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OPTIMIZATION OF HELIUM IONIZATION DETECTOR

F. ANDRAWES* and P. DENG

American Cyanamid Company, Chemical Research Division, 1937 West Main Street, P.O. Box 60, Stamford, CT 06904 (U.S.A.)

SUMMARY

The helium ionization detector has been operated at a relatively wide range of temperatures, flow-rates, and applied potentials. We used response-surface methodology to determine the optimum operating conditions for this sensitive detector.

We investigated the temperature range between 75 and 175°C, flow-rates between 5 and 35 ml/min and applied potentials between 450 and 625 V. The response to H_2, Ar, O_2, N_2, CH_4 and CO was examined.

The response to all of these gases was optimized at a detector temperature of 150°C, applied potential of 550 V and flow-rate of 5 ml/min. The characteristic negative response H_2, Ar, O_2, and N_2 was inverted to positive at a flow-rate of 5 ml/min.

INTRODUCTION

The helium ionization detector is the only universal gas chromatographic (GC) detector that is capable of detection in the ppb* range. In spite of the universitility and the high sensitivity of this detector, its use has generally been limited to the analysis of high-purity gases with packed columns. A few other applications have been reported, including the analysis of liquid samples with capillary columns[1,2].

The lack of popularity of this detector stems from insufficient understanding of its mechanism and its operating parameters. The ionization mechanism known as the Penning effect depends on the transfer of the excitation energy of the metastable helium (19.8 eV) and any other atom or molecule eluted from the analytical column[3]. This should provide an increase in the ionization current for all atoms and molecules except neon (ionization potential 21.5 eV). Unfortunately, this mechanism does not explain the decrease of the ionization currently obtained for H_2, Ar, O_2 and N_2. This negative response depends on operating conditions that have not yet been fully explored[4–6].

The factors that affect the detector's signal include carrier gas purity, temperature, flow-rate, applied potential, pressure, chromatographic column, geometry of the cell, and the activity of the radioactive source. Among these parameters the applied potential, flow-rate, and detector's temperature are often varied by the users.

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* Throughout the article the American billion (10^9) is meant.

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Carrier gas purity is one of the most important factors that influence the detector response. The effect of helium purity on the detector response, signal polarity, and linear dynamic range has been reported[4,5]. But operating this detector with an absolutely pure carrier gas may be hard to achieve.

The helium ionization detector has been operated at a wide range of parameters. The applied potential varies between 20 and 700 V, and the flow-rate varies between 20 and 80 ml/min. The detector temperature varies between ambient temperature and 200°C. In this work, we investigated the detector's optimum flow-rate, applied potential, and temperature under 31 different experimental conditions. We used an empirical quadratic response surface model to fit these data.

EXPERIMENTAL

We used a Carlo Erba HRGC 5300 gas chromatograph (Erba Instrument, Milan, Italy). The chromatograph was equipped with a flame ionization detector and a helium ionization detector. The helium ionization detector has a parallel electrode geometry. The bottom electrode contains 200 mC tritium foil. The chromatograph was fitted with a gas sampling valve and 150-μl sample loops.

Three columns were used in this work, and were packed with molecular sieve 5A, 80–100 mesh. The columns were of the following dimensions: (1) 16 ft. × 0.125 in. O.D., (2) 6 ft. × 0.125 in. O.D., and (3) 2 ft. by 0.062 in. O.D. The columns were conditioned at 150°C and operated at different temperatures. The analytical columns were operated at constant flow-rates. The detector's total flow was varied by changing the flow-rate of the make-up gas. The helium used as a carrier gas and that used for make-up were from the same cylinder. The carrier gas was a Matheson high-purity grade, and was further purified over a Supelco purifier.

We used a standard gas mixture, supplied by Matheson, containing 72 ppm H_2, 9 ppm Ar, 10 ppm O_2, 20 ppm N_2, 12 ppm CH_4, and 14 ppm CO in helium.

The detector signal was recorded on a HP-3357 Lab Automation System and on an Omega strip chart recorder at 1 mV full scale. The net detector response was calculated by dividing the peak height by the noise level in mm. The regression analysis program was run on a VAX/785 computer. However, the contour plotting program was run on a DEC-10 computer and a Calcomp 1012 plotter.

