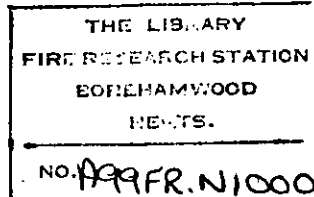




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STUDIES OF THE COMBUSTION PRODUCTS OF
CYANIDES IN A HYDROGEN DIFFUSION FLAME

by

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SUMMARY

This is a laboratory report in which is described a small-scale hydrogen diffusion flame, burning in an atmosphere of argon and oxygen, the flame being used as a means of ensuring complete combustion of hydrogen cyanide and acetonitrile fuels. Qualitative and quantitative analysis of the combustion products shows that the combustion processes of both cyanides may be similar and that the nitrogen content of each cyanide is released only as oxides of nitrogen or molecular nitrogen. The relative yields of oxides of nitrogen and molecular nitrogen are dependent upon the concentration of cyanide in the flame and the ratio N_2/NO_x varies between about 0.4 and 3.0 over the range of cyanide injection rates used in this report. A low concentration of cyanide tends to favour the production of oxides of nitrogen.

Experiments with a relatively cold flame using a vitiated diffusion flame atmosphere show that the production of oxides of nitrogen from the combustion of cyanide fuels is largely independent of flame temperature.

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1. INTRODUCTION

2. EXPERIMENTAL

- a) The burner system
- b) The motorised syringe
- c) Gas analysis
 - (i) Gas chromatography
 - (ii) Mass spectrometry
- d) Materials
 - (i) General materials
 - (ii) Hydrogen cyanide

3. RESULTS

- a) Calibration experiments
 - (i) Gas chromatography
 - (ii) Mass spectrometry
 - (iii) Flame calibrations
- b) Hydrocarbon flames
- c) Cyanide flames
 - (i) General studies
 - (ii) Quantitative analysis of products
 - (iii) Flame experiments with a vitiated atmosphere
 - (iv) Material balance for nitrogen-containing products

4. DISCUSSION

- a) General discussion
- b) Discussion of the fire behaviour of cyanides

5. CONCLUSIONS

6. ACKNOWLEDGMENTS

7. REFERENCES

8. APPENDIX

1. INTRODUCTION

When fuels are burnt in air, fixation of atmospheric nitrogen takes place with the formation of oxides of nitrogen (nitric oxide and nitrogen dioxide). This formation is temperature dependent and reversible, and the equilibrium concentration of oxides of nitrogen in a given flame system can be calculated from known kinetic data¹.

It is now becoming increasingly evident² in studies relating to pollutant emission that many combustion systems release oxides of nitrogen in quantities far greater than expected by kinetic considerations alone, and recent work has established that nitrogen, bound chemically in fuels (even at concentrations of about one tenth of one per cent) can be an important source of oxides of nitrogen.

Fires involving either natural or synthetic materials containing high proportions of bound nitrogen could therefore generate substantial quantities of oxides of nitrogen. Such oxides of nitrogen could, in principle, constitute a toxic risk to personnel subjected to the fire gases either by accident or in the course of normal fire-fighting. Oxides of nitrogen are known to be present in fire gases from nitrogen-containing fuels but little is known about the quantities involved or the magnitude of the toxic hazard.

The work of this report was undertaken in order to provide basic information about the oxides of nitrogen from the decomposition of flexible polyurethane foams (4 to 4.5 per cent by weight of nitrogen). It has been established in these laboratories that the thermal and thermal oxidative decomposition of these foams (both polyester and polyether types) produces an intermediate yellow smoke³ which subsequently decomposes at high temperatures to give a range of nitrogen-containing products of low molecular weight, particularly acetonitrile and hydrogen cyanide. These cyanides are known to be present in unburnt fire gases from polyurethane foams but when burnt may produce oxides of nitrogen. Knowledge of this conversion is of utmost importance since the toxicity of oxides of nitrogen, particularly nitrogen dioxide⁴, is approximately the same as for hydrogen cyanide when based on concentrations immediately hazardous to life. Combustion of cyanides in fires does therefore not necessarily remove the toxic risk.

In this report, a hydrogen diffusion flame is arranged to burn in a laminar flow of oxygen-argon, such that a wide range of materials under investigation can be introduced in gaseous or liquid form into the flame using a motorised syringe. Analyses of the resulting products are carried out using gas chromatography and mass spectrometry with samples extracted downstream from the burner.

A combustion system based on a hydrogen flame has been used in this work because water is the only product of combustion and this does not interfere with the analysis of nitrogen and carbon-containing products during the burning of other fuels. Argon-oxygen was chosen as the combustion atmosphere so that free nitrogen formed as a product during the burning of cyanide fuels could be analysed. The burner system is first evaluated and calibrated using n-hydrocarbon fuels up to hexane. The system is then extended to acetonitrile and hydrogen cyanide fuels and the major products identified.

