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IODINE-DOPED SELECTIVE IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY*

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SUMMARY

During initial investigations of a detector for gas chromatography based on modifications of a field-emission argon ionization detector an intriguing selective response phenomenon was identified when iodine vapor was continuously introduced into the detection chamber. The detector was of a simple design consisting of two 1.5 × 0.5 cm concave electrodes mounted in a concentric ceramic housing. With iodine continuously introduced into the housing via a thermally controlled diffusion tube, certain test compounds of interest, such as valeric acid, triethylphosphate, or aniline, provided analytically significant ionization responses while their hydrocarbon solvents and test compounds went undetected.

INTRODUCTION

The argon ionization detector (ArD), which was first described by Lovelock¹ in 1958, depends upon three separate chemical and physical processes for its operations: first, it must have a source of primary electrons; second, these electrons must contain enough energy to generate argon metastable atoms; and third, individual compounds to be detected must have ionization potential of less than that which is released upon collision with excited argon (11.6 eV). Most organic compounds do have ionization potentials less than 11.6 eV and respond well in the ArD.

Although the ArD served as the predecessor to the electron capture detector and the helium ionization detector, it has not survived the rapid and somewhat selective development of gas chromatographic (GC) detectors to become an accepted method of the day. Its requirement of a radioactive source, its non-characteristic response from one compound to another, the occurrence of a variety of response anomalies (often attributed to carrier gas contamination, column bleed, or flow fluctuations) and the continued development of the flame ionization detector (FID) with reproducible and reliable responses are some of the reasons why the ArD has not been developed into a viable detector for trace organic analysis.

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Recently, examples where the FID lacks sensitivity to perform certain analyses have generated a renewed interest in alternative methods for trace organic detection. The current popularity of photoionization detection is evidence of this need for alternatives to the FID. Perhaps it is also time to take a fresh look at the ArD for the determination of organic compounds. With modern chromatographic techniques, many operating conditions which contributed to initial limitations of the ArD are no longer so severe. Even the employment of a radioactive source of primary electrons may not be necessary.

In his initial work Lovelock¹ utilized a ⁹⁰Sr β source to generate primary electrons, but other sources also have been investigated. Among the many early publications were two short communications by Haahti and co-workers^{2,3}, which described an ArD without an apparent primary electron source. The detector of these two articles consisted of concentric electrodes 4 mm apart with an applied potential of 2000 V, creating an effective field of 5000 V/cm. Although this detector did not have an obvious source of primary electrons, it was able to detect less than a ng of the organic compound, methyl laurate.

A year later Wahlroos⁴ reproduced this work and explained that the primary electrons must arise from field-emission. Little or no work has been published on this so called "field-emission" ionization detector since 1961. This is probably due to the fact that its response appeared to be a function of contamination, that is, a "dirty" detector worked best.

Recently while investigating prebreakdown processes in high-pressure gases to determine why discharges often occur at fields much lower than can be theoretically predicted. Bortnik⁵ found that current originates from point deformations on the electrodes. Thus, the smoother and cleaner electrodes are, the more difficult it is to obtain field-emission.

To investigate response in "dirty" field-emission ionization detectors, we constructed several such detectors in which a variety of doping agents were continuously introduced into the electrode chamber.

EXPERIMENTAL

This investigation was essentially divided into two phases. In the first, a detector design which is shown in Fig. 1 was employed to survey the effect of a variety of doping agents on response for a number of test compounds.

This detector was not connected to a gas chromatograph, but rather samples were directly injected through the system in μ l quantities. An auxiliary gas entrance was used to introduce gaseous doping agents while a reactant reservoir entrance was used to introduce vapors of solid or liquid doping agents. Doping agents and test compounds were mixed at the nozzle just prior to entering the electrode region. Electrodes were made of 1.5×0.5 cm concave silver plates and were positioned so that their two edges were separated by 1 to 3 mm. The anode was connected to a Technical Measurement Model HV-4A variable-power supply, while the cathode was connected to a Keithly 417 picoammeter. Throughout these studies the detector was maintained at 200°C, with a carrier gas (helium) flow-rate of 25 ml/min. Doping agents were selected on the basis of a variety of criteria, but availability and ease of introduction into the detector were principal considerations. Some of the reagents