RESULTS

We investigated the response to H_2, Ar, O_2, N_2, CH_4 and CO, and found that changing the operating parameters changed the polarity of the response to H_2, Ar,

TABLE I

LEVELS FOR OPERATING VARIABLES

Coded level	*Applied potential (V)*	*Temperature (°C)*	*Flow-rate (ml/min)*
−1	450	75	17
0	500	125	25
+1	550	175	33

O_2 and N_2. This hindered the systematic study of these gases. The response reported here will be limited to the measurement of CH_4 and CO. The optimum response to H_2, Ar, O_2, and N_2 will be reported and discussed later in the text.

Based on previous work[4,5], we selected three levels for each of three operating variables (applied potential, temperature, and flow-rate). These levels are shown in Table I.

We used a Box and Behnken three-level design[7] to investigate the relationship between three operating variables and two responses. Initially, thirteen experiments were performed in a random sequence. For lack of replicated analyses (center points) to provide a measure of experimental error, eighteen additional analyses were obtained. This also reduces the 95% confidence limits of the predicted response. The total number of experiments was thirty-one, and they are listed in Table II.

TABLE II

DESIGNED EXPERIMENTAL DATA

Run no.	*Operating variables*			*Responses*	
	Temp.	*Voltage*	*Flow-rate*	*CH_4*	*CO*
1	−1	−1	0	11	5
2	−1	1	0	64	20
3	1	−1	0	42	22
4	1	1	0	166	70
5	−1	0	−1	32	16
6	−1	0	1	25	11
7	1	0	−1	104	50
8	1	0	1	75	33
9	0	−1	−1	52	25
10	0	−1	1	37	17
11	0	1	−1	270	122
12	0	1	1	132	60
13	0	0	0	56	48
14	−1	1	1	52	28
15	−1	−1	1	20	10
16	−1	0	0	26	14
17	−1	1	−1	61	28
18	−1	−1	−1	9	4
19	0	0	1	86	58
20	0	1	0	160	76
21	0	−1	0	46	21
22	0	0	−1	173	77
23	1	1	1	100	46
24	1	−1	1	38	16
25	1	0	0	85	37
26	1	1	−1	192	90
27	1	−1	−1	62	25
28	0	1	0	164	80
29	0	1	0	164	76
30	0	1	0	168	84
31	0	1	0	156	72

TABLE III

SIGNIFICANCE OF OPERATING VARIABLES

Response	R^2 *(%)*	*RMS*	*Level of significance (%)*
CH_4	89	648.1	>99.9
CO	91	112.2	>99.9

An empirical quadratic response surface model used to fit these data

$$Y = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} \sum_{j \geq i}^{3} b_{ij} X_i X_j$$

where Y is the appropriate response, CH_4 or CO; X_1 is voltage; X_2 is temperature; X_3 is flow-rate; b_0, b_i and b_{ij} are the parameters to be estimated by least squares.

Both linear and quadratic effects of all these operating variables were highly significant. The percentage of the total variation explained by the model (R^2), residual mean square (RMS) and the level of significance of the fitted model are shown in Table III.

