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## EFFECT OF THE SENSITIVITY SETTING OF A KATHAROMETER ON RESPONSE FACTORS AT LOW CONCENTRATIONS

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### SUMMARY

A device and procedure are described that permit the easy and precise determination of calibration graphs for the quantitative analysis of gases by gas chromatography. The study focuses on the role of the sensitivity of the thermal conductivity detector on the response data, especially when small amounts of gases are to be detected ( $< 10^{-6}$  mole). At low sensitivity the response factors for all the gases studied ( $H_2$ ,  $N_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $C_2H_4$  and  $C_4H_{10}$ ) were found to vary with the molar amounts of compound injected. No variation of the relative responses was noted at the normal sensitivity levels except for hydrogen, which exhibited an anomalous chromatographic behavior.

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### INTRODUCTION

Theoretical<sup>1,2</sup> and experimental<sup>3</sup> methods have been proposed for calculating response factor values in gas chromatography. Tabulated response factor data for a number of pure compounds are also readily available, which can be used with either flame-ionization or thermal conductivity detectors<sup>4-6</sup>. Variables such as carrier gas and carrier gas flow-rate, detector operating temperature, sample concentration, individual sensing unit and recorder attenuation have been studied as a function of the response factors<sup>7-9</sup>. Much less attention however, has been given, to the effect of the detector sensitivity on the relative response data. The object of this work was to determine whether sensitivity could affect the relative responses obtained for the major non-condensable gases ( $H_2$ ,  $N_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $C_2H_4$  and  $C_4H_{10}$ ) originating from the vacuum pyrolysis of solid fuels and which were injected in small amounts ( $10^{-5}$ – $10^{-5}$  mole) into the gas chromatograph.

### EXPERIMENTAL

#### *Apparatus and materials*

A diagram of the apparatus is illustrated in Fig. 1. The main components are a Hewlett-Packard (HP) 5730A gas chromatograph equipped with an HP hot-wire detector coupled to a HP 3380A integrator, a Perkin-Elmer Fluon Rotor gas sampling

valve (catalogue No. 454-0104), equipped with a 1-ml sampling loop, and MKS Baratron Type 220 electronic manometers with digital readout. Two-way Nupro bellow valves and three-way Whitey ball valve were used in the design. All of the test gases used were of the highest purity available and were provided by Liquid Carbonic Canada, Sherbrooke, Quebec, Canada.

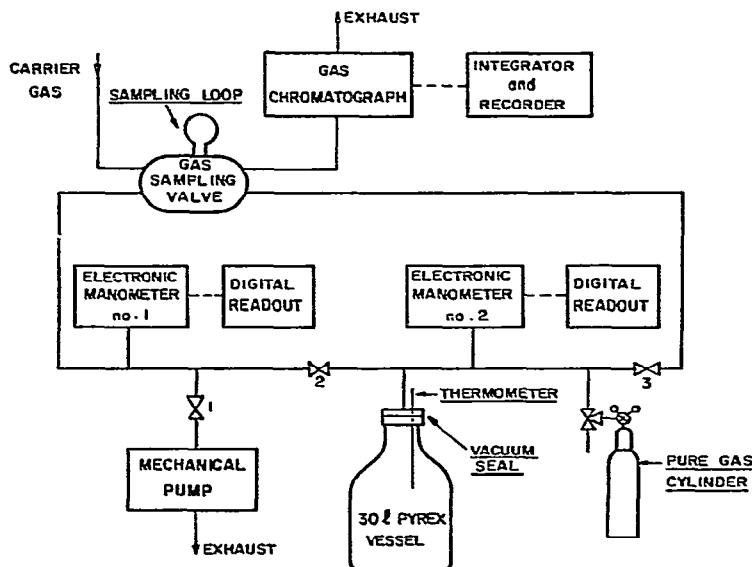


Fig. 1. Calibration apparatus for GC analysis.