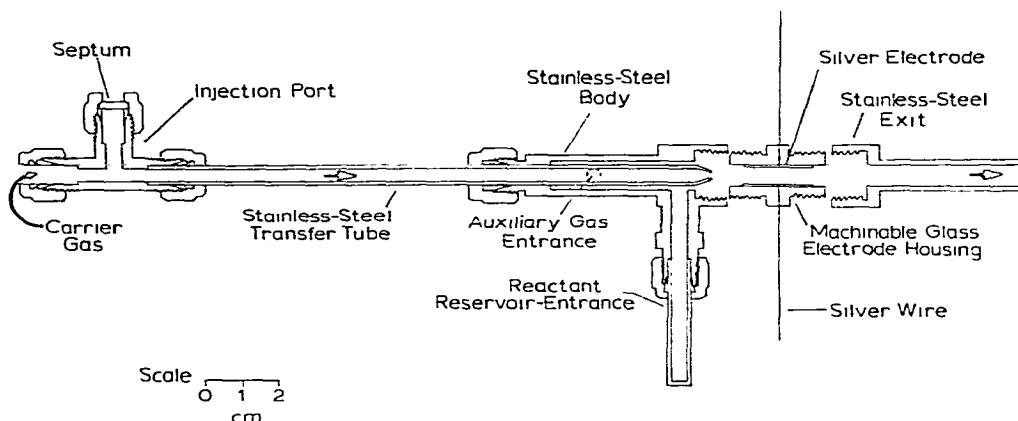


Fig. 1. Direct injection field-emission ionization detector for survey of various doping agents.

used were I_2 , Cl_2 , O_3 , NO , Ba , and $CsCl$. The detector was routinely disassembled, cleaned and the electrodes replaced after each series of tests.

After initial survey investigations, the detector was modified as shown in Fig. 2 and fitted into the thermal conductivity housing of a Varian Aerograph Model A90-Pe refurbished gas chromatograph. Fig. 3 gives a schematic picture of the entire chromatographic system. Initially, a 1/4-in. borosilicate column was installed, packed with Chromosorb W HP (80–100 mesh) that was coated with SE-30 (Supelco, Bellefonte, PA, U.S.A.). Argon carrier gas was passed through molecular sieve then split, with 25 ml/min going to the column and 10 ml/min going to the detector to serve as the transfer gas for iodine doping.

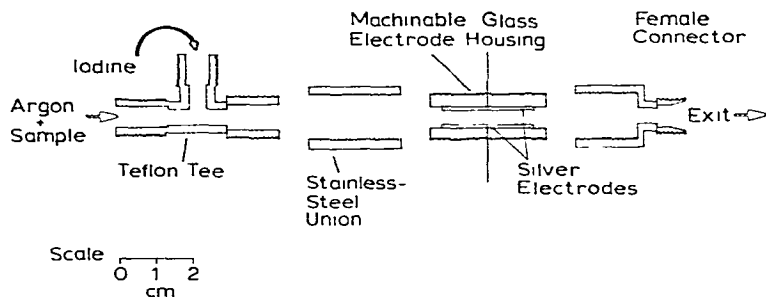


Fig. 2. Iodine-doped field-emission argon ionization detector for gas chromatography.

Iodine was introduced into the transfer gas through a diffusion tube which was submerged in an oil bath for temperature control. The oil bath was normally maintained at $120^\circ C$, the iodine transfer line, at $200^\circ C$, the detector at $250^\circ C$ and the GC column at $130^\circ C$. A fused silica capillary column coated with SE-54 (J. & W. Scientific, Orangevale, CA, U.S.A.) replaced the packed column. With this capillary system, argon was passed through molecular sieve then split with 120 ml/min going to the injection splitter and 40 ml/min going to the detector as the transfer gas. A split ratio of 1:240 allowed a 0.5 ml/min flow through the column.

