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NEW DESIGN FOR HELIUM IONIZATION DETECTION

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SUMMARY

A voltage pulse generator with variable width and interval adjust has been designed and coupled to a helium ionization detector to examine the response characteristics of sampling the detector cell's output current in a discontinuous mode. The pulser is capable of operating from 0 to 500 V at less than 1 kHz up to 333 kHz at the highest voltage. The response of the modified detector to a standard gas mixture containing Ne, H_2, Ar, O_2, N_2 and CH_4 has been examined as a function of frequency, duty cycle, and voltage. An inversion in the signal polarity for some gases was observed at certain frequency and duty cycle combinations. Noise and background current levels were significantly reduced in the pulsed mode as compared to d.c. operation. It has also been determined that the detector can be operated at higher voltages in the pulsed mode before the cell current breaks down.

INTRODUCTION

The helium ionization detector is one of the most sensitive detectors currently available for gas chromatography[1]. The detector is non-selective, meaning that it is capable of responding to all chromatographable species ranging from the permanent gases to complex organic molecules. Despite its universal response mechanism and high ionization efficiency, however, the detector has not been widely used. Factors which have contributed to its limited usage include the stringent requirements for high-sensitivity operation, instability, and variations in response for selected species as a function of chromatographic conditions[2]. The greatest sensitivity is obtained when ultrapure helium is used as the carrier gas and when contributions from the chromatographic system (*e.g.*, column bleed) to the background current are minimal[1,3–5]. Low parts-per-billion concentrations of the permanent gases can be determined under these conditions. In fact, the detector has primarily been used to analyze

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gases which can be separated on adsorption columns which have low bleed[1,3,6,7]. The universal response characteristic, which is largely an advantage, can also be troublesome, since any atmospheric diffusion in the system will reduce the sensitivity of the detector. Long periods of time may be required to stabilize the detector on initial start-up, when changing columns, or following any exposure of the system to the atmosphere. The response to the substrate or solvent may also be excessively large, requiring long periods between sample analyses in order to allow the detector to return to initial background conditions. When the detector is overloaded by high concentrations of an analyte, or if the background is high, anomalous peak shapes or polarity inversions may be obtained, making it difficult to interpret the results.

Despite these problems, there has recently been some renewed interest in the helium ionization detector. The characteristic negative responses for the permanent gases have been examined and conditions which invert the signals defined[5,8]. It was also determined that the detector could be operated in the saturation region of the field intensity with sensitivities comparable to those which can be obtained in the exponential region (*i.e.* greater than 350 V)[2]. This is due to a decrease in noise level and background current. These reductions in turn have allowed gas–liquid partition columns to be used with the detector which extends the applications to include higher-molecular-weight organics[2].

In the work reported here, modifications of an helium ionization detector which allow the output current to be sampled in a discontinuous mode by applying voltage pulses of short duration across the detector are described. The helium ionization detector has been previously operated only in a d.c. mode. Pulsed sampling techniques for the electron-capture detector have improved stability, eliminated anomalous and unreliable responses encountered in d.c. operation, and improved the linear dynamic range[9]. It also provides greater flexibility and control over the sensitivity. The response characteristics for the modified helium ionization detector were examined by analyzing a standard gas mixture at various frequencies and duty cycles. Advantages of operating the helium ionization detector in a pulsed mode are also discussed.

EXPERIMENTAL

Equipment

A Valco Model 100 H helium ionization detector was modified to operate in a pulsed mode. The detector has a coaxial cylindrical cell geometry and contains a 1 Ci scandium tritide source. A negative voltage was applied to the centered electrode and the electrometer was connected to the radioactive foil which served as the anode. The temperature of the detector was maintained at 60°C with a Valco ITC isothermal temperature controller. The detector was mounted on a Varian 3700 gas chromatograph equipped with a flame photometric detector electrometer. Separations were carried out on a 1.8 m × 2.1 mm I.D., 3.2 mm O.D. stainless-steel column, packed with Molecular Sieve 5Å (80–100 mesh). The column was operated isothermally either at 60°C or at room temperature. Ultrahigh purity helium (99.9999%, Scientific Gas Products) was used as the carrier gas at a flow of approximately 35 ml/min. A standard sample, containing 7.6 ppm H_2, 7.6 ppm CH_4, 8.0 ppm N_2, 7.5 ppm O_2, 7.5 ppm Ne, and 7.8 ppm Ar in ultrapure helium, was introduced into the column with