The gas chromatograph is equipped with a switching valve to permit the use of two columns for the analysis. The mixture passes through a 1.83 m  $\times$  3.2 mm O.D. stainless-steel column packed with 80–100-mesh Porapak Q and a 1.37 m  $\times$  3.2 mm O.D. stainless-steel column packed with 60–80-mesh molecular sieve 5A. The carrier gas is a 8% (v/v) mixture of hydrogen with a flow-rate of 25 ml/min.

### Procedure

The gas to be calibrated is first transferred from the high-pressure cylinder to a previously evacuated ( $< 10^{-1}$  torr) 30-l Pyrex vessel. This enables precise control of the sample pressure to be injected into the gas chromatograph. Before sampling the gas, the stainless-steel line and the gas sampling loop are evacuated using a mechanical pump through valve  $V_1$  while valves  $V_2$  and  $V_3$  remain closed. Once the vacuum is established,  $V_1$  is closed and the gas is admitted into the sample loop by opening  $V_3$  until the desired pressure is attained. The pressure is then read directly at the manometer head  $M_1$ . Thus a known volume of gas at a known pressure and temperature is injected in the gas chromatograph. The pressure was varied in the range 0.3–223 torr, depending on the compound being analysed, which corresponded to molar amounts between  $1.6 \cdot 10^{-8}$  and  $1.2 \cdot 10^{-5}$  mole. Mixture of gases were prepared by adding successively the individual components, while noting the partial pressures, into the receiving vessel with the manometer head  $M_2$ .

When the gas is injected, the Porapak Q and molecular sieve 5A columns are in series. After elution of the hydrogen, the polarity is changed and the Porapak Q is isolated to permit separation of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO on the molecular sieve column. After the elution of the last gas present on the molecular sieve, the carrier gas is switched back to the Porapak Q for the analysis of CO<sub>2</sub>, light hydrocarbons and a few other components.

The analysis of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO is effected isothermally at 40°C. For the other gases eluting on the Porapak Q column, the temperature is kept isothermal at 40°C for 4 min and is then raised to 200°C at a controlled rate of 8°C/min.

The gas chromatograph was run at two different sensitivity levels which corresponded to the longer life (low sensitivity) and the medium life (normal sensitivity) expectancy of the detector. Low sensitivity of the katharometer was obtained by setting the bridge current to 200 mA with the temperature of the detector controlled at 150°C. Normal sensitivity corresponded to a current of 275 mA while the temperature of the detector was decreased to 110°C. The attenuated signal output from the detector was displayed on a 4-64 mV span recorder. The slope sensitivity of the integrator was fixed at 0.3 mV/min.

## RESULTS AND DISCUSSION

The calibration data were obtained for the main pyrolytic gases mentioned above at low and normal sensitivity detector settings. Typical results are presented in Figs. 2 and 3 for CO<sub>2</sub>, CO and N<sub>2</sub> where the area response variable from the electronic integrator was plotted as a function of the number of moles of the compound analysed. The calibration graphs in Fig. 2 obtained under normal sensitivity conditions passed through the origin<sup>10,11</sup>. This was not always the case under the low sensitivity conditions, however, where it was noted that the lower portion of the graphs for all of the gases considered was slightly deflected toward the abscissa axis (Fig. 3). At low sensitivity the equations of the straight portion of the lines were calculated using the least-squares method, in which case the correlation coefficient was always better than 0.990 (4 degrees of freedom). At normal sensitivity the slopes of the resulting straight lines were calculated by taking the derivative of  $S$ , the sum of squares of the deviations of each value  $y = bx$ , with respect to  $b$ , setting it equal to zero for a minimum, and solving for  $b$ . The plots exhibited genuine linear relations with a correlation coefficient which varied between 0.993 and 0.999 (4 degrees of freedom).

The response factors were calculated following the usual procedure with nitrogen as reference. At low sensitivity the factors were found to be strongly dependent on the amount of gaseous compound injected, as shown in Fig. 4 for CH<sub>4</sub>, CO, CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Such drastic dependences between the response and the concentration were observed with heavier carrier gases at low concentrations only, while the probability of this anomalous phenomenon occurring was thought to be minimal with H<sub>2</sub> or He as carrier gas<sup>12</sup>. At normal sensitivity the response factors were easily derived from the direct ratio of the  $b$  values with respect to the reference and obviously were found to be independent of the number of moles injected. The factors are given in Table I for further comparison with other data available in the literature.