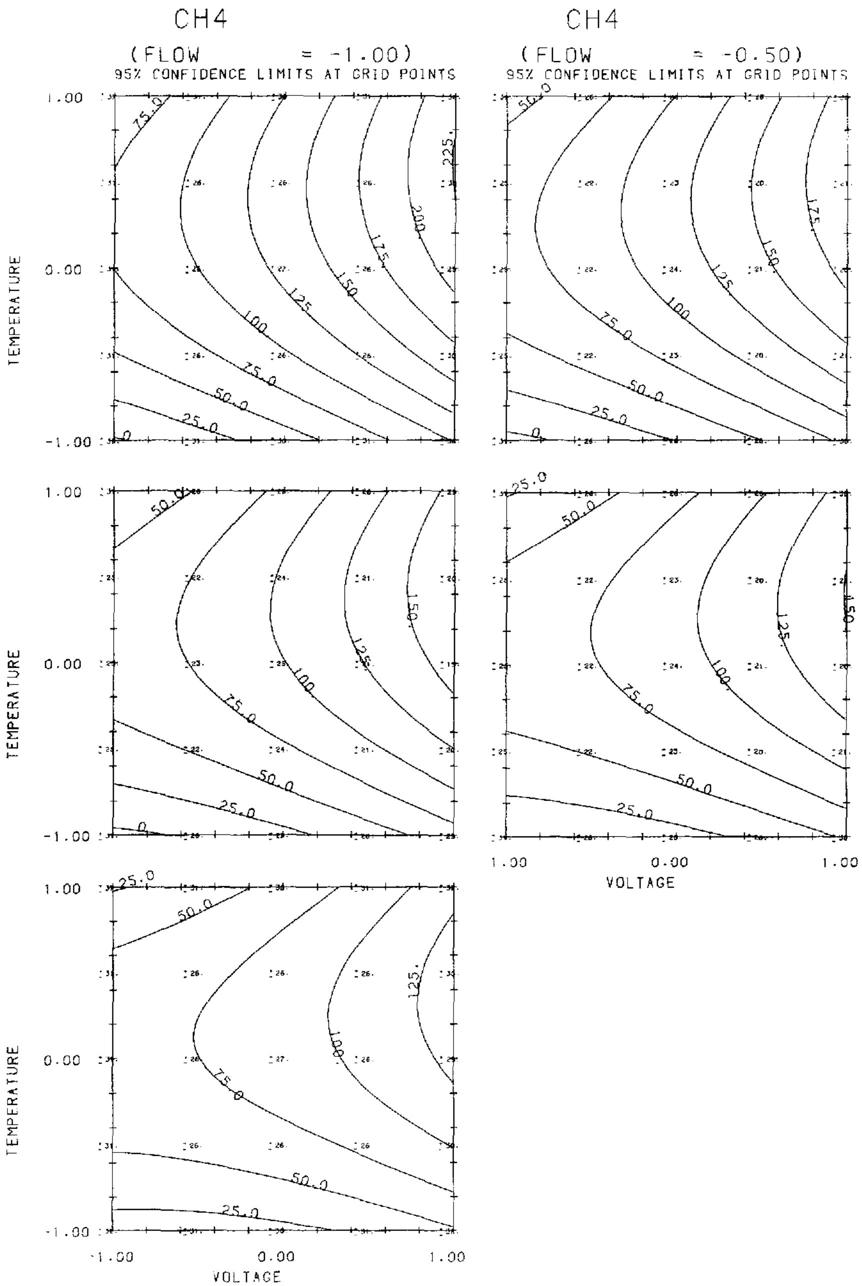
To represent the regression analysis, contour plots were made and are shown in Figs. 1 and 2. The figures show the nature of the estimated response. The values indicated by the graphs are the best estimates of the response for a given set of conditions for the operating variables. To indicate the reliability of the predicted values, half-widths of the 95% confidence limits of a predicted response are included in a 5 × 5 grid on each of these graphs. To illustrate their use, for CH_4 (second left graph in Fig. 1) at the coded level conditions: X_1 = voltage = 0.0, X_2 = temperature = 0.0, and X_3 = flow-rate = 0.0, the predicted CH_4 response is 100. The small ± 25 variation indicates that we are 95% confident that the average CH_4 lies in the interval 100 ± 25.

From the contour plots, the helium-ionization detector response is maximized at a voltage of about 550 V, a temperature between 125 and 175°C, and a flow-rate of 17 ml/min. The effect of the detector's flow-rate and applied potential are more important than the temperature effect. It seems also that further increase in applied potential and further decrease in the detector flow-rate could be investigated.

We increased the detector's applied potential to 625 V, but this was accompanied by short-term noise and the detector response was not stable. On the other hand, decreasing the detector flow-rate to 5 ml/min increased the detector's absolute response as shown in Figs. 3 and 5. Operating the detector below 5 ml/min was not practical in this investigation.

DISCUSSION

With regard to flow-rate, GC detectors can be classified by their mechanism of operation as concentration dependent, mass flow dependent, or a combination of both. For a concentration-dependent detector, the detector response has an area response inversely proportional to the volume of the carrier gas eluted with the sam-



ple. For a mass flow-rate detector, the response is theoretically independent of the volume of the carrier gas eluted with the sample, but the carrier gas flow-rate cannot be changed by more than 25% without re-optimizing the detector.