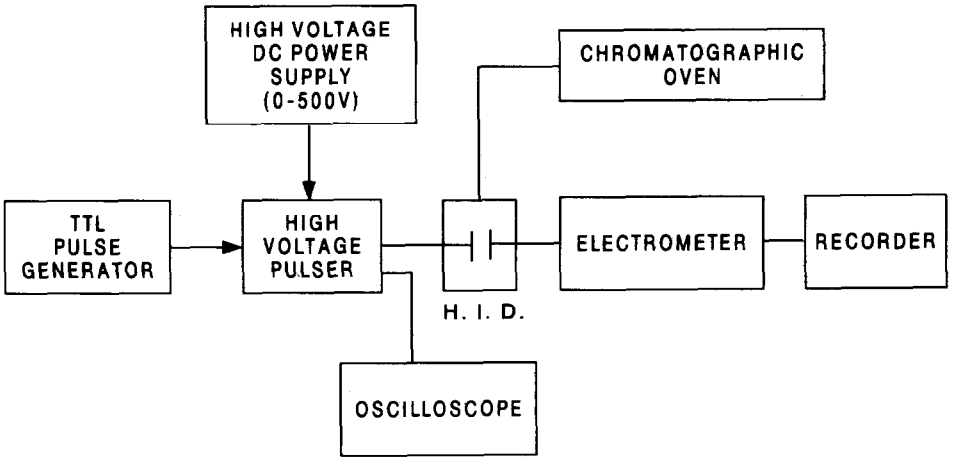

Fig. 1. Block diagram of the pulsed helium ionization detector (H.I.D.) system.

a Valco 8-port sample injection valve with 100-μl sample loops. The column was connected directly to the carrier gas tank through the injection valve, bypassing the flow controllers on the gas chromatograph.

A block diagram of the pulsed system is shown in Fig. 1. The helium ionization detector is driven in a fixed frequency mode by a high voltage pulser, which is gated by a transistor-to-transistor logic (TTL) pulse generator (Model 4001, Global Specialties, New Haven, CT, U.S.A.) and powered from an external high voltage d.c. power supply that is adjustable from 0–500 volts (Kepco, Flushing, NY, U.S.A.). Current through the detector was monitored with the flame photometric detector electrometer, the output of which was connected to a strip chart recorder. The time constants in the electrometer provide an integrated output from the pulses applied to the detector proportional to a d.c. current. The electrometer was also modified to allow direct readout of the bucking current. The pulse width and interval were monitored by a Tektronix T922 oscilloscope. Responses for the various gases were determined by measuring peak height.

High voltage pulser design

The high voltage pulser was developed specifically for the helium ionization detector to examine response characteristics of the detector as a function of pulse width, frequency, and amplitude. It is capable of providing up to 500 V negative pulses with widths ranging from 150 nsec to d.c. conditions. At 500 V, the pulser is limited to a maximum frequency of 333 kHz due to the current limitations of the high voltage power supply (40 mA) and the power dissipated in the output devices. At lower voltages, however, it can be operated at slightly higher frequencies.

A block diagram of the high voltage pulser is shown in Fig. 2. The circuitry consists of dual-gate drive channels to switch the output either to ground or to the negative high-voltage level. To drive high-voltage pulses of various widths requires d.c. coupling at the output. The output devices are complementary MOSFET transistors that have 500 V breakdown ratings. The "on" resistance of these devices is quite low (3 Ω), and they exhibit no charge storage effects typical of bipolar devices