Hydrogen has been kept apart as it exhibited anomalous chromatographic behavior even at normal sensitivity, as indicated by the non-linear calibration graphs

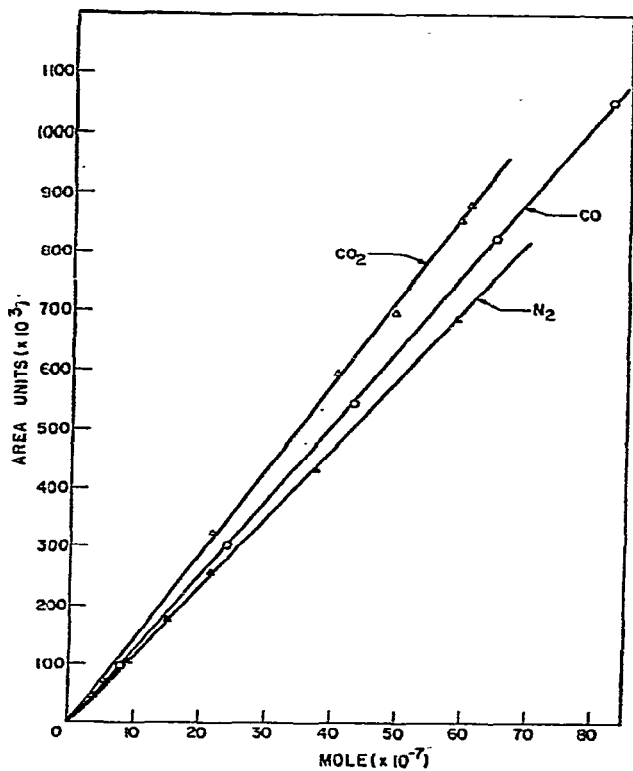


Fig. 2. Calibration graphs for CO<sub>2</sub>, CO and N<sub>2</sub>. Normal sensitivity.

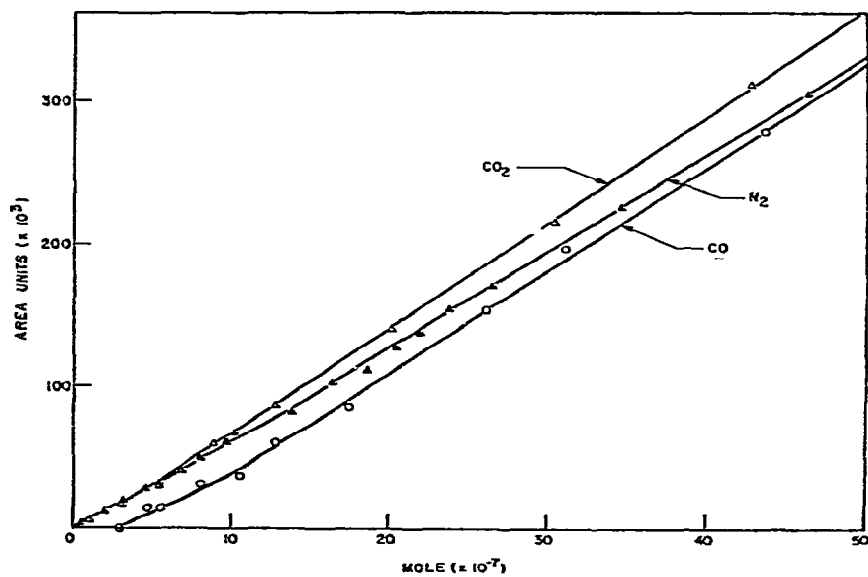


Fig. 3. Calibration graphs for CO<sub>2</sub>, CO and N<sub>2</sub>. Low sensitivity.