The mechanism of the helium ionization detector combines features of both

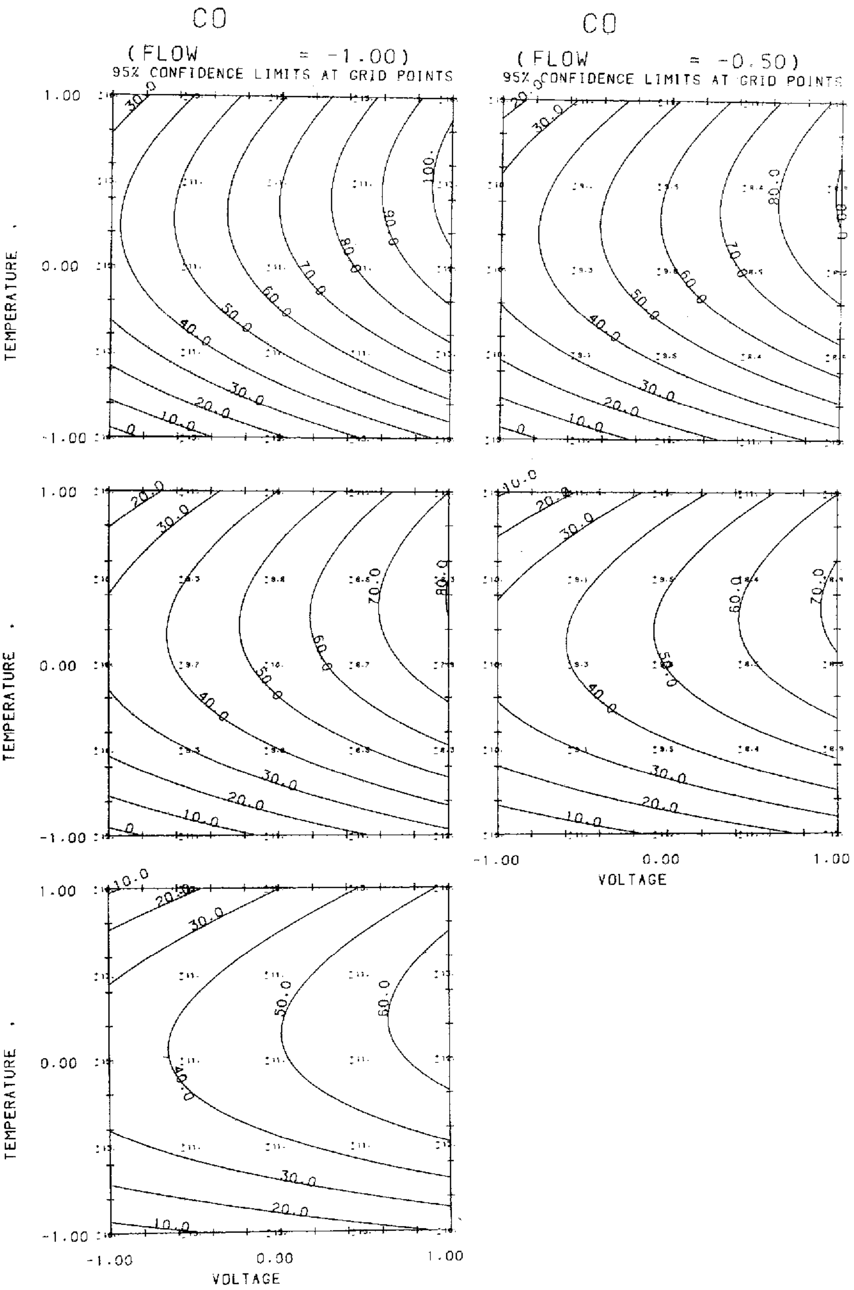


Fig. 2. Response contours to carbon monoxide.

mass flow dependence and concentration dependence. The detector's response should increase with decreasing the flow-rate, but the practical flow-rate is limited by the GC conditions and the design of the detector. If the detector is completely sealed against the atmosphere, it can be operated at a very low flow-rate, as in the case of