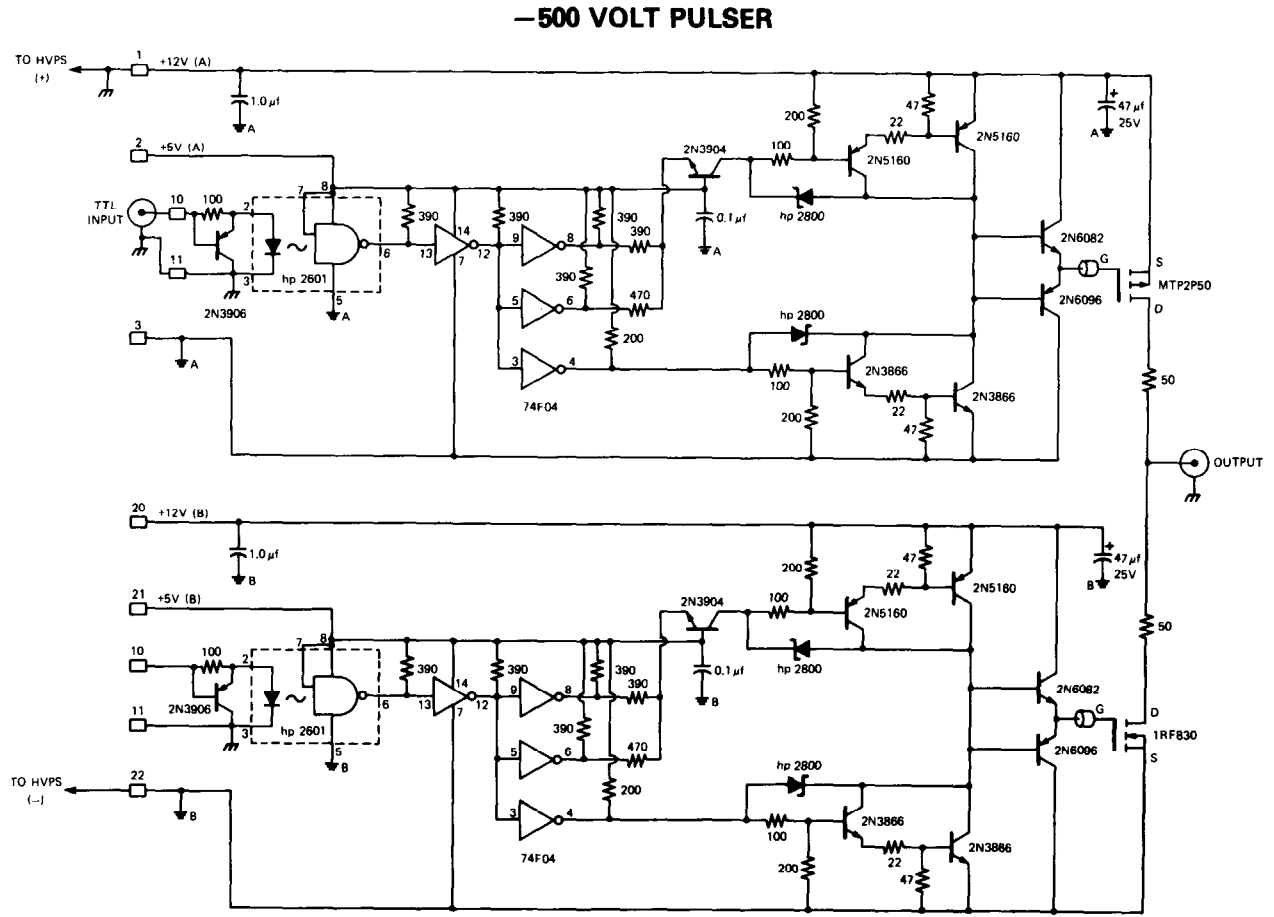

Fig. 2. Schematic diagram of the high voltage pulser.

to impair switching speed. The rise time is 50 nsec due to cable plus detector capacitances. The output devices are driven out of phase, so that only one device is on at a time. The input gate capacitance of the MOSFET is large (600 pF), requiring a high-current driver to switch the gate quickly.

Optoisolators are used on the input to provide level shifting to the complementary drivers. Drive circuits to the output MOSFET are essentially identical. They take the optoisolator level-shifted TTL output and provide a fast, high-current drive to the gate of the output MOSFET. The drive circuitry is fully complementary with non-saturating Darlington inverters, coupled to the MOSFET gates through bipolar radio frequency (RF) power transistors operating in a common collector configuration.