The yields of these products (nitrogen and oxides of nitrogen) are shown to be dependent upon the rate of cyanide injection but broadly independent of type of cyanide.

Experiments undertaken with a relatively cold flame are included to show the effect of flame temperature on product formation.

2. EXPERIMENTAL

a) The burner system

The burner system is shown diagrammatically in Fig 1. The main burner enclosure is constructed of borosilicate glass (25 mm I.D., 80 mm in height and about 40 ml in volume) and mounted vertically in a clamp. Hydrogen (about 20 ml/min) is introduced along a stainless steel tube (3.2 mm O.D and 2.0 mm I.D.) which is sealed to the glass flame enclosure with silicone rubber as shown. The tip of the hydrogen inlet tube is mounted centrally within and about 40 mm from the base of the flame enclosure. The hydrogen flame burns directly on the tip of the inlet tube in an atmosphere of oxygen - argon (normally 21% oxygen*) which is introduced as shown at about 160 ml/min and dispersed across the tube with glass 'ballotini' to give a general laminar flow near the flame zone. The flow rates of both oxygen-argon and hydrogen are monitored with precalibrated flowmeters.

Materials under investigation are introduced in gaseous or liquid form into the hydrogen inlet tube via the silicone rubber septum of injection port A using a motorised syringe.

The hydrogen inlet line, the injection port A, the flame enclosure and part of the exit lines are heated to 120°C with electrical tape as shown; this ensures

*Some experiments are recorded using a vitiated atmosphere generated by adding pure argon as a diluent.

that the liquids injected into the port are volatilised and remain in vapour form to the burner, and also prevents the condensation of water (produced from the combustion processes) within the flame enclosure. This water condenses in the cold section of the exit tube which purposely has a downward gradient to a 'U' collection tube and drain tap.

A gas sampling port B, consisting of the normal 'T' piece construction with a silicone rubber septum, is provided for the removal by syringe of samples of the gases from the burner for the analysis of carbon dioxide and oxides of nitrogen. An adjacent 'on-line' gas sampling valve coupled directly to a gas chromatograph is used for the analysis of nitrogen. This latter on-line system is necessary for nitrogen determinations because of nitrogen contamination (from the air) of samples removed by syringe methods.

For safety reasons, the entire burner system but excluding the gas sampling valve of the chromatograph is mounted within a ventilated enclosure and operated from outside via small slits within the transparent plastics front of the enclosure. This transparent front can be folded away during routine work involving non-toxic materials.

Cyanides antidotes (A and B solutions*) and also amyl nitrite capsules were available at all times within the laboratory during this study. A and B solutions were discarded and re-prepared weekly.

b) The motorised syringe

The motorised syringe unit was constructed to give a uniform feed of cyanides and calibration materials into the hydrogen flow to the burner and is shown photographically in Fig 2. The drive system consists of an OBA screwed rod, driven at 2 rpm with a synchronous clock motor, coupled to an OBA 'captive' wing nut to convert the rotary to a linear drive. The OBA wing nut locks into slots in the syringe drive plate to become 'captive' only under drive conditions and may be readily released for winding back to the start of the thread for repetition of the drive cycle. This manual resetting was necessary because the available motor was non-reversing.

*Solution A: ferrous sulphate - citric acid solution

Solution B: sodium carbonate solution

The drive plate is fixed to two tubes which in turn slide on guide rods, as shown, to give a uniform and stable drive motion. The syringe platform contains a series of spring-clamps ('Terry' clips) of different sizes in order to locate a wide range of both gas and liquid syringes.

In operation, the syringe unit is located on an adjustable horizontal table such that the syringe needle can be aligned accurately with the centre of the silicone rubber septum of the injection port A referred to in Fig 1. The entire syringe unit is then simply slid towards the injection port such that the hypodermic needle penetrates the septum and the injection cycle started.

The total drive time of the syringe was designed to be about 4 minutes in order to ensure steady-state burning conditions for a period of not less than the 1-minute required for the operation of the gas sampling valve and the removal of gas samples from port B with a syringe for chromatographic and mass spectrometric analysis of the burner gases.

The syringes used for injection of the materials to the burner using the motorised drive unit were mainly Gillette 'Scimitar' syringes for the gases and standard chromatographic glass syringes for liquids but some experiments involved a glass gas-tight syringe with a PTFE plunger. The syringe data and injection rates are recorded in Table 1. In some experiments syringes 7 and 8 were used in combination to give 5.98 ml/min injection rate. This was not possible with the gas syringes because of their relatively large size.