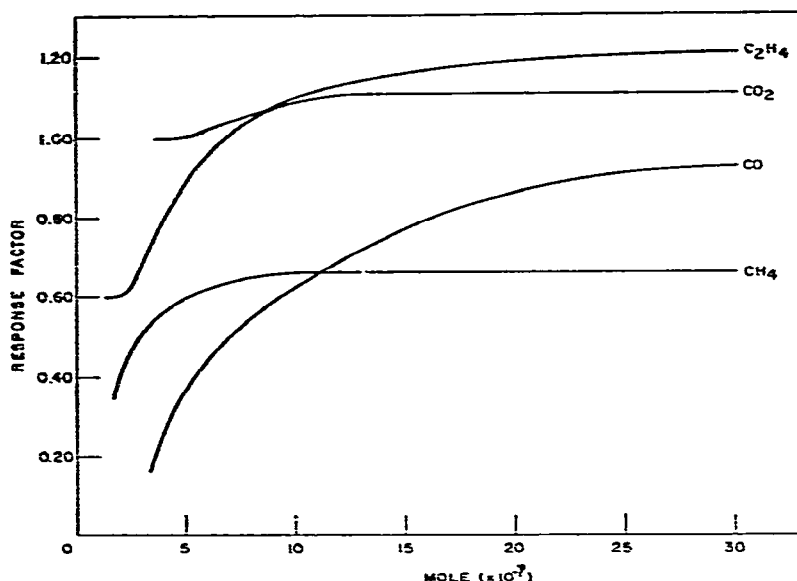


Fig. 4. Response factors for  $CO_2$ ,  $CO$ ,  $CH_4$  and  $C_2H_4$ . Reference factor: nitrogen = 1.0. Low sensitivity.

in Fig. 5. The concave-type curvature of the  $H_2$  calibration profiles at low concentrations is in sharp contrast with the convex-type curvature expected at higher concentrations<sup>14,15</sup>. The resulting response factors for  $H_2$  are given as a function of the sensitivity levels of the detector in Fig. 6. As expected, the response factor was highly dependent of the amount of gas passing through the detector.

It is necessary to examine the relative responses given by similar detectors, since Messner *et al.*<sup>7</sup> concluded that their data should be applicable to all gas chromatographs using thermal conductivity detectors and helium as carrier gas. A comparison

TABLE I

COMPARISON OF RESPONSE FACTORS TO DIFFERENT THERMAL CONDUCTIVITY DETECTORS

Gas	Response per mole relative to nitrogen		
	Present work*	Messner <i>et al.</i> <sup>7***</sup>	Guillemin <i>et al.</i> <sup>13****</sup>
$H_2$	Variable	—	—
$N_2$	1.00	1.00	1.00
$CH_4$	0.88	0.86	0.92
$CO$	1.06	1.00	1.00
$CO_2$	1.20	1.14	1.20
$C_2H_6$	1.11	1.14	1.27
$C_4H_{10}$	2.04	2.02	—

\* Carrier gas: 8%  $H_2$  in He. Normal sensitivity (275 mA, 110°C), Hewlett-Packard hot-wire detector.

\*\* Carrier gas: He. Unspecified sensitivity, thermistor-type detector.

\*\*\* Carrier gas: He. Normal sensitivity (250 mA, 95°C). Gow-Mac hot-wire detector.

