

## Notes

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### The variation with polarising voltage of the response to methane, carbon dioxide and nitrous oxide, of a macro-argon ionization detector for gas chromatography

During an investigation into the physical processes governing the operation of argon ionization detectors for gas chromatography, response curves for methane, carbon dioxide and nitrous oxide have been obtained exhibiting unexpected characteristics. In a previous communication<sup>1</sup>, using a small argon detector (LOVELOCK<sup>2</sup>) connected to a capillary column, it was found that when sampling from a 3% v/v concentration of halothane, (2-bromo-2-chloro-1,1,1-trifluoroethane), irrespective of the detector purge flow inlet-to-anode separation, an increased response was always obtained if carbon dioxide or nitrous oxide was substituted for oxygen as the diluent in the halothane sample. However, when sampling from a 2% v/v concentration of di-ethyl ether, it was found that carbon dioxide or nitrous oxide always reduced the response of the chromatograph compared to oxygen. In both cases the resolution of the column was such as to give good separation of the gas peak from the respective vapour peaks.

LOVELOCK<sup>3</sup> reporting on his original macro detector quotes a small positive response to carbon dioxide, water and methane, the latter being the greater; however in describing smaller forms of detector<sup>2</sup>, apart from methane, no response was noted for carbon dioxide, water, oxygen and nitrogen.

The present results were obtained using a macro coaxial geometry detector of the simple LOVELOCK pattern<sup>2</sup>, manufactured to high dimensional accuracy. A 6 sq. cm 40 mC tritiated titanium source was incorporated within the electrode structure, the low surface density of emission being chosen to avoid space charge distortion of the electric field. Calculated values of the field strengths for a polarising voltage of 1000 V were  $5.8 \text{ V cm}^{-1} \text{ torr}^{-1}$  and  $0.6 \text{ V cm}^{-1} \text{ torr}^{-1}$ , at the anode and cathode surfaces respectively, these being low compared to values quoted for the micro argon detector<sup>5</sup>. The detector and its associated stainless steel pipe system at ambient temperature were purged with high purity argon at 100 c.c./min, prepared by a modified form of purification train described by BERRY<sup>6</sup>, and WILKINS AND WILSON<sup>7</sup>. The humidity was continuously monitored with an electronic hydrometer at the system exhaust and kept to below 2 p.p.m. (v/v). Periodic tests confirmed that oxygen and nitrogen levels were below 0.5 and 2 p.p.m. (v/v) respectively. The detector background current in the saturation plateau region from 200 V to 1000 V, had a finite slope of  $7 \cdot 10^{-13} \text{ A V}^{-1}$ . Low concentrations of gases and vapours could be produced in the argon carrier by a continuous slow injector<sup>9</sup>.

Fig. 1 illustrates for propane, the commonly recorded<sup>3</sup> response to organic vapours having ionization potentials less than the energy of the argon metastable atom. LOVELOCK<sup>2-4</sup> considers ionization of such molecules to occur as the result of energy transferring collisions with the 11.5 eV metastable state. Fig. 2 illustrates

the response for methane, exhibiting a reversal of sign with voltage increase. It is considered that this variation could offer an explanation for some of the previously reported, rather contradictory observations at unquoted field strengths. At low applied voltages, the positive responses for methane, carbon dioxide and nitrous oxide have similar form, carbon dioxide having nearly twice the response of methane and nitrous oxide.

