

LIBRARY REFERENCE ONLY

M.O.T. AND F.O.C. 15
FIRE RESEARCH
ORGANIZATION
REFERENCE LIBRARY 70
No. A99FR-N 853



Fire Research Note No. 853

A VERSATILE CHROMATOGRAPH FOR COMBUSTION
GAS ANALYSIS

by

W. D. WOOLLEY

November 1970

FIRE
RESEARCH
STATION

**Fire Research Station,
Borehamwood,
Herts.
Tel. 01-953-6177**

F.R. Note No. 853.
November, 1970.

A VERSATILE CHROMATOGRAPH FOR COMBUSTION GAS ANALYSIS

by

W. D. Woolley

SUMMARY

A system of chemical analysis has been developed which enables both the permanent gases and organic decomposition products from fires and other thermal decomposition processes to be studied with a single chromatograph. It consists of molecular sieve and silica gel columns with individual injection ports built into the inlet of a conventional organic research chromatograph.

A simple method of peak area normalization is suggested for calculating the percentages of oxygen, nitrogen, carbon monoxide and carbon dioxide in dry combustion gases which avoids the need for accurate sample injection and frequent sensitivity checks. The general method is demonstrated by using sensitivity factors available in the literature and analysing air and also two commercial gases of known compositions. For convenience, all normalizations of the integrator counts in this work have been undertaken using a short programme in an electronic desk computer.

KEY WORDS: Combustion products, gas chromatography.

Crown copyright

This report has not been published and should be considered as confidential advance information. No reference should be made to it in any publication without the written consent of the Director of Fire Research.

	Page
1. INTRODUCTION	1
2. EXPERIMENTAL AND RESULTS	
a) The chromatographic system	2
b) Gas analysis by a normalization method	3
c) Analyses of air and commercial gas mixtures	5
(i) Oxygen-nitrogen analyses of air	5
(ii) Analyses of commercial gas mixtures	6
3. DISCUSSION	7
4. REFERENCES	9
5. APPENDIX	10

A VERSATILE CHROMATOGRAPH FOR COMBUSTION GAS ANALYSIS

by

W. D. Woolley

1. INTRODUCTION

A research gas chromatograph, fitted with simultaneous flame ionization and thermal conductivity detectors with electronic integration facilities, was available for the studies of various organic decomposition products from fires and related laboratory tests^{1,2,3}. The permanent gases (oxygen, nitrogen, carbon monoxide and carbon dioxide) from these tests were analysed using a small laboratory chromatograph with a poor sensitivity and output not readily compatible with the electronic integrator.

The first section of this note outlines a simple system, consisting of a molecular sieve column for the separation of oxygen, nitrogen and carbon monoxide and a silica gel column for carbon dioxide analyses, which has been attached to the inlet of the research chromatograph without altering the normal performance of the instrument. In this way, both the permanent gases and organic materials from fire tests can be analysed with the one instrument, backed with full integration facilities.

During the chromatography of the permanent gases it has been the normal practice, particularly with carbon dioxide analyses using silica gel, to calibrate the instrument for each specific gas and hence analyse unknown mixtures by reference to the calibration graphs rather than by using direct normalization methods. This has been necessary since the composite peak (oxygen, nitrogen and carbon monoxide), eluted very rapidly from the silica gel during analyses of carbon dioxide, is a sharp peak and not easily integrated by standard methods.

With the introduction of automatic electronic integrators the peak areas of these relatively sharp peaks can be determined easily.

The second part of this report outlines a simple normalization technique for calculating the percentages of oxygen, nitrogen, carbon monoxide and carbon dioxide in combustion gases directly from integrator areas. For the method a gas sample is analysed by molecular sieve giving areas for oxygen, nitrogen and carbon monoxide. A second sample is then injected into silica gel and the areas of the composite and carbon dioxide peaks are obtained.

An overall normalization then gives directly the percentages of the four gases in the mixture.

The normalization method eliminates the need for accurate gas injections since the two samples injected into the chromatograph can be of different, and if necessary of unknown volumes. Further, the method automatically compensates for day to day changes in the sensitivity of the chromatograph and hence avoids frequent sensitivity checks. The method is limited, however, in that the calculated percentages of the four gases are based on the assumption that no other gases are present.