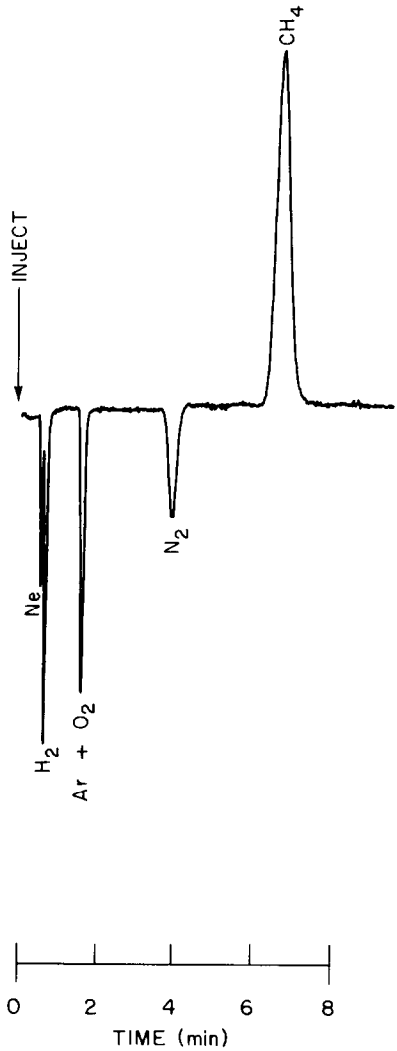

Fig. 3. Detector response to standard gas mixture. Column temperature, ambient. Frequency, 20 kHz; duty cycle, 80%; 350-V pulses.

The drive circuits in the high voltage pulser are extremely fast, high current, and non-saturating. The voltage applied to the detector is not distorted or reduced in amplitude by the loading effects of the cable and detector capacitance because of the low output impedance of the pulser. Overall, the high voltage pulser allows high frequency operation at high voltages.

RESULTS

The response of the detector to the standard gas mixture was examined at various frequencies and duty cycles at various voltages. The chromatogram shown in Fig. 3 was obtained at 350 V, 20 kHz and 80% duty cycle. The response to Ne, H_2, Ar + O_2, and N_2 was negative, which is characteristic of the helium ionization detector when ultrapure helium is used as the carrier gas[5]. Argon and O_2 were not resolved on the analytical column used. The magnitude of the response for CH_4 was approximately 50% of that obtained at 350 V d.c., while the other gases gave about

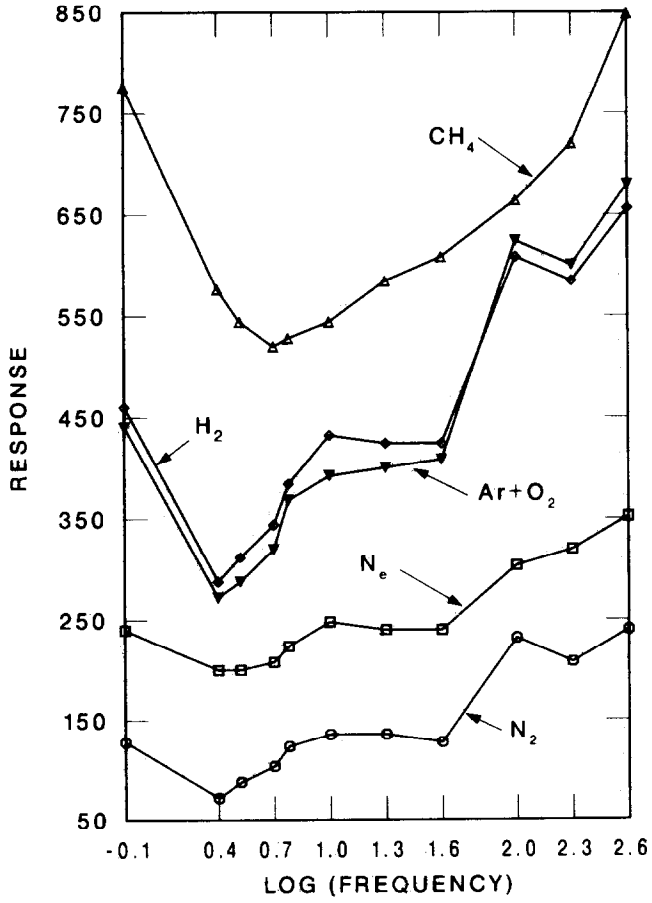

Fig. 4. Response of Ne, H_2, Ar + O_2, N_2, and CH_4 as a function of frequency. Duty cycle, 80%; 350-V pulses. Data collected with column at room temperature.

30% of their response at d.c. conditions. The noise level, however, was substantially reduced in the pulsed mode (*i.e.* by a factor of 3 under the given conditions) and the background current was approximately halved.