Table 1. Syringe injection data using motorised drive

Syringe number	Type	Body material*	Total capacity	Injection rate (mean values)
1	Gas	P	20 ml	3.40 ml/min
2	Gas	P	10 ml	1.99 ml/min
3	Gas	P	5 ml	1.22 ml/min
4	Gas	P	2 ml	0.639 ml/min
5	Gas	P	1 ml	0.171 ml/min
6	Liquid	G	50 μ l	8.26 μ l/min
7	Liquid	G	25 μ l	4.14 μ l/min
8	Liquid	G	10 μ l	1.84 μ l/min
9	Gas	GP	5 ml	0.818 ml/min

* P - Plastics 'scimitar' syringe

G - Glass body, fixed needle

GP - Glass body, PTFE plunger

c) Gas analysis

(i) Gas chromatography

The percentages of carbon dioxide and nitrogen in the oxygen-argon stream from the burner were analysed by gas chromatography. Samples for carbon dioxide analyses (0.5 ml) were removed from sampling port B (of Fig 1) in the conventional way using a syringe and analysed using a Porapak Q column (1.5 m x 3.2 mm) operated at 25°C. Nitrogen analyses were undertaken using an on-line gas sampling valve (0.5 ml) coupled to the chromatograph with a molecular sieve column (0.5 m x 4.8 mm) at 25°C.

For simplicity in the overall analytical system, the Porapak Q and molecular sieve columns were both fitted into one thermal conductivity instrument. During analyses on one column the second column became the reference column for the detector and vice-versa. This system worked effectively but had the disadvantage that simultaneous analyses were not possible.

In all analyses, peak areas were obtained using an automatic electronic integrator with print-out facilities. Details of the calibration of the chromatograph and the use of a normalization method⁵ for calculating the gas percentages are given in the results section.

(ii) Mass spectrometry

Analyses of the percentage of oxides of nitrogen in the gas stream from the burner were obtained by mass spectrometry using a fast scanning version of the GEC-AEI MS20 with a modified inlet system. Basically this instrument is equipped with a Biemann separator (helium separator) for normal gas chromatography-mass spectrometry and was modified by isolating the chromatograph and fitting the special inlet system to the separator as shown diagrammatically in Fig 3. This consists of a helium supply S at a rate slightly greater than that removed by the pumps of the separator as indicated by a positive reading on the flowmeter F. This ensures a steady flow of helium to the separator.

Samples (0.5 ml) of the oxygen-argon stream from the burner are injected into the injection port I (via a silicone rubber septum) and are carried to the flow stabilizer with the helium supply. The flow stabilizer (about 25 ml) ensures, by mixing, that the sample is introduced into the mass spectrometer (via the separator) over a sufficiently long period for easy analysis. This analysis is effected by monitoring the total ion current (ie the pressure) of the mass spectrometer and recording the mass spectrum at the maximum value.

In this work it was originally hoped to monitor nitrogen dioxide and nitric oxide at m/e values of 46 and 30 respectively. In practice it was found that the nitrogen dioxide dissociated into nitric oxide inside the low pressure inlet system and enabled the total oxides of nitrogen to be monitored at m/e 30. No m/e 46 was found throughout this study. Monitoring the total oxides of nitrogen as m/e 30 proved to be an advantage in simplifying the overall analytical procedure.

This system also enabled other species in the oxygen-argon stream to be monitored simply by adjusting the m/e scan range of the mass spectrometer to the appropriate range.

d) Materials

(i) General materials

Acetonitrile was obtained commercially as high purity grade. Nitrogen dioxide and nitric oxide were also obtained commercially. Nitrogen dioxide was thermostatted at 28°C and assumed to be 80 per cent associated as the dimer (ie dinitrogen tetroxide).

All hydrocarbons used in the preliminary flame studies were of high purity grade and obtained in lectures bottles (C_1 to C_4 hydrocarbons) or as liquids (C_5 and C_6 hydrocarbons).

(ii) Hydrogen cyanide

Liquid hydrogen cyanide (yellow) is termed prussic acid and boils to a colourless gas at 26°C ; it is therefore not easily used entirely in liquid or entirely in gaseous form for injection into the burner system with a syringe and a special gas handling system as shown in Fig 4 was glass-blown together for preparing mixtures of hydrogen cyanide and argon directly in a syringe.

Hydrogen cyanide was prepared by the action of dilute sulphuric acid (50:50) on potassium cyanide using a flow of argon to carry the hydrogen cyanide through a drying tube (Magnesium Perchlorate) and into the gas handling system. Hydrogen cyanide was frozen into trap TR1 using methanol slurry at -100°C with the remaining argon passing to waste through tap T2. The hydrogen cyanide was purified by conventional 'trap to trap' distillation under vacuum using traps TR1 and TR2 and finally stored at reduced pressure in the reservoir R.