Finally, the general repeatability and accuracy of the normalization method is demonstrated by repetitive analyses of air and two commercial gas mixtures.

2. EXPERIMENTAL AND RESULTS

a) The chromatographic system

The layout of the chromatograph is shown diagrammatically in Fig. 1. For the modification, one of the normal helium flow lines from the flow meter F_1 to the injection port I_1 is split and taken externally from the chromatograph with copper tubing (3.2 mm o.d.). Two columns (molecular sieve and silica gel respectively), each fitted with separate injection ports (X and Y) are fitted in series in the loop as shown. The helium carrier gas passes through the two columns, enters the research chromatograph via the injection port I_1 and then flows through the main column (Porapak Q) of the chromatograph in the normal manner. The molecular sieve (5A, 30-60 mesh) and the silica gel (30-60 mesh) are packed in copper tubing (4.8 mm o.d.) of lengths 0.2 and 0.25 m respectively, coiled and strapped to the sides of the chromatograph. The columns were operated at room temperature without any temperature control. No external reference columns were required. The injection ports (X and Y) were constructed simply by inserting a rubber diaphragm into one arm of a brass 'T' union and coupled to the column with compression fittings.

Fig. 2 shows the traces, obtained with the modified single chromatographic system, of the permanent gases and also the general phenolic products obtained during the thermal decomposition of a phenol-formaldehyde resin in air. For this study the main columns of the chromatograph were Porapak Q columns (2 m x 3.2 mm o.d. in stainless steel) with overall flow rates of 30 ml/min as monitored by flow meters F_1 and F_2 as shown in Fig. 1.

In Fig. 2(a) oxygen, nitrogen and carbon monoxide are separated by the molecular sieve by injection at X, pass unchanged through the silica gel and Porapak Q (operated isothermally at 80°C)* and are detected by the thermal conductivity detector. Carbon dioxide is retained permanently by the molecular sieve.

In Fig. 2(b) carbon dioxide is separated from the oxygen nitrogen and carbon monoxide (composite peak) by the silica gel column by injection at Y. The carbon dioxide and the composite peak pass unchanged through the Porapak Q (again at 80°C) and are analysed by the thermal conductivity detector.

In Fig. 2(c) the phenolic materials are separated by conventional temperature programming (at 4°C/min) with the Porapak Q column by injecting a solution of the materials in methanol into injection port I₁. In this case the organics were analysed by flame ionisation detection.

b) Gas analysis by a normalization method

The response factors for the gas chromatographic analysis of many common materials by flame ionization and thermal conductivity detectors have recently been recorded by Dietz⁴. The values for oxygen, nitrogen, carbon monoxide and carbon dioxide for thermal conductivity detection have been extracted from this data and are shown in Table 1. For convenience the response factors have been corrected to give a response factor of nitrogen as unity. All response factors quoted in this report will refer to these modified figures. During the chromatographic analysis of the materials, the peak area divided by the response factor gives the true peak area. Normalizing the true peak areas then gives the volume percentages of the gases.

Table 1

Response factors of permanent gases
to thermal conductivity detectors

Permanent Gas	Response factors as given by Dietz	Response factors with nitrogen as unity
Oxygen	40	0.953
Nitrogen	42	1.000
Carbon monoxide	42	1.000
Carbon dioxide	48	1.143

* Excessively high temperatures of the Porapak column were avoided in order to prevent any oxidation of the column packing taking place during the analysis of oxygen-containing gases. No evidence of oxygen removal by the Porapak Q was detected below 150°C.

As outlined earlier the injection of a mixture of gases into the molecular sieve column gives a separation of oxygen, nitrogen and carbon monoxide with carbon dioxide being permanently retained on the column as shown in Fig. 2(a). The relative percentages of oxygen, nitrogen and carbon monoxide (i.e. assuming carbon dioxide to be absent) may be directly determined by correcting the three peak areas to true peak areas, followed by a simple normalization. For example, if the peak areas of oxygen, nitrogen and carbon monoxide are 953, 5000 and 1000 units respectively then the true peak areas are 1000, 5000 and 1000 units with relative percentages (P^1) of 14.3, 71.4 and 14.3% respectively.