Frequency effects were examined from 0.8 to 400 KHz at 80% duty cycle with 350-V pulses at the detector. The results shown in Fig. 4 indicate that an enhanced response for all the gases examined is obtained at high frequencies or at the low frequency (0.8 kHz). Noise levels in all cases were less than in the d.c. mode, although they increased with decreasing frequency. At the lowest frequency examined (0.8 kHz), the pulse width is relatively large (1 msec), and under this condition, the response of the detector may have more d.c. character, resulting in higher noise levels and greater magnitude of response. At 400 kHz, CH_4 gave 76% of the d.c. signal and the noise level was reduced by 50%.

The effects of duty cycle within a narrow range of frequencies (5, 10, 20, and 40 kHz) were also examined at 350 V. For this set of studies, the column was operated at 60°C. The results for CH_4 and N_2 are shown in Figs. 5 and 6, respectively. Re-

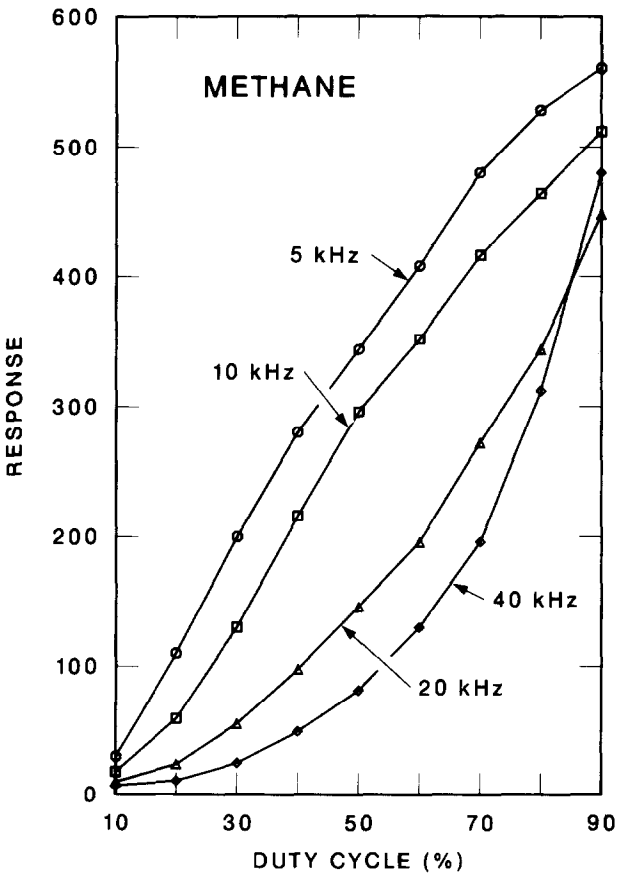

Fig. 5. Response of methane as a function of duty cycle and frequency. Column temperature, 60°C; 350-V pulses.

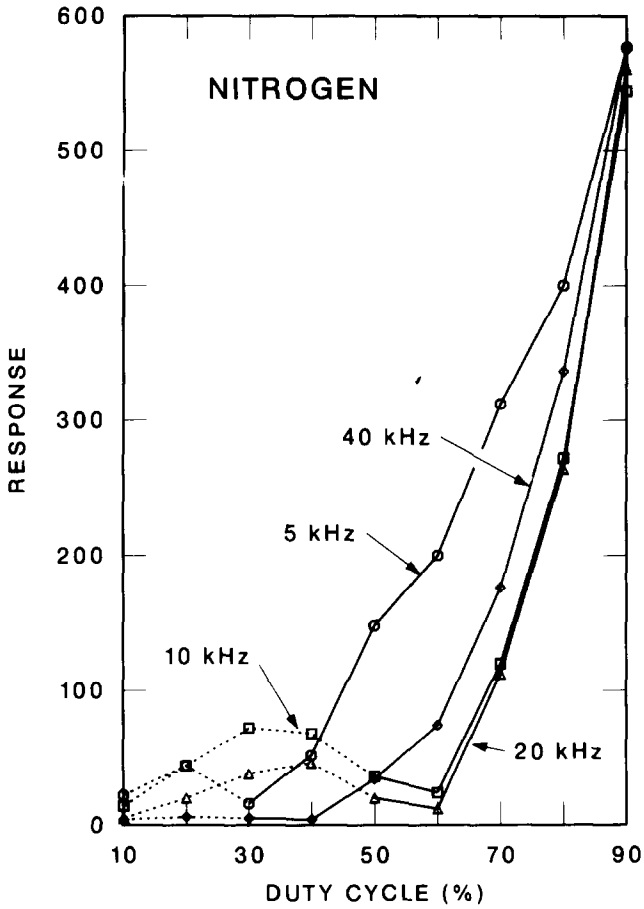

Fig. 6. Response of nitrogen as a function of duty cycle and frequency. Conditions as in Fig. 5. Dotted lines correspond to inverted (positive) signal; solid line, negative signal.