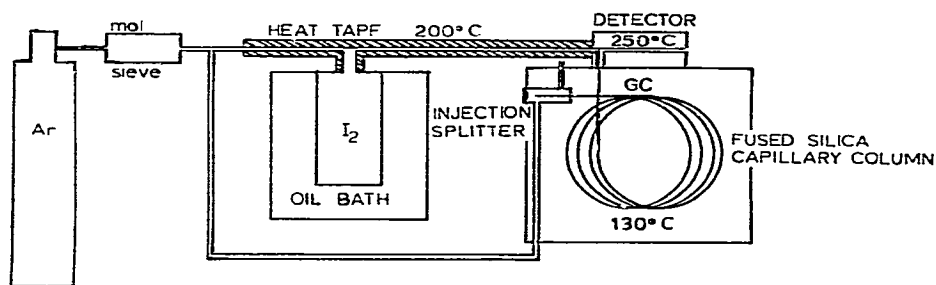


Fig. 3. Schematic of chromatographic system.

A lab-built FID was connected to the exit of the ArD to confirm retention times of test compounds.

RESULTS AND DISCUSSION

With a 400-V potential placed across the electrodes, most of the doping agents tested produced no background current or provided no response for test compounds. Halides, however, produced both. Thus, the results that we obtained when iodine was the doping agent will be the focus of this discussion.

A plot of background current as a function of the oil bath temperature as shown in Fig. 4 demonstrates that the quantity of iodine in the detector affected the amount of current flowing in the cell. The intensity of a compound's response was also related to the amount of iodine present in the detector. In Fig. 5, response, which was obtained for repetitive injections of 10 μg of valeric acid, is plotted as a function of the background current of the detector. In general, the detector was operated with a background current between 0.1 and 0.4 nA.

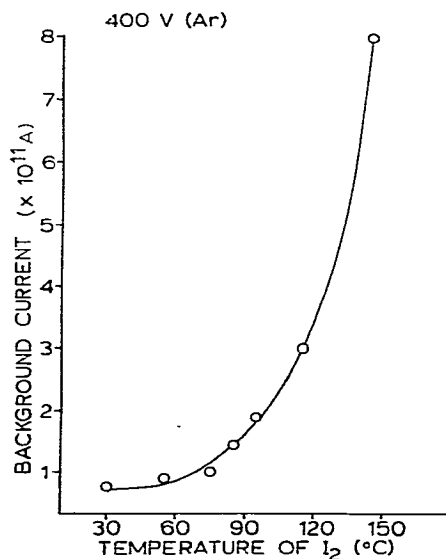


Fig. 4. Background current dependence upon iodine concentration in detector.

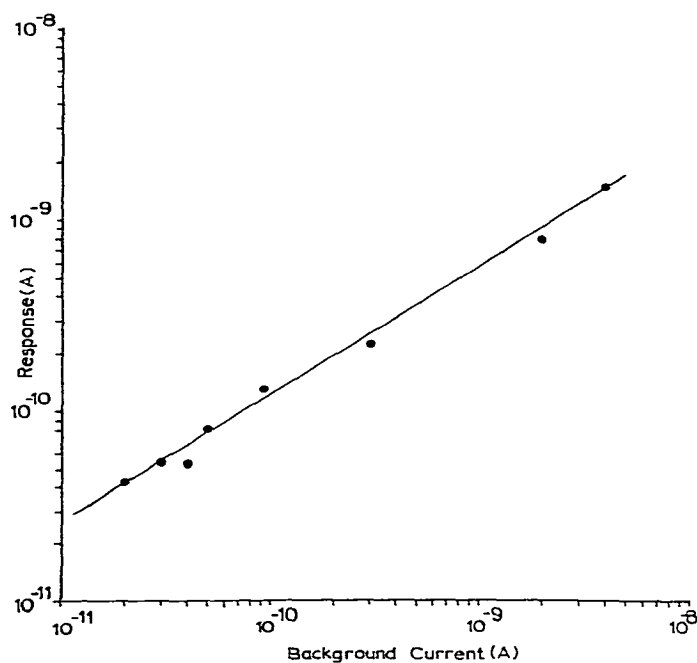


Fig. 5. Peak height responses of 10 μ g valeric acid as a function of increasing background current (increasing iodine concentration) at a constant applied potential of 400 V.

TABLE I

COMPARATIVE RESPONSES IN pE VALUES FOR TEST COMPOUNDS IN IODINE-DOPED DETECTOR

N.R. = No response.

