

COMPARISON OF HELIUM AND ARGON IN IONIZATION DETECTORS

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The action of argon ionization detectors for gas chromatography has been ascribed by LOVELOCK^{1,2} to the occurrence of inelastic collisions between metastable excited argon atoms and molecules of other gases. As a result of these collisions, the excited argon imparts its energy to the second species of molecule and itself returns to the ground state. If the second molecular species has an ionization potential below 11.6 eV, the energy of the lowest excited state of argon, the collision results in ionization and a consequent increase in the number of charge carriers. The magnitude of the resulting increase in electrical conductivity may be taken as a measure of the concentration of the second molecular species.

On the basis of this hypothesis, an increase in sensitivity was predicted if helium were substituted for the argon since the excited states of helium are more energetic (more than 20 eV) than those of argon. When helium was used experimentally, however, "high baseline currents" and low sensitivity were observed^{3,4}, and gases with high ionization potentials such as oxygen or nitrogen caused diminution of the current flow in these detectors. This behavior was attributed to the presence of impurities in the helium. Upon collision with excited helium, the impurity molecules were ionized, which caused high baseline current. The excited helium returned to the ground state, so that the addition of more nitrogen or oxygen to the gas stream only interfered with the process of creating excited states and so reduced the total current.

When purified helium was used⁵ oxygen and nitrogen caused the predicted increases in current and highly sensitive detection of these gases was found possible. This was reported to require exhaustive purification of the helium.

We have previously reported finding that helium supplied commercially is sufficiently pure for this last effect if the design of the detector cell is modified somewhat and if reasonable care is exercised in making gas connections⁶. This observation permitted us to evaluate the use of helium in an ionization detector, to determine the response to atmospheric gases and to organic vapors containing a variety of functional groups, and to compare these responses to those obtained when argon was used.

MATERIALS AND METHODS

A detector cell composed of a coaxial rod and cylinder was used (Fig. 1). Polytetrafluoroethylene ("Teflon") was used as insulator and mechanical mounting of the center electrode. Care was taken in the construction of this cell so that no leakage of

gas occurred between the insulator and the central electrode, or at the junction of the insulator and the cylinder. A self sustained, direct current electric discharge was excited between the central electrode and the cylinder⁷.

A high negative potential from a North Hills Electronics Co. Model CS 120 Constant Current Source was put on the cylinder, while the central anode was

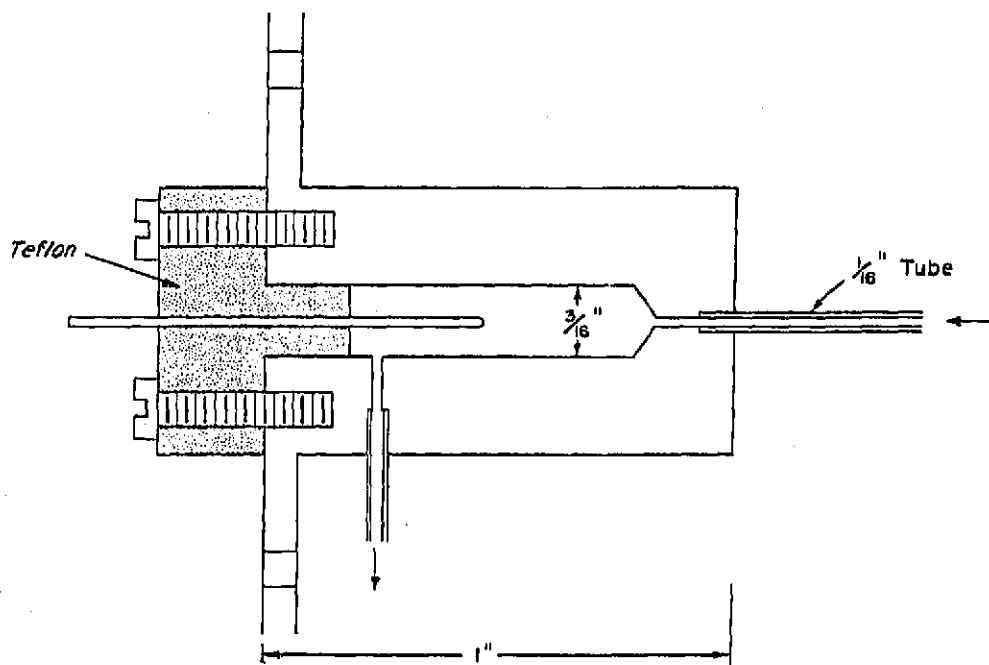


Fig. 1. Longitudinal section of a detector cell (schematic).

grounded. One μA was put through the gas in the detector. A signal proportional to the voltage necessary to cause this current to flow was recorded, using appropriate zero suppression.