sponse curves for Ar + O_2 and H_2 were similar to N_2. Above 50% duty cycle, Ne also resembled N_2, while at lower values, measurements could not be obtained due to changes in the H_2 signal and the incomplete separation between these 2 peaks. Methane clearly increased in response as the duty cycle was increased at all frequencies. At 5 and 10 kHz, the increase was relatively linear, while at 20 and 40 kHz, the increase was exponential. The lower frequencies within this set also provided greater signals for a given duty cycle. For a given pulse width, however, the response was greater at the higher frequencies. For the remaining gases at high duty cycles (80 to 90%), the responses were similar, irrespective of frequency. At the lower duty cycles, some interesting and unexpected results were obtained. N_2 and Ar + O_2 were found to change polarity from their normal negative signal to positive. Hydrogen also showed inversion, although the lack of resolution between H_2 and Ne makes it difficult to determine whether the response for H_2 is fully positive with Ne remaining negative or whether H_2 and Ne have some bipolar character. A chromatogram show-

ing the inverted signals, obtained at 350 V, 30% duty cycle and 10 kHz, is shown in Fig. 7. Within the set of conditions examined, the lowest negative response for Ne, H_2, Ar + O_2, and N_2 was obtained at 30 or 40% duty cycle, 40 kHz, and the greatest positive response (or bipolar in the case of Ne and H_2) was obtained at 30% duty cycle, 10 kHz. Signal inversions in Fig. 6 are indicated with dotted lines.

Conditions under which changes in polarity could be obtained were further examined by varying the frequency from 2 to 160 kHz at different duty cycles. Reversals for one or more peaks occurred only within the range of 3 to 45 kHz when the duty cycles were less than 60% and when the analytical column was operated at

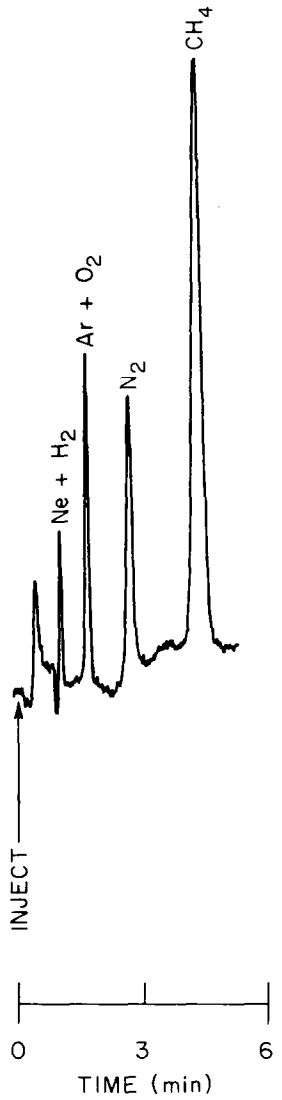

Fig. 7. Detector response to standard gas mixture. Column temperature, ambient. Frequency, 10 kHz; duty cycle, 30%; 350-V pulses.