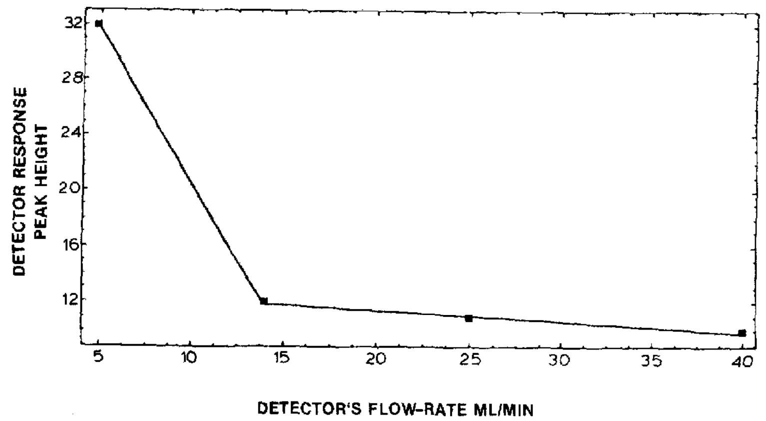


Fig. 3. Effect of flow-rate on detector response to carbon monoxide.

this work. Any increase in flow-rate decreases the detector's response. If the detector is not completely sealed against the atmosphere, a minimum flow-rate is required to minimize atmospheric diffusion. After this minimum flow is achieved, any increase in the detector's flow will decreasse the detector's response.

Fig. 3 shows the effect of flow-rate on the detector's response to CO. Fig. 3 is typical for a detector that is sealed against the atmosphere. Fig. 4 shows a hypothetical curve for a detector that is not fully sealed against the atmosphere[8,9].

Fig. 3 shows an initial high slope at a flow-rate below 12 ml/min and low slope at higher flow-rates. This may suggest that at low flow-rates the concentration dependency mechanism prevails but at higher flow-rates the mass flow-dependence mechanism prevails.

Decreasing the detector's flow-rate decreased the magnitude of the negative response to H_2, Ar, O_2 and N_2. At a flow-rate of about 5 ml/min the response to

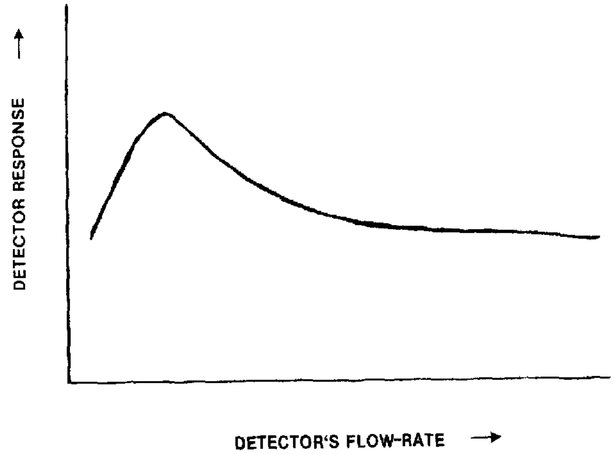


Fig. 4. Hypothetical effect of flow-rate on detector response for a detector that is not fully sealed against the atmosphere.