A gas tight syringe of 20 ml capacity (syringe number 1 of Table 1) was attached to the gas handling system at tap T4 using a short length of plastics tubing of negligible 'dead' volume. The syringe was then evacuated, filled to a certain pressure (as recorded by manometer M) with hydrogen cyanide and then filled to atmospheric pressure with argon. In this way syringes filled with hydrogen cyanide up to about 80 per cent of total capacity could be obtained.

3. RESULTS

a) Calibration experiments

(i) Gas chromatography

The volume percentages of carbon dioxide and nitrogen in the oxygen-argon stream from the burner were obtained chromatographically using the apparatus outlined in the experimental section. A typical chromatogram of the separation of nitrogen from a composite peak of oxygen-argon using the molecular sieve column is given in Fig 5(a). This column also elutes carbon monoxide if present, but adsorbs carbon dioxide irreversibly. The carbon dioxide separation, again from a composite peak of oxygen-argon and nitrogen using the Porapak Q column is shown in Fig 5(b).

For calibration purposes, 0 to 1 ml-samples of carbon dioxide, nitrogen and oxygen (21%) - argon were injected in turn into the chromatograph on the respective column and the thermal conductivity response to each gas

obtained accurately by a graphical method and recorded in Table 2. The experimental response to pure argon is also included for guidance during the vitiation of the oxygen (21%) - argon in combustion work. During an analysis the peak area divided by the relative response gives the true peak area which may be converted to volume percentages using a simple normalization technique developed⁵ in these laboratories for combustion studies and when applied in this instance consists of:

Firstly an analysis using the Porapak Q column with normalization of true peak areas to give the true percentage of carbon dioxide in the gases. The remainder (oxygen (21%) - argon with small quantity of nitrogen) being assumed to have the same relative response as oxygen (21%) - argon alone.

Secondly an analysis using the molecular sieve column with normalization of the true peak areas to give the relative percentages of nitrogen and oxygen (21%) - argon in the gases; carbon dioxide being irreversibly adsorbed on the column.

Thirdly an overall normalization of (i) and (ii) to give the true percentages of nitrogen and carbon dioxide in the oxygen (21%) - argon.

This method of analysis has been shown to be both versatile and reliable. It has the advantage that it does not require accurate injection techniques and eliminates frequent sensitivity checks since all calculations are relative.

Throughout this report, analyses have been carried out assuming that the relative response of oxygen-argon is unity. As seen from Table 2, vitiation of the oxygen during combustion will introduce an error, but even with complete vitiation to pure argon, the overall analytical error will not exceed 4%.

Table 2. Thermal conductivity response data for gas analysis

Gas	Absolute response (arbitrary units per ml)	Relative response*
Argon	5250	1.039
Oxygen (21%) - argon	5050	1.000
Carbon dioxide	5450	1.079
Nitrogen	4950	0.980

*With oxygen (21%) - argon as unity

(ii) Mass spectrometry

The percentage of oxides of nitrogen in the oxygen-argon from the burner were analysed by mass spectrometry as outlined earlier. In this particular inlet system nitrogen dioxide was found to be entirely converted to nitric oxide such that oxides of nitrogen (ie mixtures of nitric oxide and nitrogen dioxide) could be conveniently monitored at m/e 30.

Calibration experiments were undertaken by injecting dilute mixtures of nitrogen dioxide in oxygen-argon into the mass spectrometer and monitoring the peak height at m/e 30 as shown graphically in Fig 6. For these experiments the dilute calibration gases were prepared by adding known volumes of nitrogen dioxide (assumed to be 80% associated as dinitrogen tetroxide) with a syringe to a glass flask containing oxygen (21%) - argon and mixing with glass balls.

Experiments carried out by fitting a thin silica tube, surrounded with a tube furnace at 850°C , into the helium flow line between the injection port and flow stabilizer of Fig 3 confirmed that the calibration graph of Fig 6 was valid for both nitrogen dioxide and nitric oxide.

Throughout this report oxides of nitrogen (ie mixtures of nitric oxide and nitrogen dioxide) will be reported simply as oxides of nitrogen on a volume percentage basis.

(iii) Flame calibrations

During preliminary flame work, the hydrogen flow to the burner was arbitrarily set at 19 ml/min* in order to produce a flame stable to a wide range of oxygen-argon flows. Estimations made by adding methane to the flame (with the motorised syringe) showed that an efficient combustion system was produced at oxygen-argon flows in excess of about 100 ml/min and yielded carbon dioxide without any carbon monoxide**, and no unburnt methane.