Compound	Blank	Iodine
Valeric acid	N.R.	5.9
<i>tert.</i> -Butyl chloride (TBC)	N.R.	6.7
Aniline	N.R.	8.8
Butanal	N.R.	8.7
Triethylphosphate	N.R.	7.4
Dibutylamine	N.R.	7.1
Acetone	N.R.	N.R.
Octene	N.R.	N.R.
Methanol	N.R.	N.R.
Benzene	N.R.	N.R.
Acetonitrile	N.R.	N.R.
Hexanes	N.R.	N.R.
Carbon disulfide	N.R.	N.R.

Table I lists a number of test compounds and their responses when iodine was and was not added to the detector. Compound responses are reported as the negative log of the ionization efficiencies, pE :

$$pE = -\log \frac{\text{response in coulombs/mole}}{96,487 \text{ coulombs/mole}}$$

When iodine was not present in the detector, none of the test compounds responded. But, with iodine vapor in the detector several tested compounds gave a significant response at the μg level. In order of decreasing responses they were valeric acid, *tert.*-butyl chloride, dibutylamine, triethyl phosphate, butanal and aniline. Fig. 6 shows representative peaks for these responding compounds. These broad, rather tailing, peaks are indicative of chromatography in a 1/4-in. packed column which was interfaced to the detector through a metal transfer line. When a capillary column was installed, peaks were much sharper and more symmetrical.

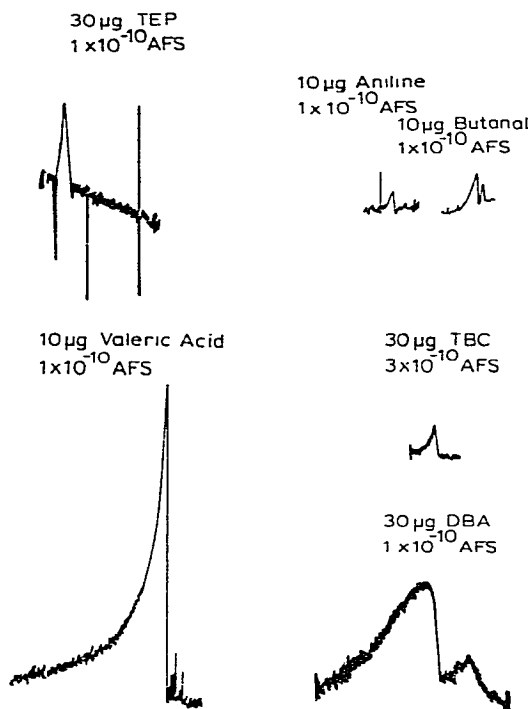


Fig. 6. Representative chromatograms of test compounds with an applied potential of 400 V.

Calibration graphs shown in Fig. 7 indicate that the iodine-doped detector is linear over at least two orders of magnitude, but they also reveal that the response of the detector is not as sensitive as is often needed. The minimum detectable quantities for these two compounds were found to be about 100 ng. Although this was the best sensitivity that could be obtained during this study, it should be pointed out that the data were generated with second- or third-hand equipment. With a more stable power supply and amplifier, baseline noise may be reduced considerably, permitting measurements at more sensitive settings.

Selectivity of this detector, however, can be quite spectacular. Fig. 8a shows a FID tracing of 10 μg of triethylphosphate. The off-scale peak is the solvent (hexane)