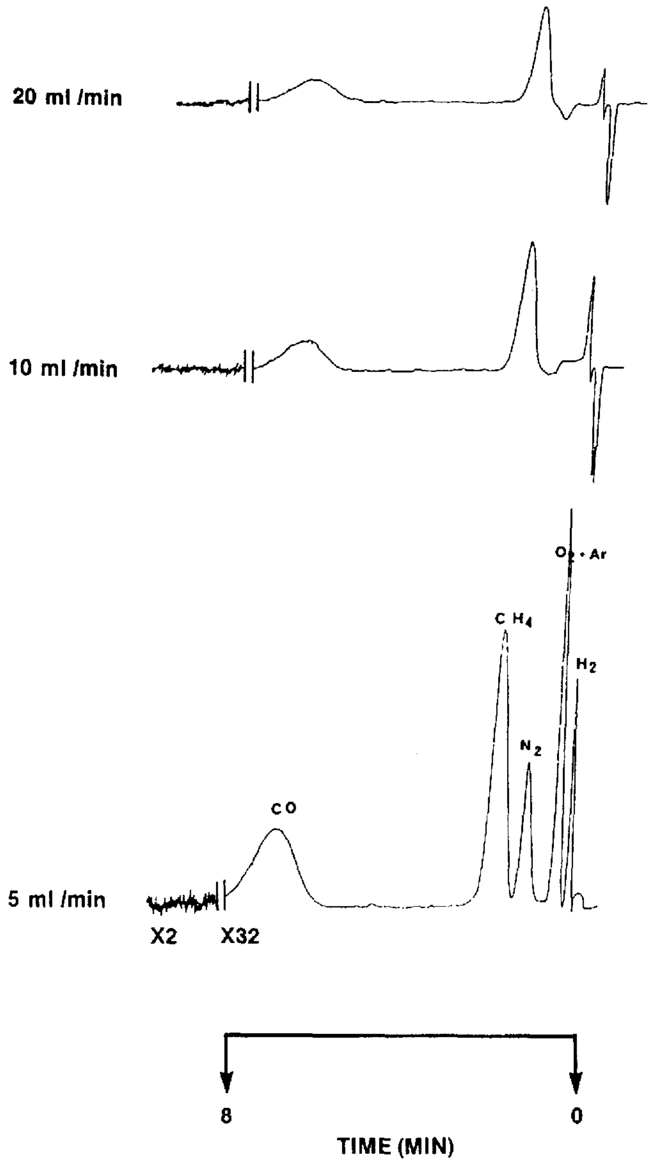


Fig. 5. Detector response to standard mixture at different detector flow-rates. Column 2 ft. × 0.06 in. O.D., packed with molecular sieve 5A, temperature 20°C.

these gases is fully positive, as shown in Fig. 5. Inversion of the response to these gases has previously been achieved by adding small concentrations of these gases to the helium carrier gas[4,5]. From this work, it seems that the same result can be achieved by decreasing the detector flow-rate. In addition, at flow of 5 ml/min the detector's response to these gases was maximized.

If the inversion in polarity observed in this work is a result of atmospheric diffusion through the detector cell, the response to CH_4 and CO would have decreased[4] instead of increased as shown in Fig. 4. The inversion in polarity at low flow-rate is probably the result of increasing the residence time of these gases in the detector cell. It is possible that at low flow-rate the Penning effect prevails, while at higher flow-rate other mechanisms, such as electron capture, electron mobility, and cross-section mechanisms may compete to produce the negative response.

Helium ionization detection (HID) dependence on the applied potential has been previously reported[10]. Normally the detector is operated at high voltage, *i.e.*, in the multiplication region of the volt–ampere curve (about 400 V), but it has also been operated at low voltage, *i.e.*, in the saturation region of the volt–ampere curve (20–200 V)[2]. Good sensitivity has been reported at both low and high voltages.

The optimum applied potential depends on the cell geometry, the stability of the electronic circuits, and the polarization voltage source. At high applied potential, the noise level and the detector's response are especially dependent on the stability of the power supply, but at low applied potential the noise level and the detector's response are independent of the power supply.

In this work, the detector response was maximized at 550 V. Above this level the high-frequency noise level was acceptable, but short-term noise was high. At such high voltage the back-ground current is extremely dependent on flow-rate and voltage fluctuation. If the short-term noise can be reduced, this detector can be operated at higher voltage and greater sensitivity.The detector temperature has not been fully studied. Most of the HID systems utilize tritium foil as a radioactive source. The safety limit for this source is between 180 and 200°C. We found that the maximum response was obtained at a detector temperature between 125 and 175°C. Maintaining the detector at this temperature is also important in keeping the detector clean. This source limits the upper temperature to 200°C, but other sources, not yet tested for HID applications, have allowed a temperature limit of up to 350°C[11].

We investigated the stability of this detector over a period of one day and nine days. Table IV shows the relative standard deviation (R.S.D.) of 16 analyses of the standard mixture in a period of 8 h. The pooled standard deviation of nine days is also shown in Table IV.

The numbers reported in Table IV shows a high precision for such a small concentration. The numbers reported for Ar + O_2 and N_2 are higher than the rest of the gases. This is probably due to a small atmospheric leakage through the gas sampling valve.

The work we report here should facilitate operating this detector at maximum sensitivity, and should help in designing better detectors. If a new helium ionization

TABLE IV

PRECISION OF THE HID RESPONSE

Gas	*Concentration (ppm)*	*R.S.D. in 8 h (%)*	*R.S.D. in 9 days (%)*
H_2	72	1.1	3.6
Ar + O_2	19	2.3	7.6
N_2	20	2.0	6.6
CH_4	12	0.8	3.2
CO	14	1.0	3.5

detector were designed with a very small volume and a very small flow-rate, the response would be high and positive to all gases and compounds.

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