With the silica gel column oxygen, nitrogen and carbon monoxide are eluted as a composite peak followed by carbon dioxide, as shown in Fig. 2(b). The response factor (R) for the composite peak is given by:-

$$R = 0.953 A + 1.0 (B + C) \quad \dots\dots\dots (1)$$

where A, B and C are the fractional amounts (by volumes) of oxygen, nitrogen and carbon monoxide respectively (i.e. $A + B + C = 1$). In combustion gases, A is invariably less than 0.2 (i.e. 20% oxygen) and the response factor (R) of equation (1) may be approximated to unity with a maximum error of less than 1%.

Thus the percentage of carbon dioxide can be determined using response factors of 1.00 and 1.143 for the composite and carbon dioxide peaks respectively. The percentage of carbon dioxide calculated in this way is the true percentage in the mixture. For example if the peak areas for the composite and the carbon dioxide peaks are 6000 and 1143 units respectively then the true peak areas are 6000 and 1000 units with true percentages of 85.7 and 14.3% respectively.

The relative percentages (P^1) of oxygen, nitrogen and carbon monoxide in the mixture determined on the molecular sieve column may now be converted to true percentages by normalization to P composite or $(100 - P_{CO_2})$. Thus the true percentages (P) of oxygen, nitrogen and carbon monoxide are given by:-

$$P_{O_2} = \frac{P^1_{O_2}}{100} (100 - P_{CO_2})$$

$$P_{N_2} = \frac{P^1_{N_2}}{100} (100 - P_{CO_2})$$

$$P_{CO} = \frac{P^1_{CO}}{100} (100 - P_{CO_2})$$

Thus in the above example the true percentages in the mixture are 12.2, 61.3, 12.2 and 14.3 for oxygen, nitrogen, carbon monoxide and carbon dioxide respectively, calculated from peak areas only obtained from the injection of two unknown (but approximately 0.5 ml) quantities of gas into the chromatograph. The total analysis time as shown in Fig. 2(a) or 2(b) is approximately 12 minutes.

Finally, it should be emphasised that although molecular sieve separates oxygen, nitrogen and carbon monoxide, argon (approximately 1% of the atmosphere) is eluted with oxygen. Dietz⁴ records the response factor of argon to thermal conductivity detectors as 42 (i.e. the same as nitrogen). Since the percentage of argon is small and the response factor approximately the same as for oxygen, the total oxygen and argon of combustion gases can be determined assuming the whole peak to have the response factor of oxygen.

In combustion gas analysis, the oxygen content of the gas is often expressed as the oxygen - argon content. If necessary, this can be corrected to oxygen content alone since in air the nitrogen - argon ratio is a fixed quantity.

c) Analyses of air and commercial gas mixtures

In order to demonstrate the general method of area normalization, a series of chromatographic analyses were undertaken using firstly air and secondly two commercial gas mixtures containing oxygen, nitrogen, carbon monoxide and carbon dioxide at concentrations typically encountered in fire gases.

(i) Oxygen-nitrogen analyses of air

The integrator counts (in arbitrary units) for 5 repetitive analyses of air (approximately 0.5 ml) with the molecular sieve column are shown in Appendix 1. The percentages of oxygen and nitrogen in each sample is given in Table 2, obtained simply by dividing the oxygen and nitrogen areas by 0.953 and 1.000 respectively and then normalizing the true peak areas to obtain the percentages of each gas. It should be noted that the values quoted for oxygen are total oxygen and argon percentages. Air contains nitrogen, oxygen and argon as 78.09, 20.95 and 0.93 per cent respectively⁵. For the purposes of this report, air will be regarded as containing nitrogen and total oxygen and argon as 78.11 and 21.89 per cent respectively in order to ensure a complete total of 100 per cent.

Table 2. Chromatographic analyses of oxygen and nitrogen in air by the normalization method

	Chromatographic values (per cent)					Mean values (per cent)	Expected values (per cent)	Error per cent
	Oxygen*	21.33	21.40	21.45	21.40	21.43	21.40 \pm 0.07	21.89
Nitrogen	78.67	78.60	78.55	78.60	78.57	78.60 \pm 0.05	78.11	+ 0.6

* As oxygen and argon

Also recorded in Table 2 are the mean chromatographic values with the maximum experimental deviations, the expected values and the error percentages for the two gases. In each case the maximum experimental deviation is small but the mean value of oxygen is somewhat lower (2.3%) than expected.