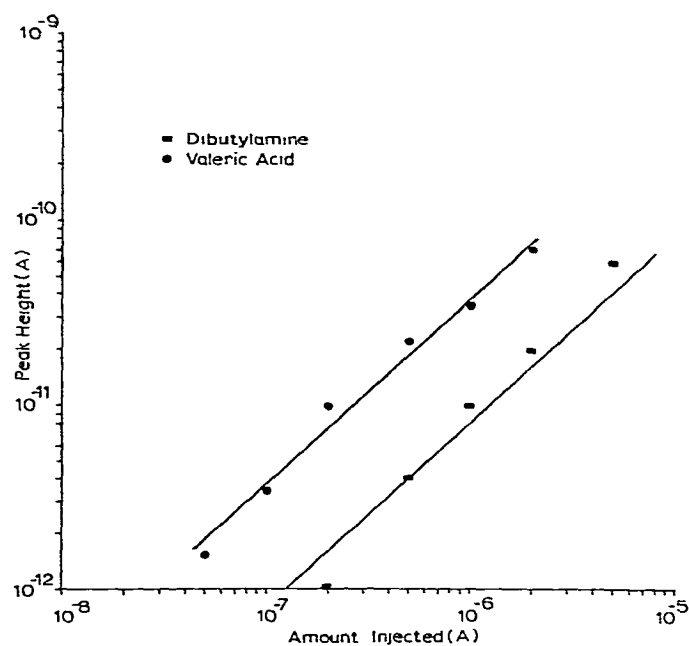


Fig. 7. Calibration curves for valeric acid and dibutylamine.

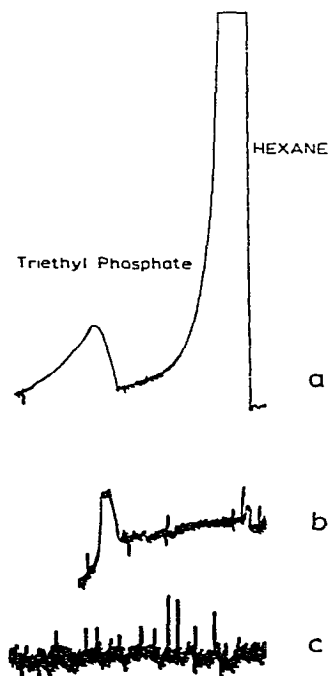


Fig. 8. Comparison of FID and iodine-doped field-emission ionization detector (applied voltage = 400 V) for triethyl phosphate (TEP) in hexane. (a), FID tracing of $10\ \mu\text{g}$ TEP in $1\ \mu\text{l}$ hexane; (b) iodine-doped field-emission ArD tracing of $30\ \mu\text{g}$ TEP in $3\ \mu\text{l}$ hexane; (c) non-iodine-doped field-emission ArD tracing of $10\ \mu\text{g}$ TEP in $1\ \mu\text{l}$ hexane.

and the smaller peak is the standard (triethylphosphate). Fig. 8b shows a tracing of the iodine-doped detector when three times the amount of this test mixture was injected. As can be seen, hexane did not respond while triethylphosphate produced an easily identifiable peak. Fig. 8c is a blank obtained at a higher sensitivity to show that the detector does not respond without iodine in the system. Fig. 9 shows responses for propanoic acid, hexane and aniline when direct injections were split and chromatographed on a fused silica capillary column. In the iodine-doped mode propanoic acid and aniline responded while hexane did not. Note that the potential across the electrodes is only 300 V.

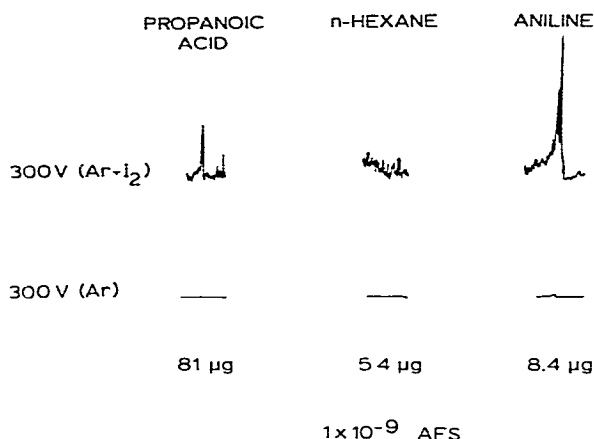


Fig. 9. Responses for the iodine-doped and non-doped ArD for propanoic acid, hexane and aniline at an applied voltage of 300 V.

Throughout these studies the electrode potential was maintained at or below 400 V to avoid a non-selective response which is indicative of the field-emission ionization detector discussed in the Introduction. When the potential was increased to 700 V, an extremely sensitive and non-selective response was obtained. Fig. 10 shows that in this mode both acetic acid and hexane produce very strong responses.

