture is as small as this is almost impossible. In view of the success of ionization methods for *quantitative* gas analysis it seemed worth exploring the possibility that a sensitive ionization method for *qualitative* analysis could be developed. The mass spectrometer is available for this purpose but it is an expensive instrument and at present too insensitive for the latest techniques of gas chromatography. The most promising approach appeared to be one based on the differences in electron affinity which apparently exist between the principal classes of organic compounds. This paper describes the basis and application of this simple but sensitive method of qualitative gas analysis.

Physical Basis of the Method.—In an ionized gas the negative charge carriers may be either free electrons or negative molecular ions. An important process leading to the formation of negative ions is the reversible reaction in which neutral molecules (M^0) capture free electrons (e^-)

$$M^0 + e^- \rightleftharpoons M^- + \text{energy}$$

The energy liberated by the reaction or required to dissociate the negative ion is called the electron affinity of the molecule. Electron affinities of different molecular species vary over a wide spectrum of energy so that the electron affinity of a given compound is a property potentially useful in its characterization. It must be emphasized, however, that the process described above for the reversible interaction between free electrons and neutral molecules is true only in a broad sense. The interaction of electrons with neutral molecules and the dissociation of negative ions are both complex processes[4] and only rarely are the energies involved equivalent. Nevertheless from a practical viewpoint the measurement of apparent dissociation energies or apparent electron affinities is sufficient for the needs of qualitative analysis.

With many organic compounds the electron affinity is determined principally by the predominant functional group present in the molecule particularly when this includes some atom other than carbon or hydrogen. The size and configuration of the hydrocarbon moiety has relatively little effect. The electron affinities of such classes of compounds as esters, ethers, ketones and alcohols are all different and it is possible to assign an unknown organic compound to a class following the measurement of its electron affinity.

In classical physics relatively complex methods have been used in the precise determination of electron affinities. For the measurement of apparent electron affinities, however, simpler methods are sufficient. One of these requires merely an ionization chamber containing a source of ionizing radiation and some means of measuring the current which flows in the chamber at different applied potentials. To measure the electron affinity of a given gas or vapor the current flow in the chamber at different applied potentials is observed; first when the chamber is filled with an inert gas and then with the same inert gas containing a small quantity of test vapor or gas. In this context an inert gas is one which has a negative affinity for free electrons, *i.e.*, hydrogen, nitrogen and the noble gases.

The voltage current relationships of an ionization chamber containing nitrogen and nitrogen contaminated with various vapors is illustrated in Fig. 1. With pure nitrogen in the chamber the current is seen to rise rapidly with increasing

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[1] This investigation was supported by grants from the National Heart Institute, National Institutes of Health (H-3558), the National Dairy Council and The Nutrition Foundation.

[2] I. G. McWilliam and R. A. Dewar, *Nature*, **182**, 760 (1958).

[3] J. E. Lovelock, *J. Chromatography*, **1**, 35 (1958).

[4] H. S. W. Massey, "Negative Ions," Cambridge University Press, New York, N. Y., 1950.

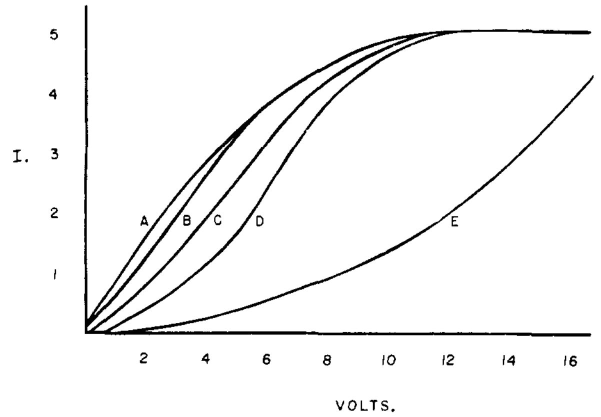

Fig. 1.—The voltage–current (I) relationships of an ionization chamber containing nitrogen (curve A) and nitrogen containing various organic molecules in the gas phase (B, hydrocarbon; C, ester; D, alcohol; E, halogenated hydrocarbon).