(ii) Analyses of commercial gas mixtures

Two commercial gas mixtures containing oxygen, nitrogen, carbon monoxide and carbon dioxide were obtained for these tests. The integrator counts (i.e. peak areas) obtained during 5 repetitive chromatographic analyses of gas mixture 1 using the molecular sieve and silica gel columns in turn as outlined in a previous section are recorded in Appendix 2 (a).

The percentages of each gas in the mixture calculated directly from the peak areas using the complete normalization technique with sensitivities as recorded by Dietz are given in Table 3.

Table 3. Chromatographic analyses of gas mixture 1 by the complete normalization method.

	Chromatographic values (per cent)					Mean values (per cent)	Expected values (per cent)	Error per cent
	Carbon dioxide	12.49	12.61	12.60	12.63	12.44	12.55 \pm 0.11	12.4 \pm 0.1
Oxygen	5.08	5.07	5.08	5.09	5.10	5.08 \pm 0.02	5.35 \pm 0.05	- 5.3
Nitrogen	76.01	75.86	75.98	76.09	76.25	76.04 \pm 0.18	75.80*	+ 0.3
Carbon monoxide	6.41	6.47	6.33	6.18	6.22	6.32 \pm 0.15	6.45 \pm 0.05	- 2.1

* By difference

In all cases the normalization calculations have been undertaken using an electronic desk computer with programming facilities. The programme, which is stored indefinitely on a magnetic card is designed to display the final true percentages of the mixture directly from the peak areas. For comparison, the relevant hand calculation of one of the 5 gas analyses is shown in Appendix 2(b).

Also recorded in Table 3 are the mean chromatographic values with the maximum experimental deviations, the expected values with the manufacturer's stated tolerances and the error percentages of the gases. It should be noted that the error percentages are based upon expected values without tolerances.

The equivalent data of 5 repetitive analyses of gas mixture 2 are recorded together with the relevant expected values and error percentages in Table 4.

Table 4. Chromatographic analyses of gas mixture 2 by the complete normalization method.

	Chromatographic values (per cent)					Mean values (per cent)	Expected values (per cent)	Error per cent
Carbon dioxide	11.23	11.25	11.20	11.23	11.16	11.21 ± 0.05	10.9 ± 0.1	+ 2.8
Oxygen	12.91	12.89	12.90	12.91	13.01	12.92 ± 0.09	13.6 ± 0.1	- 5.3
Nitrogen	75.00	74.97	75.01	74.92	74.94	74.97 ± 0.05	74.67*	- 0.4
Carbon Monoxide	0.87	0.89	0.89	0.95	0.90	0.90 ± 0.05	0.83 ± 0.05	+ 7.8

* By difference

3. DISCUSSION

The system clearly demonstrates that a research gas chromatograph, fitted for general organic analyses, can be modified with a special inlet system for the study of the permanent combustion gases. The modification does not interfere in any way with the general performance of the instrument, although organic and inorganic analyses cannot, of course, be undertaken at the same time.

The repetitive analyses of air and the commercial gas mixtures show the general method of peak area normalization to be a fast and reliable way of analysing the compositions of combustion gases. The repeatability of analyses is good but there are certain trends in the mean chromatographic values. For example oxygen is 2.3 per cent low in the analyses of air and 5.3 per cent low in both commercial gases. Carbon dioxide tends to be slightly larger than expected (1.2 and 2.8 per cent for gas mixtures 1 and 2 respectively). The error per cent of nitrogen is good and varies only between - 0.4 and + 0.6 per cent throughout the analyses. Carbon monoxide is 2.3 per cent lower and 7.8 per cent larger than expected with gas mixtures 1 and 2 respectively. The large error in this latter value may be due partly to the low absolute value of the carbon monoxide involved. For example, the electronic integrator automatically integrates all chromatographic signals above the base line during the elution of a component. With small peak areas, background electronic noise, which is automatically integrated, may be significant. It should also be noted that the error per cent of the manufacturer's stated composition of carbon monoxide in this gas is $\pm 6\%$.