When studying the effect of addition of atmospheric gases, the inlet tube of the detector was connected to the outlet of a glass gas chromatography column, 3 ft. long, containing molecular sieve 5 A, 30–50 mesh. A silicone rubber seal was used to make the glass-to-metal connection. A 10 μl syringe (Hamilton Co.) was used to inject samples of air into this column through a silicone rubber septum. To evaluate the response of the detector to concentrations of oxygen and nitrogen smaller than those obtainable by injecting 1 μl of air, additional carrier gas was supplied to the detector cell using a "T" connection. To evaluate the response of the detector to organic vapor, a capillary column, stainless-steel, 0.010 in. inside diameter, 100 ft. long coated with Apiezon L was used to supply graded quantities of vapor. Despite using a stream divider to reduce the time constant of the inlet, whereby more than 99% of the gas was vented and less than 1% entered the column, and despite brisk (100 cc/min) dilution flow at the detector, the detector was overloaded when 1 μl liquid samples of organic materials were injected into the inlet. A series of solutions were prepared containing 1% test material in either toluene or isooctane, and a second series of 2% solutions of the same materials in these solvents. Each of the materials tested was well separated from either isooctane or toluene by the column so that the sensitivity of

the detector to it could be determined by injecting 3 μ l samples of their solutions in these solvents. The response of the detector to each test substance was determined by measuring the area of the peaks after establishing that peak area was linearly related to the quantity injected.

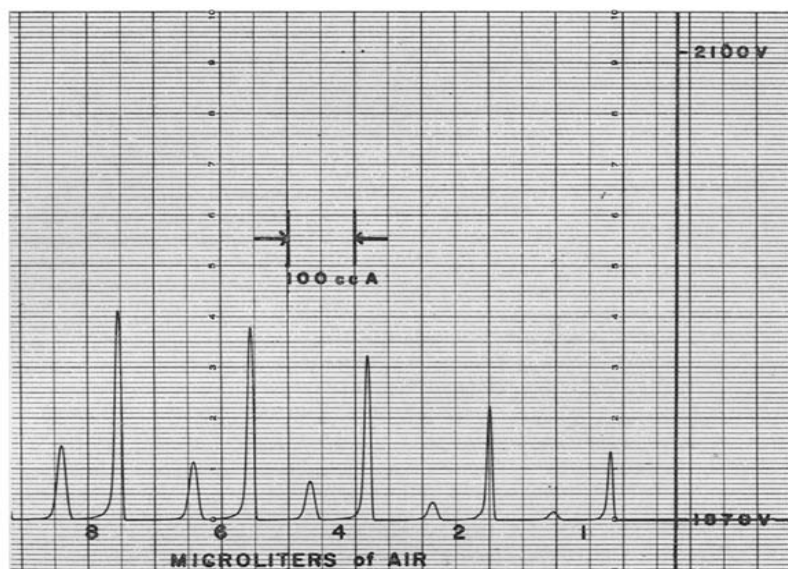


Fig. 2. A series of air samples, analyzed by a molecular sieve column, detected by an argon discharge.

RESULTS

Atmospheric gases

The response of an argon discharge to a series of air samples by a molecular sieve column is shown in Fig. 2. The baseline voltage is 1870 V. The presence of either oxygen or nitrogen caused an increase in this voltage. The effect of oxygen was comparatively much greater.

The response of a helium discharge to a similar series of samples is shown in Fig. 3. This series of analyses was done using a freshly installed, incompletely activated column so that the gas reaching the detector cell may be assumed to have contained contaminating gases. The baseline voltage was 500 V. Both oxygen and nitrogen raised the voltage (decreased the conductivity) of the discharge. The sensitivity to nitrogen and oxygen was more nearly comparable.

The sensitivity of the argon discharge or the impure helium discharge to oxygen or nitrogen decreased with increasing concentration of these gases. The decrease in sensitivity was somewhat specific. When, for example, the helium discharge was deliberately contaminated with nitrogen, the sensitivity of the discharge to both oxygen and nitrogen was decreased, but the decrease was relatively greater with respect to nitrogen. When the gas was deliberately contaminated with oxygen, the sensitivity to both gases again decreased. Under this circumstance, the sensitivity to oxygen decreased more. Contamination of the gas in the detector with air gave the expected intermediate result.