voltage and the saturation current of the chamber is soon reached with a relatively small applied potential (curve A). When a vapor with an affinity for free electrons is also present the initial rise of current with applied potential is less steep and the potential required for the establishment of a saturation current is higher than with pure nitrogen (curves B, C, D and E). The differences between the various responses shown in Fig. 1 may be explained as follows. In an ionized pure inert gas the negative charge carriers are all free electrons. These have a small probability of recombining with positive ions and are also highly mobile so that a relatively small potential is needed to collect them without loss at the anode and permit the flow of a saturation current in the chamber. When a vapor with an affinity for free electrons is present in the ionized inert gas some of the free electrons will be captured by the inert gas molecules to form negative molecular ions. Negative ions are slow moving and combine more readily with positive ions than do free electrons. For these reasons the collection of negative ions is more difficult than the collection of electrons and a higher potential is therefore needed to establish the flow of a current. When a relatively high potential is applied to the ionization chamber the negative ions may receive sufficient energy from the electric field, between collisions with inert gas molecules, to dissociate. When the potential is high enough to dissociate all of the negative ions, the flow of a saturation current in the chamber again becomes possible. Thus the potential needed to establish the flow of a saturation current or some convenient proportion of it will be related to the electron affinity of the gas within the chamber. For a given compound the value of this potential will depend not only upon the electron affinity of the compound but also on the shape of the chamber and the temperature and pressure of the gas within it. The relative values for different compounds under constant conditions should, however, be consistent.

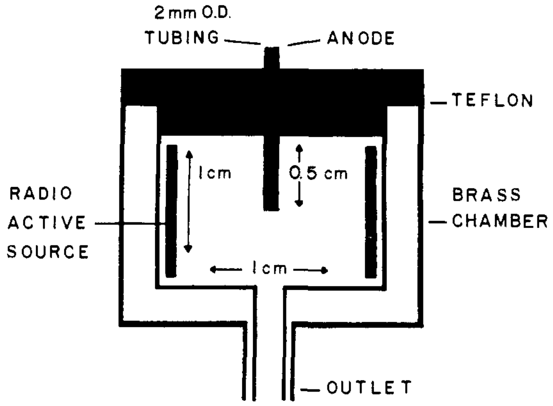

Fig. 2.—Ionization chamber (simplified).

Experimental

Apparatus.—A suitable ionization chamber is illustrated in Fig. 2. It consists of a brass body enclosing a cylindrical chamber 1 cm. in diameter by 1 cm. deep. The negative charge carriers are collected at an anode consisting of a short length of 0.2-cm. diameter brass tubing supported coaxially by a polytetrafluoroethylene insulator at the center of the chamber. The gas was ionized by including a sealed α-radiation source which in this instance consisted of 50 microcuries of radium. The current flowing when potentials of between 0 and 100 volts were applied to the chamber was measured in terms of the potential developed across a resistance of approximately 100 megohms in series with the chamber and the source of potential. The signal after electronic impedance transformation was recorded automatically using a potentiometric recorder.

The serial introduction of the vapors of different compounds in a stream of inert gas (in these experiments helium) was most conveniently arranged by connecting the chamber to a chromatograph column. In these experiments the column used was 100 feet long, 0.01 inch internal diameter, and made from metal capillary tubing. It was coated internally with a thin layer of squalane. The response of the method to different classes of compound was determined by applying the same mixture of compounds repeatedly to the column and comparing the chromatograms obtained when the chamber potential was varied between each application.

Results and Discussion

The results of a typical experiment are shown in Fig. 3. The chromatograms show for each class of compounds the following general behavior. At low applied potentials there is a decrease in current flow as the vapor enters the detector. At higher potentials this negative response becomes less and may disappear completely as with hydrocarbons at 5 volts in Fig. 3. At still higher applied potentials the response becomes positive, *i.e.*, there is an increase in current flowing in the detector when vapor is present.

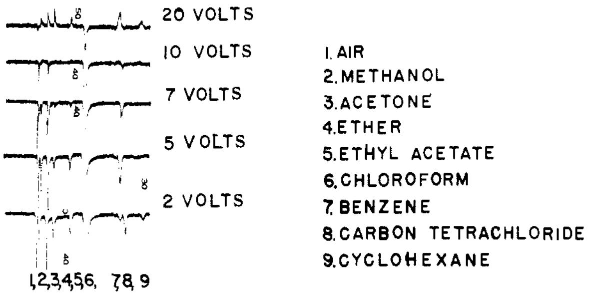

Fig. 3.—The affinity of various functional groups for free electrons at different applied potentials.