A possible solution to the relatively low oxygen values, as indicated by the normalization method, is to modify the response factors of oxygen given in Table 1 on the basis of a specific instrumental bias. In this way the oxygen content of air by chromatography could be corrected to the expected value. This would reduce, but not eliminate the error percentages of oxygen in gas mixtures 1 and 2.

In conclusion, the normalization method is a fast and reliable method of gas analysis. Without modification it is ideally suited for the analysis of combustion gases from fires and related experiments where speed and ease of analysis rather than high accuracy are the dominating factors.

With care and by introducing certain experimental modifications to the response factors, the general accuracy of the method could, if necessary, be improved.

4. REFERENCES

1. WOOLLEY, W. D., A study and toxic evaluation of the thermal decomposition products of PVC in air and nitrogen, F.R. Note No. 769, 1969.
2. WOOLLEY, W. D. and WADLEY, ANN I., Studies of phosgene production during the thermal decomposition of PVC in air, F.R. Note No. 776, 1969.
3. WOOLLEY, W. D. and WADLEY, ANN I., The decomposition products of phenol-formaldehyde laminates, Parts 1 and 2, F.R. Notes in preparation.
4. DIETZ, W. A., Response factors for Gas Chromatographic Analyses, J. Gas Chromatography, 1967, 5 (2), pp 68-71.
5. Handbook of Chemistry and Physics, Chemical Rubber Pub. Co., 41st Edition, p 3379.

5. APPENDIX

Appendix 1.

Peak areas (arbitrary units) of oxygen and nitrogen recorded during analyses of air with the molecular sieve column.

Oxygen	Nitrogen
86680	335900
82830	319600
88440	340200
87570	337800
84520	325500

Appendix 2(a).

Peak areas (arbitrary units) of composite, carbon dioxide, oxygen, nitrogen and carbon monoxide recorded during analyses of gas mixture 1.

Composite	Carbon dioxide	Oxygen	Nitrogen	Carbon monoxide
305000*	49730*	21290*	334500*	28220*
428000	70510	21130	332200	28330
353300	58190	20460	321500	26800
400600	66160	21440	336500	27340
361100	58570	20780	328600	26640

* Used in Appendix 2(b).

Appendix 2(b).

Calculation of gas composition by the complete normalization method of the first analysis given in Appendix 2(a). All areas are quoted in arbitrary units.

(i) Silica gel analysis

area of composite peak = 305000

area of carbon dioxide peak = 49730

thus

true area of composite peak = 305000

true area of carbon dioxide peak = $\frac{49730}{1.143} = 43508$

thus

true percentage of composite gases = $\frac{305000 \times 100}{305000 + 43508} = 87.51$

true percentage of carbon dioxide = $\frac{43508 \times 100}{305000 + 43508} = 12.49$

(ii) Molecular sieve analysis

area of oxygen peak = 21290

area of nitrogen peak = 334500

area of carbon monoxide peak = 28220

thus

true area of oxygen peak = $\frac{21290}{0.953} = 22363$

true area of nitrogen peak = 334500

true area of carbon monoxide peak = 28220

thus

relative percentage of oxygen = $\frac{22363 \times 100}{22363 + 334500 + 28220} = 5.81$

relative percentage of nitrogen = $\frac{334500 \times 100}{22363 + 334500 + 28220} = 86.86$

relative percentage of carbon monoxide = $\frac{28220 \times 100}{22363 + 334500 + 28220} = 7.33$

and

$$\text{true percentage of oxygen} = 5.81 \times \frac{87.51}{100} = 5.08$$

$$\text{true percentage of nitrogen} = 86.86 \times \frac{87.51}{100} = 76.01$$

$$\text{true percentage of carbon monoxide} = 7.33 \times \frac{87.51}{100} = 6.41$$