Fig. 4 shows the responses obtained with the same experimental helium dis-

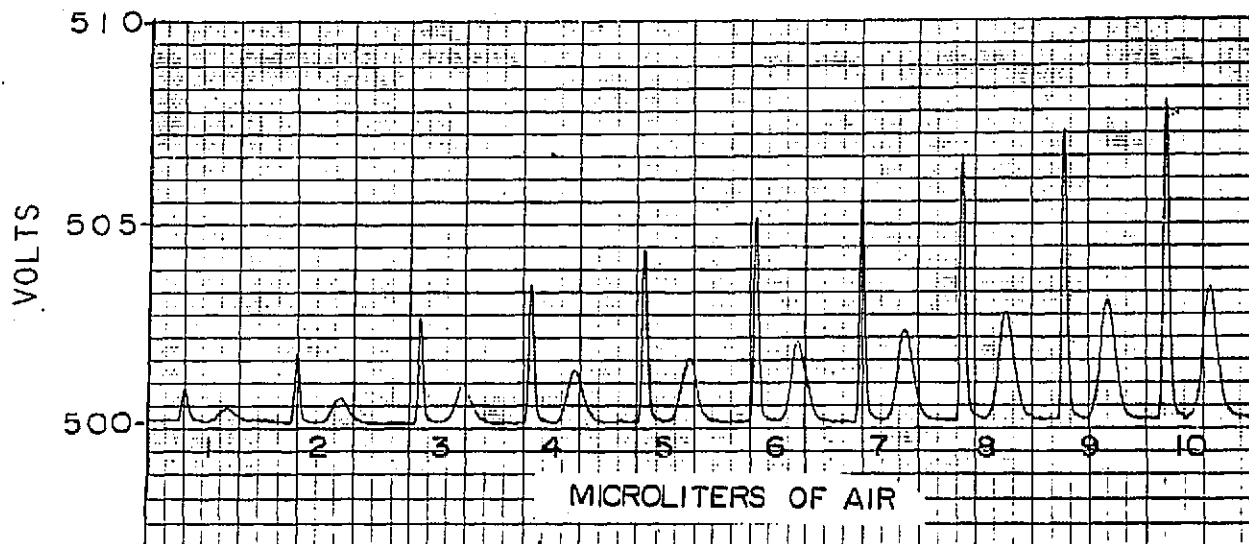


Fig. 3. A series of air samples, analyzed by a molecular sieve column, detected by an "impure" helium discharge.

charge setup as above except that the column had been "activated" by heating at 200° overnight with helium flowing through it. The baseline voltage increased from 500 to 800 V. Addition of either nitrogen or oxygen now increased the conductivity of the discharge (lowered the voltage). The sensitivity to both was greatly increased. It was necessary to add a dilution flow of 1000 cc of helium per minute to the detector to avoid overloading. Despite this dilution, the response to oxygen showed overloading at concentrations that resulted when 10 μ l samples of oxygen were analyzed. More than twice this concentration of nitrogen in the helium was required to overload the detector. As may also be seen, the minimum voltage of the discharge reached when

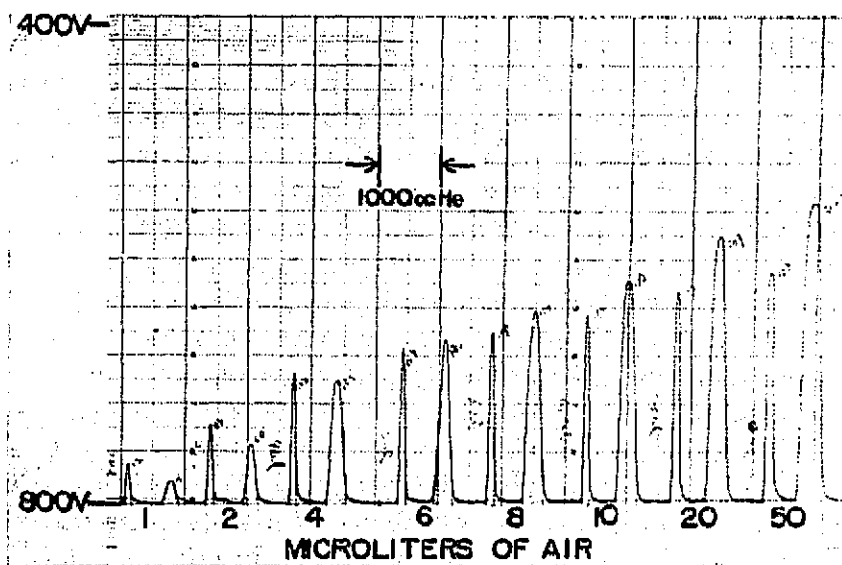


Fig. 4. A series of air samples, analyzed by a molecular sieve column, detected by a "pure" helium discharge.

oxygen was added to the helium was greater than the minimum reached when nitrogen was added.