Unless otherwise stated in this report all flame experiments were carried out at the hydrogen flow rate of 19 ml/min with an oxygen-argon flow of either 160 or 170 ml/min. This latter variation, checked by overall flow calibrations, corresponded to the 'inject' or 'bypass' position of the gas sampling valve respectively.

* This does not imply that exactly 19 ml/min is vital for a stable flame but corresponds to an easily resettable value on the precalibrated hydrogen flowmeter.

**Carbon monoxide is eluted from the molecular sieve column; the detection limit is 0.05%.

The total oxygen availability under these flow conditions is 34 to 36 ml/min respectively with 9.5 ml/min consumed by the hydrogen leaving an excess of about 25 ml/min for the combustion of added fuels.

Flame calibrations were then undertaken by injecting samples of nitrogen and carbon dioxide in turn into the flame with the motorised syringe and analysing the composition of the gases from the burner. The relationships between the experimental and theoretical compositions of the gases are shown graphically in Fig 7 and 8.

The theoretical value in each case is calculated from the rate of injection of each gas (with the syringe) and the oxygen-argon flow from the burner and assumes that water is condensed from the system.

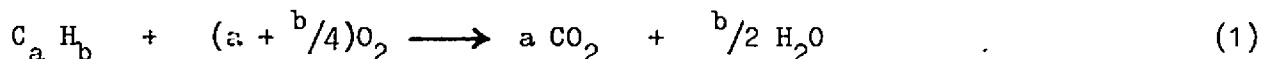
With carbon dioxide there is an almost exact agreement between the experimental and theoretical values whereas the nitrogen shows some deviation from the theoretical and also a small background reading at zero nitrogen injection. No oxides of nitrogen were detected during the nitrogen calibration work and it was therefore assumed that the experimental deviation from the theoretical was caused by an analytical discrepancy (probably caused by the analysis of a small nitrogen peak following a large oxygen-argon composite on the molecular sieve column, with calibration using only pure nitrogen). The nitrogen 'background' at zero injection rate of nitrogen in Fig 8 was found to be due to nitrogen contamination of the burner gases, particularly the hydrogen supply. As a result, in all analyses the experimental percentage of nitrogen was converted to the theoretical percentage by the data of Fig 8. No corrections were made to the carbon dioxide data.

b) Hydrocarbon flames

In order to ascertain the general combustion characteristics of the flame, a number of experiments were carried out using saturated hydrocarbon fuels and the resulting carbon dioxide in the gas stream from the burner monitored experimentally.

Fig 9 shows the general linear relationship between the experimental percentage of carbon dioxide in the gas stream from the burner and the theoretical, produced by the injection of various quantities of n-hexane into the flame. The syringe sizes were chosen to give up to about 6 per cent carbon dioxide and the relevant data for the injections are given in Appendix I. The experimental points plotted in Fig 9 are mean values of several determinations.

The theoretical percentage of carbon dioxide represents the calculated percentage in the vitiated oxygen-argon stream from the burner and assumes that the hydrocarbon combustion is given in general terms by



Thus if the oxygen (21%)-argon flow to the burner is 170 ml/min, hydrogen is introduced at 19 ml/min and the rate of injection of hydrocarbon in vapour form is F ml/min then the theoretical percentage of carbon dioxide is given by:

$$\text{Theoretical carbon dioxide (\%)} = \frac{F.a. (100)}{170 - (9.5 + F(a + b/4)) + F.a.} \quad (2)$$

As shown in Fig 9 there is linear relationship between the experimental and theoretical values over the 6 per cent working range. All future experiments will be designed to fit within this linear combustion range, which is more than adequate for normal working.

Within this combustion region, samples of C_1 to C_6 hydrocarbons were introduced into the flame in turn and the percentages of carbon dioxide in the gas stream from the burner obtained experimentally and the relevant data recorded in Appendix II. This is shown graphically in Fig 10 as carbon dioxide to hydrocarbon mole ratio as a function of carbon number for the hydrocarbon. The mole (or volume) ratio is the ratio between the rate of production of carbon dioxide and the rate of injection of vapour hydrocarbon. The rate of production of carbon dioxide is calculated from the experimental percentage of carbon dioxide in the gases from the burner and the calculated flow from the burner, given in general terms from equations (1) and (2) as

$$\text{Total flow from burner (ml/min)} = 170 - (9.5 + F(a + b/4)) + F.a. \quad (3)$$

In Fig 10 there is a good general agreement between the expected molar yields of hydrocarbons and the corresponding carbon number of the hydrocarbon.