This transition from a negative to a positive response as the potential increases is most evident when helium is used as the carrier gas and may be explained as follows: At all applied potentials there is an increase in the rate of ion production by the primary radiation when vapor is present. This is due to the fact that the ionization cross section of organic molecules is greater than that of helium. At low applied potentials where electron capture takes place the loss of ions by recombination however always exceeds the gain in numbers of ions by the cross section effect. Thus at a sufficiently low potential all substances with an affinity for free electrons cause, by their presence in the detector, a decrease in current. At intermediate potentials where some dissociation of the negative ions takes place, the two effects may counterbalance so the response vanishes.

The potential at which the transition from a positive to a negative response occurs varies slightly with both the vapor concentration and the carrier gas used but is sufficiently constant for the characterization of the major classes of organic compounds.

The chromatograms show how it is possible to distinguish between the different classes of compound when as many as six classes are present in a mixture. Similar experiments using different members of each of the classes represented in Fig. 3 indicated that with a wide range of compounds the applied potential at which the transition from negative to positive response occurred was independent of the size of the hydrocarbon moiety of the compound.

The potentialities of the method are perhaps best illustrated in the chromatograms shown in Fig. 4. In this experiment quantitative chromatograms using an "argon" detector are compared with qualitative chromatograms using the electron capture device. In the first chromatograms the separation of a 22-component hydrocarbon mixture is shown. In the second the same mixture contained in addition 5% of a mixture of two ketones (3 pentanone and 2-methyl-3-pentanone). The identification of the two ketones amidst the forest of hydrocarbon spikes would have been a formidable task with the conventional quantitative method. Using the qualitative method, however, the presence of the two ketones is clearly distinguished.

The requirements of a *qualitative* detector for gas chromatography are that it should be able to distinguish between as many classes of compound as possible and perform this function when the quantity of compound available is one microgram or less. The ability to provide precise *quantitative* analysis simultaneously with the qualitative analysis would be desirable but it is not essential, for excellent quantitative detectors are available which could be used in series or parallel with the qualitative detector. For these reasons no attempts were made in these experiments to assess the quantitative response of the device described above. During the emergence of a peak from a chromatograph column the vapor concentration rises from zero to a maximum and then decays. The observed responses were always consistent during the emergence of a peak and thus the qualitative response appears to be independent of concentration. It is tolerably certain, however, that except for very low concentrations the quantitative response of the device will not vary linearly with vapor concentration.

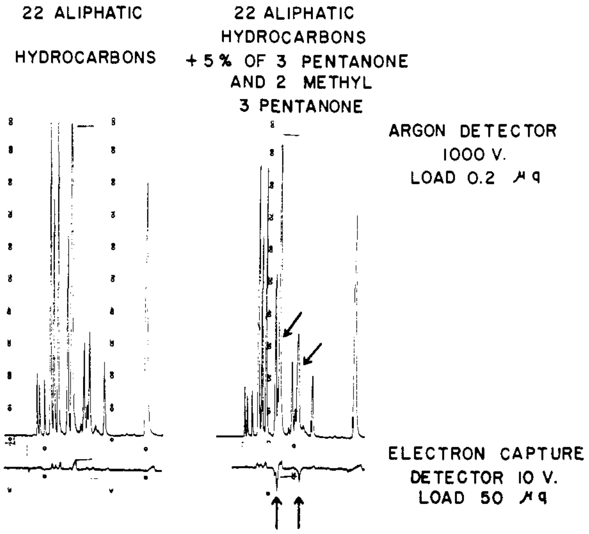

Fig. 4.—Quantitative chromatogram (left) using an "argon" detector compared with qualitative chromatogram (right) using the electron capture device.

The apparatus was constructed to explore the possibilities of using electron affinity spectroscopy as a method of *qualitative* analysis. No attempt was made to design it specifically for the requirements of the method at this time. In spite of this a high sensitivity and a considerable power of resolution was found. Preliminary experiments using a pulsed instead of a steady source of potential and a more sophisticated chamber design suggest that the sensitivity and resolution can be still further increased.

The simple detector is suitable for use with nitrogen, hydrogen or helium as a carrier gas. Argon cannot be used, for when this gas is irradiated metastable atoms are produced; these on collision with vapor molecules produce ions which offset the effects provided by electron capture. It may be feasible, however, to arrange the apparatus and its operating parameters in such a manner that only the free electrons come in contact with the organic molecules in the gas phase. Under these conditions argon may then be used as a carrier gas, thus providing the great convenience of simultaneous quantitative and qualitative analysis.

This method of spectroscopy offers a promising basis for automatic gas analysis and qualitative gas chromatography.

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