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During the period from August 1, 1961 to January 31, 1963 our laboratory has concerned itself primarily with the development of a suitable gas chromatographic detection system capable of meeting many of the requirements necessary for the use of this extraordinarily powerful analytical technique in the determination of the presence of organic compounds on the surfaces of the Moon and Mars. In addition, in this regard it was decided to seek a monitoring system that would approach an ideal i.e. A single, simple and robust detection device which is highly sensitive to both atmospheric gases and organic vapors.

The practical development of such a device would afford extraordinary flexability and versatility in that

a) it would simplify the determination of the individual components of atmospheric gases as well as mixtures of organic substances

b) it would simplify the analysis of gases as well as smaller chemical fragments released during the pyrolysis of organic compounds

c) it would simplify instrument requirements in that a single detector would be available which would provide exceedingly good sensitivity to gases as well as organic compounds. Moreover it was hoped that this could be accomplished with the use of single carrier gas

d) it would simplify weight requirements by conceivably reducing the number of detectors required to successfully fulfill all aspects of the Surveyor mission as well as further space ventures such as the Mariner atmospheric analysis and soft lander probes.

As the work proceeded, a new, simple, and highly sensitive gas chromatographic detection system for the analysis of both gases and organic vapors was developed. The detector, containing a 200 mc. tritium source, was an ionization chamber characterized by a low internal volume and concentric electrodes 1mm. apart. Utilizing argon as a specific carrier gas, this detector at an applied potential of 1 to 2 volts when maintained at 150° to $200^{o}C$. provided an excellent response to test samples of permanent gases. The limit of detection approached 10^{-12} moles per second per 25 ml. of carrier gas. The substantial increase in current emitted from the detector at these low field strengths was originally thought to be due to one or two mechanisms. This involved either alterations in electron drift velocity caused by the addition of complex molecules to argon and/or a phenomenon implicating collisions between excited argon atoms (A*) and fixed gas molecules (M) to produce complex ions (AM)

$$\text{i.e.} \quad A^* + M - AM^+ + e^-$$

By operating the same unit at a higher voltage (150 to 250 volts) the sensitivities for organic vapors were comparable to or greater than that noted for the small 1cm. detector described by Lovelock. This increase in response arose in part from a lower noise level and from the configuration of the electrodes

which minimized ion recombination processes. The mechanism of ionization of organic compounds whose ionization potentials were below the excitation potential of argon (11 6 e.v.) in addition to the classical Penning effect was thought to also involve addition processes such as complex ion formation.

Recently in order to further elucidate the mechanism responsible for the ionization of permanent gases in this system, studies utilizing higher molecular weight monoatomic gases of high purity as the eluting gas have been carried out. The response to various polyatomic sample gases, using krypton (m.w. 83.8) or xenon (m.w. 131.3) as carrier was approximately two or three times greater, respectively, than that previously noted with argon.

From these observations it became apparent that both the existance of a sensitivity maximum with increasing voltage (1-2v) and the comparatively large current which was derived from the detector at these low field strengths could be best explained by relative alterations in electron drift velocity caused by the addition of trace quantities of test samples of complex molecules to the monoatomic carrier gas. The magnitude of response elicited by these substances appeared to have a direct correlation to the molecular weight of the carrier and the relative temperatures of the electrons within the ionized gas.

Apparently the presence of complex polyatomic gaseous molecules in the chamber cause the free electrons to undergo inelastic impacts which result in a transfer of energy between the particles. In this instance it is presumed

that the electrons lose their energy by exciting the vibrational and rotational states in these molecules. The overall effect of this lowering in the average energy of the electrons results in an increase in their drift velocity. This reduces the probability of ion recombination reactions by decreasing the free electron density within the ionization chamber. Under these circumstances these reactions tend to facilitate the collection of free electrons at the anode giving rise to a relatively large signal. Thus when polyatomic samples are analyzed in this system the resultant increase in electron drift velocity effect is greater for xenon > krypton > argon > neon > helium when each of these substances are used as the carrier gas.

In contrast, with only monoatomic carrier gas (either A, Kr or Xe) flowing within the ionization chamber the free electrons engage in elastic collisions with the particular monoatomic gas atoms. In this case the electron drift velocity in these rare gases is relatively low. Thus, under these conditions, in an applied field, the electron temperature is increased considerably above that of the gas, making collection at the anode relatively inefficient. This would account for the lack of a distinct sensitivity maximum and the comparatively poor response (minimal level of detection less than 3×10^{-8} mole/sec. at a flow rate of 25 ml./min. of carrier gas) which was observed when test samples of the various monoatomic gases such as Ne, A, Kr, and Xe were introduced into the system containing different monoatomic carrier gases.

The modest response elicited when helium was analyzed (minimal level of detection 1×10^{-10} moles/sec. per 25 ml./min. of carrier gas) appears to be in exception. The precise mechanism responsible for the response here is unknown and may be related to two effects, a) the large difference between the two masses in as much as the fractional energy loss of the electron engaged in collision will be greater for He than for A, Kr, or Xe, b) the relative magnitude of change in the mobilities of the respective ions.

This work has resulted in the following publications:

1. Lipsky, S.R. and M.M. Shahin, "Sensitive Ionization System for the Detection of Permanent Gases and Organic Vapors by Gas Chromatography", Nature, 197, 626, 1963.
2. Shahin, M.M. and Lipsky, S.R., "The Mechanisms of Operation of a New and Highly Sensitive Ionization System for the Detection of Permanent Gases and Organic Vapors by Gas Chromatography", Analytical Chemistry, 35, 467, 1963.
3. Lipsky, S.R. and Shahin, M.M., "Observations on the Use of Xenon and Krypton as Carrier Gases for a Highly Sensitive Detection System for Gas Chromatography - submitted for publication Nature 1963.