This work confirmed that the general combustion conditions of the flame were sufficiently satisfactory for a study of acetonitrile and hydrogen cyanide experiments.

c) Cyanide flames

(i) General studies

Acetonitrile (Mol. wt 41.05 and density 0.78 g.ml^{-1}) was injected into the burner system in liquid form using syringes of capacities 10, 25, 10 + 25*, and 50 μl . The upper limit of 50 μl was chosen in order to maintain the combustion well within the linear range established from hydrocarbon experiments. The syringe capacities and rates of injection of both liquid or vapour are summarised in Table 3.

Table 3. Injection data for acetonitrile flames

Syringe(s) (μl)	Liquid flow rate ($\mu\text{l}/\text{min}$)	Vapour flow rate [†] (ml/min)
10	1.84	0.844
25	4.14	1.90
10 + 25	5.98	2.74
50	8.26	3.79

[†] At room temperature

In this work carbon dioxide and nitrogen were detected by gas chromatography with no evidence of carbon monoxide or unburnt acetonitrile. Mass spectrometry confirmed this, and also showed the presence of oxides of nitrogen but no other species were detected.

The production of these species (ie carbon dioxide, nitrogen and oxides of nitrogen) may be considered with three equations:



*ie 10 and 25 μl syringes used simultaneously.

For acetonitrile injected at a flow rate F ml/min (ie vapour) then the alteration in the flow rate of gases from the burner ΔR

where

ΔR = Flow rate of products - rate of oxygen consumption
by acetonitrile

is given by

$$\Delta R = -\frac{1}{4} F \text{ for equation (4) and (5)}$$

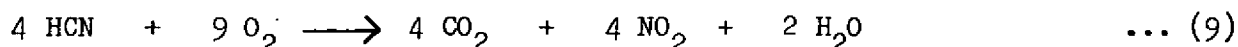
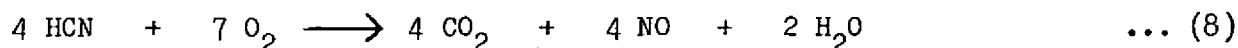
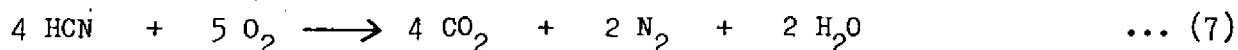
$$\Delta R = -\frac{3}{4} F \text{ for equation (6)}$$

For $F \ll 3.79$ ml/min (Table 3) and the oxygen (21%) - argon to the burner is 160 ml/min* with a hydrogen flow of 19 ml/min (ie net flow from the burner, without acetonitrile injection, of 150.5 ml/min) the alteration to the flow from the burner by the injection of acetonitrile is small. Hence the percentages of carbon dioxide, nitrogen and oxides of nitrogen in the gases from the burner formed theoretically as in equation (4), (5) or (6) are directly proportional to the added acetonitrile.

Hydrogen cyanide injections were carried out, as explained in the experimental section, with a 20 - ml syringe filled with various amounts of gaseous hydrogen cyanide up to about 80 per cent of syringe capacity with the remainder being pure argon.

The products detected in this study were identical to those observed during the work with acetonitrile, namely carbon dioxide, nitrogen and oxides of nitrogen. No other products were detected.

The overall combustion equations can be considered as



and ΔR , defined in the same terms as for acetonitrile is given by

$$\Delta R = \frac{1}{4} F \text{ for equations (7) and (8)}$$

and $\Delta R = \frac{3}{4} F \text{ for equations (9)}$

where F is the injection flow rate of hydrogen cyanide.

*Nitrogen determinations involve the use of the gas sampling valve which restricts the gas flow from the burner and reduces the flow from 170 to 160 ml/min.

Since $F \leq 2.63$ ml/min, ΔR is small and can again be neglected in relation to the overall gas flow from the burner.

The argon, injected into the flame with the hydrogen cyanide is more important but even at zero hydrogen cyanide in the syringe the argon injection rate of 3.40 ml/min alters the total flow from the burner by only 2 per cent. This error decreases with increased injection rates of hydrogen cyanide and was considered sufficiently small to assume direct proportionality between the percentages products (based theoretically on equations (7), (8) and (9)) in the gas stream from the burner and the rate of injection of hydrogen cyanide.

A direct theoretical relationship of this kind for both acetonitrile and hydrogen cyanide also enables direct comparisons to be made between the two cyanides as shown later.

(ii) Quantitative analysis of products

The percentages of carbon dioxide, nitrogen and oxides of nitrogen in the gas stream from the burner are recorded in Appendix III and IV for the injections of acetonitrile and hydrogen cyanide. For acetonitrile injections, up to 6 experiments were carried out for 4 syringe sizes whereas the experiments with hydrogen cyanide involved 'single point' determinations at 8 different injection rates.