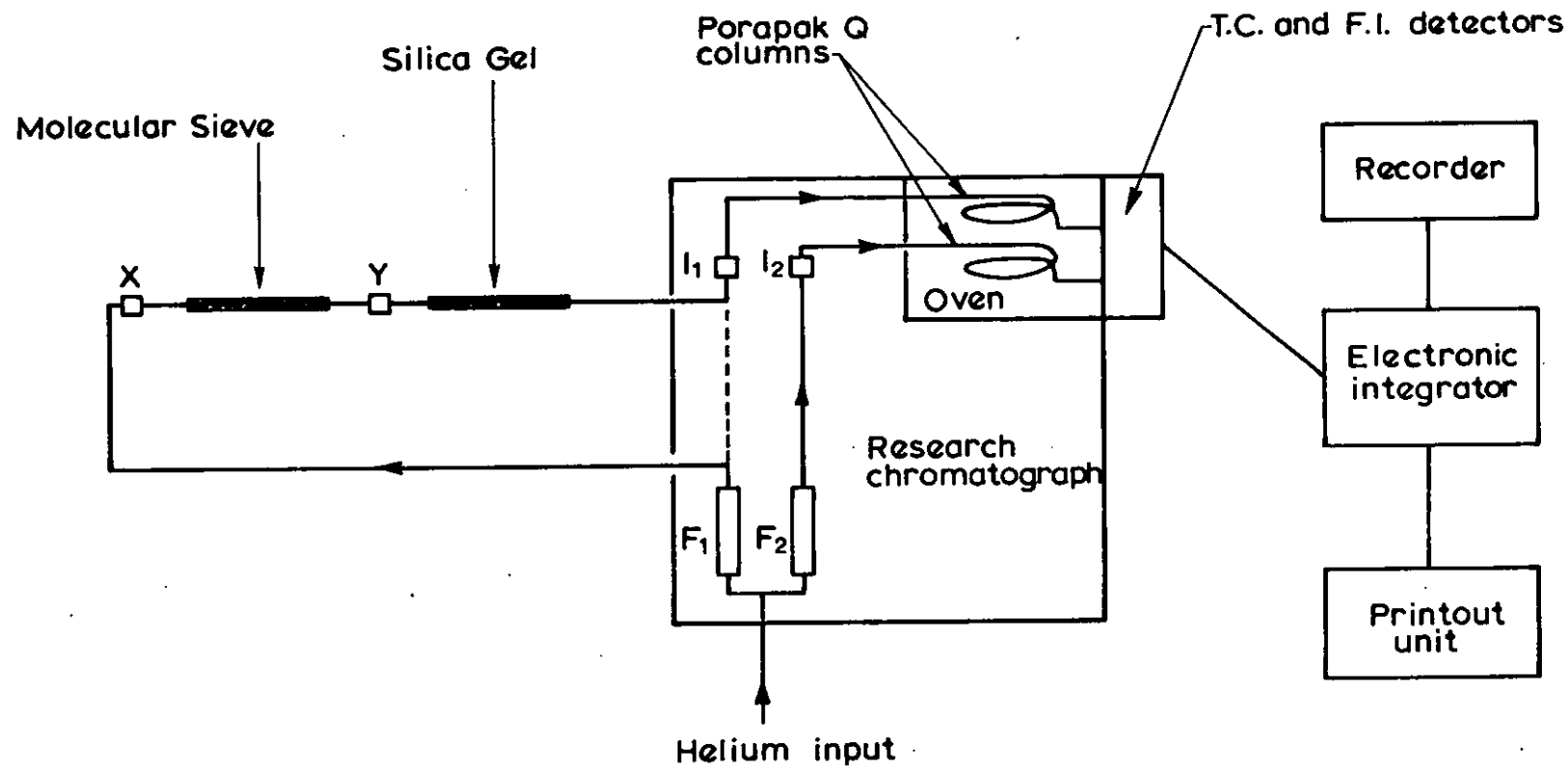
and directly from (i)

$$\text{true percentage of carbon dioxide} = 12.49$$

Appendix 3.

Peak areas (arbitrary units) of composite, carbon dioxide, oxygen, nitrogen and carbon monoxide recorded during analyses of gas mixture 2.