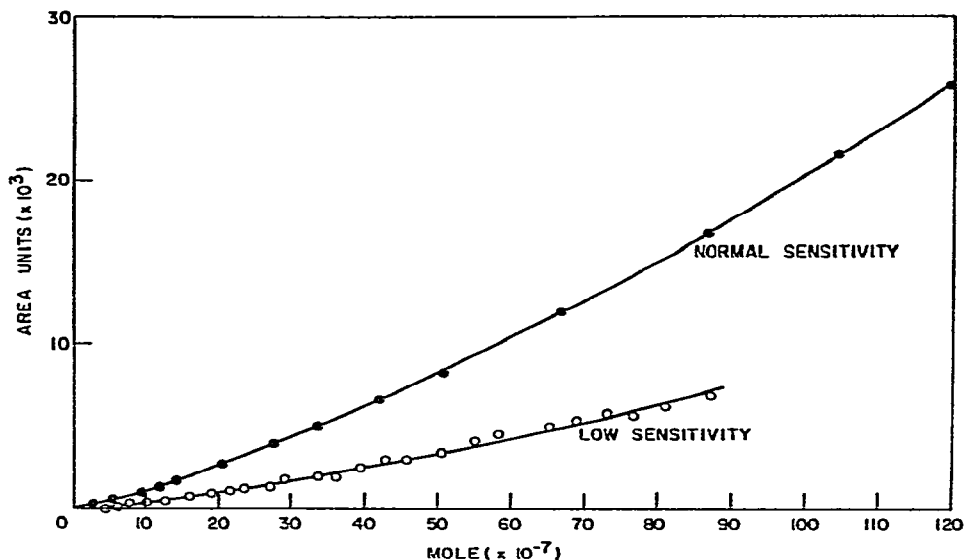


Fig. 5. Calibration graphs for  $H_2$ . Low and normal sensitivity.

of their results and those of other investigators using similar instruments is shown in Table I. Although some agreement can be found in the results, there is, as yet, not enough published work on relative responses to show the extent to which the claimed reproducibility exists.

The resulting response factors were tested against a synthetic blend at known composition of  $H_2$ ,  $CH_4$ ,  $CO$  and  $CO_2$ . Five analyses of the same blend were run at a

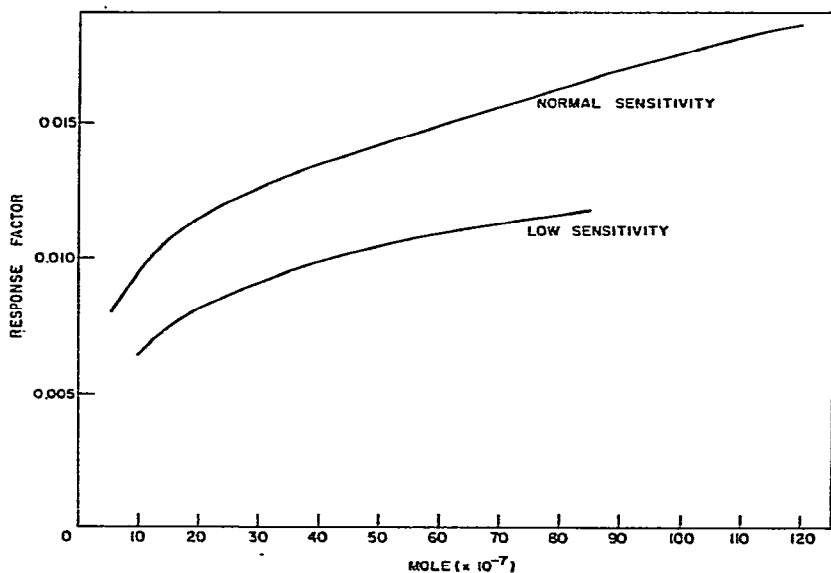


Fig. 6. Response factors for  $H_2$ . Reference factor: nitrogen = 1.0. Low and normal sensitivity.

sample pressure of 350 torr with the 1-ml sampling loop. The detection was performed with the normal sensitivity setting of the katharometer. The resulting average values are presented in Table II. Based on the specified true molar percentages, the relative error is not higher than 2.6% in the worst instance.

TABLE II

## ANALYSIS OF SYNTHETIC BLEND

Normal sensitivity. Sample volume: 1 ml. Total pressure: 350 torr.

Gas	True molar %	Observed molar %	% Error
H <sub>2</sub>	25.70	26.36	2.6
CH <sub>4</sub>	18.32	18.53	1.1
CO	22.34	21.79	2.5
CO <sub>2</sub>	33.64	33.32	1.0

## CONCLUSION

When injecting small amounts of gases into the gas chromatograph the relative responses provided by the katharometer are significantly influenced by the sensitivity of the detector. At low sensitivity, the response factors vary with the amount of compound injected, but at normal sensitivity the relative responses for all the gases considered except H<sub>2</sub> are constant with respect to the reference. In contrast the response factor for H<sub>2</sub> is very sensitive to the carrier gas flow-rate, as its calibration graph is not linear with respect to the reference. Close control of the carrier gas flow-rate is therefore strongly recommended.

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