The yields of carbon dioxide (as a percentage in the gas stream from the burner) for the various injection rates of the cyanides are given as experimental points (mean values for acetonitrile and single point determinations for hydrogen cyanide) in Fig 11. The line through each set of points is the theoretical carbon dioxide yield assuming complete combustion. These two lines have slopes in the ratio of 2:1 because of the overall stoichiometry of the relevant combustion equations.

The equivalent data for the yields of nitrogen for the cyanide injections (mean points for acetonitrile and single point determinations for hydrogen cyanide) are given in Fig 12. As seen, there is a broad agreement between the yields of nitrogen from both acetonitrile and hydrogen cyanide, but all points lie below the theoretical line, as would be expected since some nitrogen* is involved in the formation of oxides of nitrogen. The theoretical line shown in Fig 12 is the same line for both acetonitrile and hydrogen cyanide

*but not necessarily as free nitrogen

since the injection flow rate scale is recorded in VAPOUR terms, and hence the molar injection rates of the two materials are equivalent. The slope of this theoretical line is of course 0.5 and 0.25 times the slope of the carbon dioxide lines of hydrogen cyanide and acetonitrile respectively given in Fig 11. The acetonitrile point marked (x) in Fig 12 is in error for reasons not understood. Any subsequent data plotted graphically using this point will be marked (x).

The production of oxides of nitrogen in equivalent terms are shown in Fig 13. No attempt has been made to include a theoretical line and the dotted line through the points is drawn by eye. It is interesting to note that, as observed for nitrogen production, there is agreement between the yields of oxides of nitrogen from both cyanides when plotted in this way.

(iii) Flame experiments with a vitiated atmosphere

A series of experiments (similar to those carried out in the previous section) were undertaken with a relatively cold flame. This flame was produced by reducing the oxygen concentration in the burner enclosure to about 10% yet still keeping the oxygen availability constant. This was achieved by maintaining the oxygen (21%)–argon flow to the burner at the standard level of 160 ml/min but introducing a further supply of pure argon, also at 160 ml/min, in such a way as to ensure complete premixing before the gases entered the flame enclosure.

The resulting flame was somewhat less stable than the standard flame but once alight, burnt without any problems.

The yields of carbon dioxide, nitrogen and oxides of nitrogen (as percentages in the gas stream from the burner) are recorded in Appendix V for the injection of acetonitrile and hydrogen cyanide; only single point determinations were carried out for acetonitrile.

The yields of carbon dioxide for the various injections are shown (as experimental points) with respect to the injection rate of cyanide (both as vapour) in Fig 14. The lines through the points represent the theoretical behaviour assuming complete combustion.

The equivalent yields of nitrogen and oxides of nitrogen for this study are shown graphically in Fig 15. The dotted lines through each set of points are drawn by eye and the solid line represents the theoretical nitrogen recovery.

As in the standard burning conditions, there is agreement of the yields of nitrogen and oxides of nitrogen between the two cyanides when plotted in this way.

(iv) Material balance for nitrogen-containing products

It has been established that complete combustion of both cyanides to carbon dioxide takes place under both burning conditions (ie standard and vitiated atmospheres). The only nitrogen-containing products detected are nitrogen and oxides of nitrogen. On theoretical considerations, one mole of acetonitrile or hydrogen cyanide would produce on combustion 0.5 moles of nitrogen or 1 mole of oxides of nitrogen. Thus in this combustion study the function $(N_2 + \frac{1}{2} NO)$ where nitrogen and oxides of nitrogen are measured on a volume basis (ie a gas percentage) should be equivalent to the theoretical nitrogen production.

The function $(N_2 + \frac{1}{2} NO)$ for the various cyanide experiments are tabulated in Appendix V1 and shown graphically as experimental points in Fig 16. The solid line through each set of points represents the theoretical nitrogen yield in each case showing the complete material balance of the experimental yields of nitrogen and oxides of nitrogen.

The slopes of the theoretical lines for the standard and cool flame yields in Fig 16 are not exactly in the ratio of 2:1 due to oxygen consumption by the flame*.

This work establishes the full material balance for the nitrogen content of the two cyanides in the formation of nitrogen and oxides of nitrogen under both flame conditions. Relative proportions of nitrogen and oxides of nitrogen can be considered using the ratio N_2/NO_x as a function of cyanide injection rate. The relevant data for N_2/NO_x for the various cyanide injections are given in Appendix VI and the data shown graphically in Fig 17.