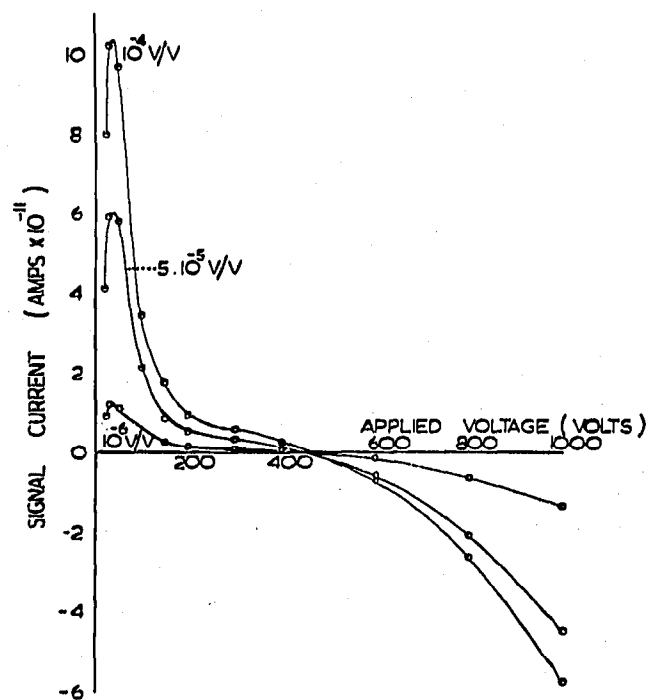
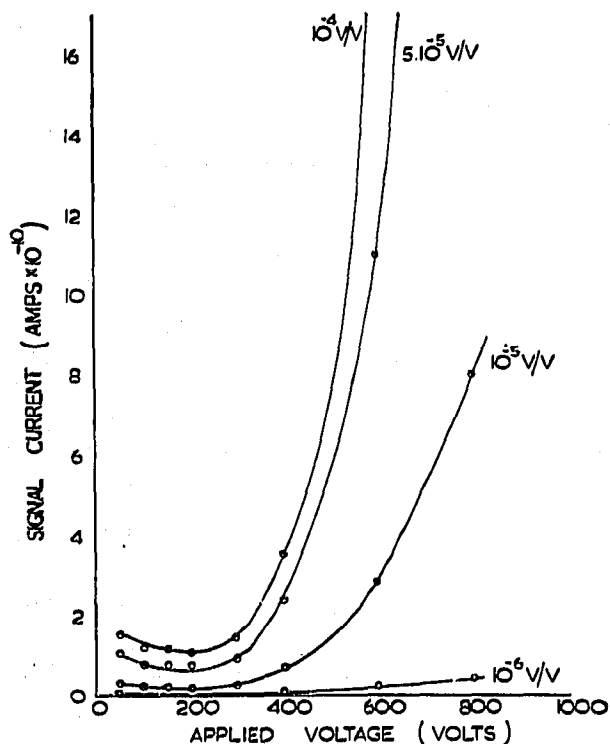


Fig. 1. Response *versus* polarizing voltage for an argon ionization detector to various concentrations of propane.

Fig. 2. Response *versus* polarizing voltage of an argon ionization detector to various concentrations of methane.

The negative response observed at the high voltage region is approximately identical for all three vapours. At 30 V, when the response for all three gases is a maximum, the response for carbon dioxide coincides with that for propane, considering a concentration of 100 p.p.m. (v/v).

Since the ionization potentials of methane, carbon dioxide and nitrous oxide, 12.98, 13.8, 12.9 eV, respectively<sup>10</sup>, are higher than the argon atomic metastable level, LOVELOCK predicts that no response to these substances should result. If they are present as an impurity with an ionizable organic, it is reported<sup>2</sup> that the efficiency of response to the latter is reduced through nonionizing collisions of the impurity reducing the argon metastable state population. However, SHARPE<sup>11</sup>, measuring ionization chamber currents resulting from complete absorption of alpha particles, observed that 2 to 5 % carbon dioxide added to argon produced an approximate 1% increase of current. COLLI AND FACCHINI<sup>12</sup>, studying argon mixture filled geiger counters at near atmospheric pressure, considered that the carbon dioxide quenched

the argon metastable level, resulting in resonant dissociation forming carbon monoxide.

STRICKLER AND ARAKAWA<sup>13</sup>, studying optical emission from argon mixtures under high density alpha particle bombardment, postulate the existence of a 14.5 eV excitation state of argon due to the observation of rapid quenching of a 2200 Å band by carbon dioxide and methane. HURST, BORTNER AND GLICK<sup>14</sup> also propose such a state having a sufficiently long lifetime to cause ionization of such added gases in argon. However, the existence of such a state could not easily explain the present results.

SHAHIN AND LIPSKY<sup>15</sup>, using a heated detector of small electrode separation, recorded results of some similarity to those of the authors. These they considered to be caused by the variation of the free electron drift velocity or by the formation of complex molecular ions. In the present results, it is likewise considered that since the positive response occurs predominantly in the recombination limited zone, a lowering of the primary electron temperature by inelastic collisions with the added gas molecules could lower the recombination coefficient, thus resulting in the current peak recorded, as the process would conceivably cease at saturation voltages.

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*Research Department of Anaesthetics,  
Royal College of Surgeons of England,  
Lincoln's Inn Fields, London W.C. 2 (Great Britain)*

D. W. HILL  
H. A. NEWELL

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