Composite	Carbon dioxide	Oxygen	Nitrogen	Carbon monoxide
344000	49690	45950	280500	3239
341800	49480	46320	283000	3357
302500	43590	46990	287100	3397
341000	49240	44540	271600	3427
342000	49060	46340	280400	3354



I_1, I_2 = Normal chromatographic injection ports

F_1, F_2 = Flow meters

X, Y = New injection ports

FIG. 1. LAYOUT OF MODIFIED CHROMATOGRAPH

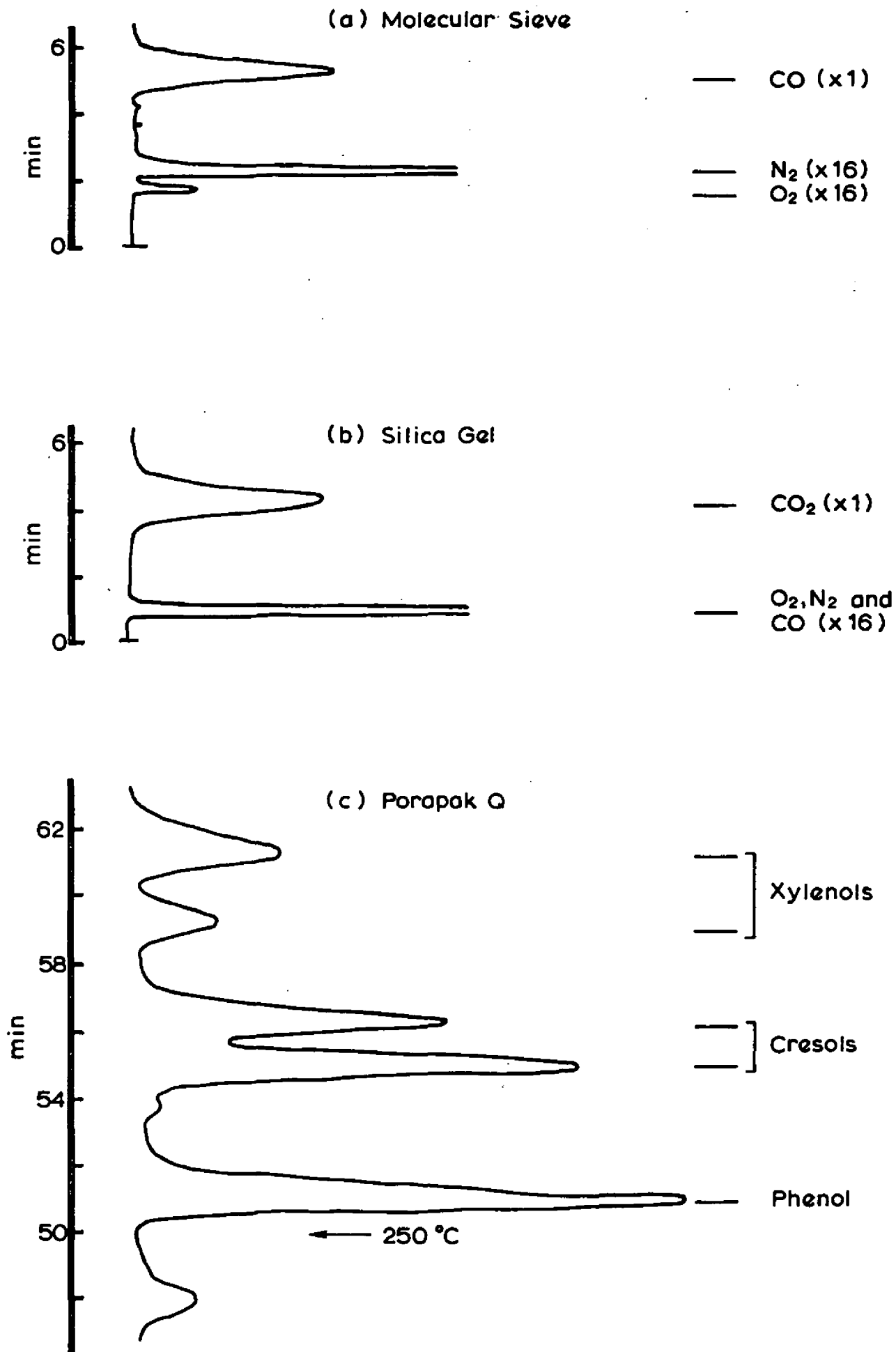


FIG.2. COMBUSTION GAS ANALYSIS WITH MOLECULAR SIEVE, SILICA GEL AND PORAPAK Q COLUMNS