It was possible to monitor the process of outgassing the molecular sieve column by observing the voltage and the response of the helium detector. When the column was freshly installed the voltage across the helium discharge ranged from 600 to 700 V, and oxygen and nitrogen both caused increases in voltage. The sensitivity was comparatively low, but within several hours, the voltage dropped to 550 V, and the sensitivity to both oxygen and nitrogen increased. Both continued to cause increases in voltage. With still further outgassing, but without a marked change in voltage, the sensitivity to low concentrations of nitrogen decreased. At this point low concentrations of nitrogen decreased the voltage while oxygen continued to increase the voltage. The response to oxygen then also changed toward increasing the conductivity of the gas.

The sensitivity, when the helium was sufficiently pure so that addition of oxygen and nitrogen caused decreases in the voltages (increased conductivity) was at least two orders of magnitude greater than that of the "impure helium" system in which these gases decreased the conductivity.

By repeatedly heating the molecular sieve column to 200° with helium flowing through it and then allowing it to cool, and by repeatedly heating the detector cell to 200°, we were able to raise the voltage across the helium discharge to a maximum of 1100 V. This was accomplished with considerable experimental difficulty. Sensitivity to oxygen and nitrogen increased with the increase in voltage. Disconnecting the detector from the column for less than ten seconds returned the voltage to 600 V and required repeated baking of the detector cell before the voltage could be raised again. We postulated that contamination of the electrode surfaces with water was responsible for a major part of this effect.

TABLE I
RESPONSE OF ARGON AND HELIUM DISCHARGES TO ORGANIC COMPOUNDS

	Argon			Helium		
	Response per mole	Response per unit wt.	Response per gram C	Response per mole	Response per unit wt.	Response per gram C
Chlorobenzene	2.28	1.49	1.95	0.92	0.58	0.74
Toluene	2.14	1.72	1.57	1.62	1.28	1.15
Fluorobenzene	1.47	1.11	1.24	0.71	0.55	0.60
Benzene	1.38	1.29	1.17	1.15	1.06	0.95
Iso-octane	1.16	0.74	0.74	1.43	0.81	0.89
Cyclohexane	1.09	0.93	0.91	1.43	1.23	1.19
Heptane	1.04	0.75	0.74	1.34	0.97	0.95
Pentane	1.00	1.00	1.00	1.00	1.00	1.00
Acetone	0.57	0.71	0.95	0.42	0.59	0.78
Methylene chloride	0.52	0.43	2.59	0.81	0.70	4.06
Chloroform	0.42	0.26	2.22	0.97	0.59	4.85
Ether	0.42	0.66	0.53	0.44	0.69	0.54
Methyl ethyl ketone	0.38	0.40	0.50	1.13	1.14	1.41
Carbon tetrachloride	0.38	0.19	2.04	1.14	0.54	5.66

Organic vapors

The response of both argon and helium discharges to organic compounds with different functional groups was variable (Table I). Within a series of closely related compounds, such as the aliphatic hydrocarbons, pentane, cyclohexane, heptane, and isooctane, or the halogenated hydrocarbons, the response appeared to be related to the number of molecules of these substances introduced, rather than to the weight.

The responses of the argon discharge to compounds within this limited group may be classified into the responses to aliphatic hydrocarbons, which were all similar, the responses to aromatic hydrocarbons, including toluene, benzene, chlorobenzene, and fluorobenzene which were greater and the responses to compounds containing oxygen such as acetone and those containing halogens, which were less.

The responses of the helium discharge to the same group of compounds were grossly similar. The discharge was most sensitive to toluene. The sensitivities per mole to aliphatic hydrocarbons, halogenated aromatics, and halogenated aliphatics were all equal. In the group of compounds tested, only diethyl ether and acetone were detected with lower sensitivity. The helium discharge showed somewhat less variability of response than the argon discharge. This was only a matter of degree rather than an easily discernible qualitative difference.

DISCUSSION

A stable electric discharge in a gas requires that free electrons be released at a rate equal to the rate at which they are lost. This requires that a population of ions and excited gas molecules exist in just sufficient concentration to cause the release of these electrons. If the discharge is self-sustained, this population of electrons, ions and excited molecules must be maintained without dependence on any source of initiating electrons. A stable gas discharge thus implies a rather unique condition of the gas.