Unfortunately, a concise and complete explanation of all the results reported here is beyond the scope of the data available. However, partial explanations may be possible. At high voltages primary electrons, presumably produced from field-emission processes, gain enough energy to excite argon or helium atoms to the metastable state. These energetic atoms ionize samples to produce the sensitive and non-selective responses which are characteristic of the argon or helium ionization detectors. At lower voltages primary electrons do not gain enough energy to excite the carrier gas and the non-selective ionization effect is lost. Iodine however has an ionization potential of only 9.3 eV and may be ionized at the lower voltages to produce the background current which is observed only when iodine is introduced into the detector.

Why the presence of iodine selectively enhances the ionization of certain organic compounds is less clear and further investigations are needed before speculating on this mechanism. Currently, little information is available on the operation of this

700 V (Ar)

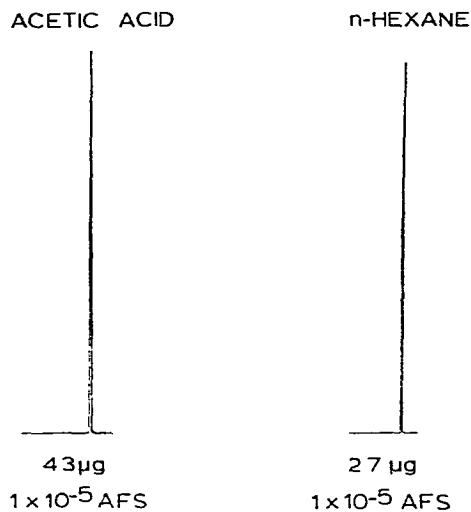


Fig. 10. Responses in ArD for acetic acid and hexane at applied voltage of 700 V.

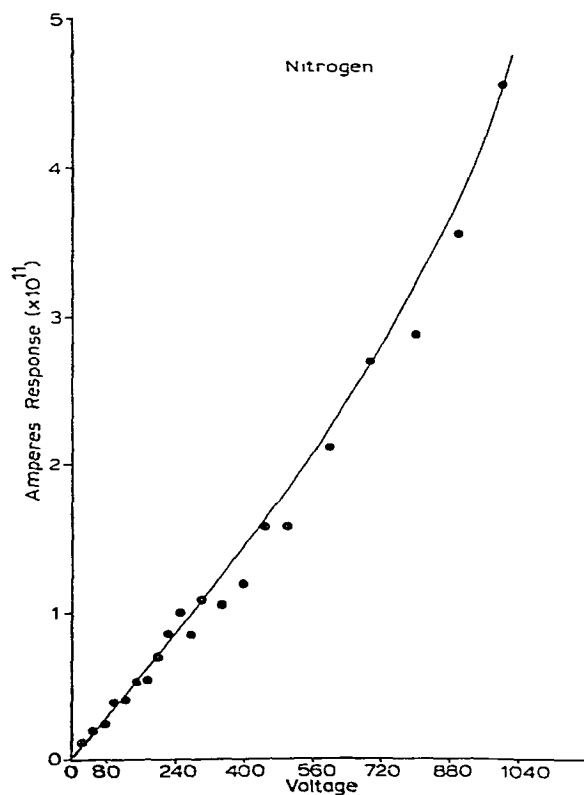


Fig. 11. Responses in nitrogen of 2.5- μ l injections of 1-nitropropane in detector configuration of Fig. 1 as a function of applied voltage with chlorine as doping agent.

selective mode in gases other than argon or helium. It does appear, however, that these gases are not necessary for the halide induced response. For example, Fig. 11 shows the response of nitropropane in chlorine-doped nitrogen. As the voltage is increased so is the response, yet when chlorine is not added to the nitrogen, no response is obtained.

CONCLUSIONS

Although this study was more qualitative than quantitative and many questions concerning the analytical utility and mechanisms of both the iodine-doped and non-doped mode of operation exist, some general conclusions may be made:

(a) A strong non-selective response for organics can be obtained in a field-emission argon ionization detector similar to that which was first observed in 1959 by Haahti and Nikkari².

(b) Selective responses for a variety of compounds such as acids and amines can be obtained in the presence of iodine vapor at voltages too low to achieve the non-selective response.

(c) Additional investigations of this iodine-doped detector with carrier gases other than argon or helium may lead to more sensitive selective responses.

(d) Further investigations of the non-doped field-emission argon (or helium) ionization detector may lead to the development of a sensitive non-selective detector with advantages similar to those of the photoionization detector.

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