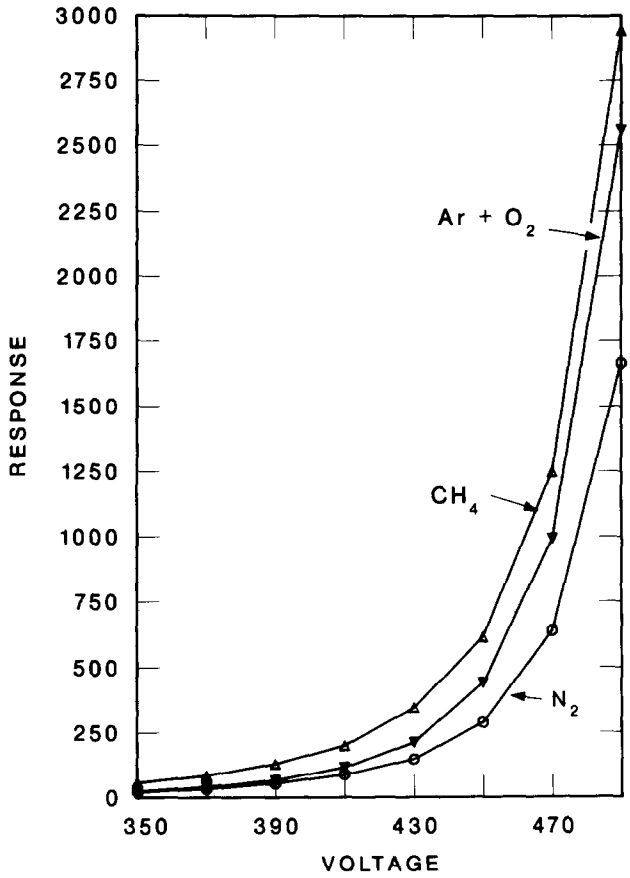

Fig. 8. Response of N_2, Ar + O_2, and CH_4 as a function of voltage. Frequency, 5 kHz; duty cycle, 20%. For comparison with other curves, response value should be increased by factor of 2.

greater than room temperature. The magnitude of the inverted responses also increased exponentially with increasing voltage, as shown in Fig. 8. These data were collected at 5 kHz, 20% duty cycle. When the detector was operated with d.c. conditions the typical volt–ampere curve for the helium ionization detector was obtained[2]. For a given set of pulsed conditions, the same type of curve was obtained, except that the three regions (collection, saturation, and multiplication) were shifted to higher voltages. In the pulsed mode the helium ionization detector could also be operated up to 500 V for some frequencies and duty cycles, while in the d.c. mode the detector was found to breakdown at 460 V.

DISCUSSION

Modification of the helium ionization detector to operate in a pulsed rather than a d.c. mode has led to some significant and interesting results. The noise and background current levels were substantially reduced in the pulsed mode. It was also determined that the detector could be used at higher voltages before the cell current

would break down. Since the response increases exponentially at higher voltages, operation under these conditions may provide significant increases in sensitivity. Detection limits for the gases analyzed are currently being determined so that the exact effects on sensitivity can be ascertained. Some trends, however, for pulsed operation were noted. The highest response for all gases was obtained at high frequencies and at high duty cycles.

Sampling the detector's output current in a pulsed mode also resulted in an unexpected inversion in the signal polarity for H_2, Ar + O_2, and N_2 at certain frequency and duty cycle combinations. Although the mechanism responsible for the inversion phenomenon is not understood at this time, it seems likely that the impurity or background level in the detector is largely responsible for the reversals. They occurred only at elevated column temperatures where the background current was relatively high. It has been previously determined that, if the carrier stream to the detector is doped with low concentrations (ppm) of some additives, the signal polarity for H_2, Ar, O_2, and N_2 can be inverted to positive[5,8]. While low levels of these gases can be satisfactorily quantitated in the negative mode, the upper detection limit is only approximately 100 ppm[5]. Higher levels produce deformed W-shaped peaks. When the peaks are inverted to positive, the upper detection limit improves. The maximum analyzable concentration then depends upon the type of dopant and the level at which it is added to the carrier. H_2, N_2, O_2, and Ar have been used as additives. There are several disadvantages to increasing the upper detection limit of the helium ionization detector in this manner, however. The addition of a dopant requires some calibration and is time-consuming. It also makes it difficult to analyze samples for the added gas. Operating the helium ionization detector in a pulsed mode, however, may provide a means of readily inverting the signal polarity of the gases that normally provide a negative response. Depending upon the analytical requirements, the response may be easily adjusted to cover a broad range simply by varying the frequency and/or duty cycle.

Pulsed operation for another ionization detector, the electron-capture detector, was described over two decades ago[10]. The resulting improvements in signal reliability, linearity, and stability were so marked that most electron-capture detectors are now operated in either a fixed pulse or variable pulsed constant current mode. Although the electron-capture and helium ionization detectors operate on different principles, it appears that pulsed operation may also have distinct advantages for helium ionization detector's performance. The preliminary findings reported here suggest an increase in sensitivity, linearity, and stability. The pulser which was developed for this work, unlike the electron-capture detectors, is capable of operating at high voltages. It also provides the operator broad control over the detector's output.

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