In the usual operation of an ionization detector, a given voltage is impressed across the electrodes of the detector cell and the current is measured. The voltage chosen may, however, be less than optimal for maximum sensitivity when one gas is used, while yet large enough to result in destructive currents when other gases are used. Since the experiments reported here were designed specifically to compare the effects of using different gases, an attempt was made to use comparable conditions, and the use of a constant current, self-sustained, gas discharge was selected. This defined the conditions of excitation of the gas necessary for maintaining a self-sustained gas discharge as the conditions at which the effects of using different gases were compared.

Since the electrical characteristics of a self-sustained discharge are by definition independent of the level of radioactivity present, no radioactive source was required.

The voltage across the discharge depends primarily upon the composition of the gas. Because of this and because it is independent of the current in the same manner that the voltage across a voltage regulator tube is independent of the current, it is a better variable to follow than the current. Although the effect of small changes in current is small, the current was held constant electronically. A constant current system tends to be more stable especially when the test materials reduce the electrical conductivity of the gas.

Each of the discharges tested was found to be sensitive to each of the atmospheric gases and organic vapors added. LOVELOCK has reported¹ that the argon ionization detector is insensitive to nitrogen. We have noted that the sensitivities of the "impure" helium discharge and the argon discharge to a given atmospheric gas decreased with increasing concentration of that gas and postulated that different levels of impurities in the argon may explain the differences in the results reported from different laboratories.

By painstaking attention to the details of leaktight construction of the detector cell and by prolonged outgassing of the molecular sieve column, the connecting tubing, and the detector cell itself, we were able to cause the voltage across a "pure" helium system to rise to 1100 V when the effluent of a molecular sieve column alone was put through the detector. When the effluent of a capillary column was added, however, we were not able to obtain a voltage higher than 700 V. Since this same voltage could have indicated either moderate contamination of the helium or rather pure helium, we have determined which of the two it did actually indicate by injecting air into the capillary column. The responses to organic vapors described were each obtained using helium that responded to the addition of air with an increase in electrical conductivity, or what we described as "pure" helium.

This same test was not useful when the argon discharge was used, since the response of the argon discharge to air was always in the direction of decreased conductivity. Since the presence of relatively large concentrations of air in the argon reduces the increase of its conductivity when organic vapors are added, the ability of organic vapors to drop the voltage to 500 V was taken as evidence that the argon was not grossly contaminated with air.

The sensitivity of the pure helium system to oxygen, nitrogen and argon was greater than that of any of the other discharges described. The sensitivity of the same discharge to organic vapors was comparable to the sensitivity of the argon discharge to these vapors and was greater, approximately in proportion to the purity of the helium, than the sensitivity of the impure or contaminated helium system. Since this increase in sensitivity was obtained concomitantly with increase in sensitivity to oxygen and nitrogen, any real increase in sensitivity in terms of increased signal to noise ratio is achieved only through a great deal of effort.

Despite increased sensitivity to oxygen, the response of the pure helium discharge to organic compounds containing oxygen was still less than to similar compounds containing only carbon and hydrogen. Failure to obtain a marked improvement in nonspecificity of response over that obtained using the argon discharge, combined with the increase in experimental difficulty make its comparative usefulness for detection of organic materials, except under unusual circumstances, somewhat doubtful.

SUMMARY

Sensitive detection of atmospheric gases and organic vapors using ionization detectors has been accomplished with either helium or argon carrier gas. Addition of permanent gases in low concentration increased the electrical conductivity of an electric discharge excited in helium, while addition of higher concentrations of the same gases decreased it. Addition of permanent gases to an argon discharge reduced its conductivity.

Addition of small concentrations of organic vapors to either an argon or a helium discharge increased its conductivity. The sensitivity of both helium and argon discharges to compounds with different functional groups varied. The variation in sensitivity of the helium discharge, although somewhat less than that of the argon discharge, was found to be still pronounced.

REFERENCES

- ¹ J. E. LOVELOCK, *J. Chromatog.*, 1 (1958) 35.
- ² J. E. LOVELOCK, *Anal. Chem.*, 33 (1961) 162.
- ³ R. LANDOWNE AND S. LIPSKY, *Nature*, 198 (1961) 571.
- ⁴ J. F. ELLIS AND C. W. FORREST, *Anal. Chim. Acta*, 24 (1961) 329.
- ⁵ R. BERRY, *Nature*, 188 (1960) 579.
- ⁶ A. KARMEN, L. GIUFFRIDA AND R. L. BOWMAN, *Nature*, 191 (1961) 906.
- ⁷ A. KARMEN AND R. L. BOWMAN, *Proc. 3rd Intern. Symposium on Gas Chromatography (I.S.A.)*, East Lansing, Michigan, U.S.A., 1961.

J. Chromatog., 9 (1962) 13-20