This figure demonstrates a general linear dependence of N_2/NO_x as a function of the cyanide injection rate. Statistical analysis of the data shows that the relationships for standard and vitiated atmospheres are linear and the best straight lines given by

$$\text{Line A : } N_2/NO_x = 0.68 (\text{I.R.}) + 0.36$$

with correlation factor 0.99

$$\text{Line B : } N_2/NO_x = 0.56 (\text{I.R.}) + 0.39$$

with correlation factor 0.97

where I.R. is the injection rate of cyanide.

*In the vitiated flame experiments oxygen (21%)-argon and pure argon are each introduced to the flame at 160 ml/min.

4. DISCUSSION

a) General discussion

This report demonstrates that a hydrogen flame with means of the motorised injection of fuels into the flame is a versatile means of studying the reactions and end products of various combustion systems. The flame unit, together with gas chromatography and mass spectrometry can be used both qualitatively and quantitatively as shown by the work involving hydrocarbon fuels injected into the flame as either liquids or gases. The only product detected (other than water) is carbon dioxide which accounts for all the available carbon in the fuels.

This is also true for the cyanide fuels, where the only carbon containing product is carbon dioxide formed in quantities as stoichiometrically predicted under both burning conditions (ie standard and vitiated atmospheres). This confirms that all the cyanide fuel is being burnt and is consistent with the experimental absence of any unburnt cyanides during mass spectrometry.

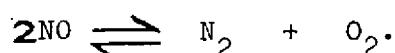
The only products detected which contain nitrogen during the burning of the cyanides are molecular nitrogen and oxides of nitrogen NO_x . It has been shown by material balance calculations that, under both standard and vitiated burning conditions, these products account for the entire nitrogen content of the two cyanide fuels.

When based on an injection rate of cyanides in vapour (ie molar) terms the yields of both oxides of nitrogen and molecular nitrogen are in agreement for both cyanides. The reason for this is not understood but may be associated with the same intermediate species being involved from both acetonitrile and hydrogen cyanide (eg cyanide radicals). Alternatively acetonitrile may decompose to hydrogen cyanide in the hot preflame zone and hence burn as hydrogen cyanide. The concentration of these intermediate species (or hydrogen cyanide) in the flame in each case will be dependent upon the injection rate of the cyanides and this may help to explain the observed relation between the ratio of the yields of oxides of nitrogen and nitrogen and the volume injection rate of the cyanides.

The general combustion of the cyanides to oxides of nitrogen and molecular nitrogen are quite similar under both flame conditions. The vitiated flame will be relatively cold in comparison with the standard flame but tends to produce yields of oxides of nitrogen and molecular nitrogen which are slightly

richer in nitrogen than observed during standard burning condition (see Fig 17). Lines A and B in Fig 16 represent the best straight lines through each set of N_2/NO_x points for the standard and vitiated flames respectively. The lines appear to be slightly different although the intercept at zero cyanide injection rates are similar and of the order of 0.4. The vitiated atmosphere tends to favour the production of oxides of nitrogen more than the standard flame.

In flames burning in air, oxides of nitrogen are generated by free atom reactions involving an overall equilibrium:



The formation of oxides of nitrogen from atmospheric nitrogen is often referred to as 'fixation'. The equilibrium is strongly temperature dependent with high temperature favouring the production of NO.

No attempts will be made in this report to assess the equilibrium conditions related to the distribution of oxides of nitrogen and molecular nitrogen because of the many uncertainties involved in the calculation and particularly the estimations of the flame temperatures.

It is experimentally known that the injection of nitrogen into the 'normal' flame during the calibration experiments of section 3(a) (iii) even at concentrations sufficient to produce an excess of 2 per cent nitrogen (Fig 8) in the flow stream from the burner produced no detectable oxides of nitrogen. The limit of detection by mass spectrometry with this particular system is 5 ppm such that the ratio of nitrogen to oxides of nitrogen is greater than 4000. Under conditions of vitiated combustion the ratio is likely to be very much greater than this figure.

In the experiments with added cyanides the nitrogen to oxides of nitrogen ratio is similar for both standard and vitiated combustion and lies between about 0.4 and 3.

It therefore seems clear that the quantities of the oxides of nitrogen formed during the combustion of cyanide fuels are very much in excess of the quantities expected from the normal fixation routes. It is concluded that the nitrogen content of cyanides is much more active in producing oxides of nitrogen than molecular nitrogen via fixation.

b) Discussion of the fire behaviour of cyanides

For technical reasons it has been necessary to carry out the combustion study of this report by burning cyanides in a hydrogen diffusion flame. This flame is not completely typical of full scale fires but may be realistic in the sense that the hydrogen provides a combustion system which ensures the complete combustion of the cyanides. Under these conditions the nitrogen content of both hydrogen cyanide and acetonitrile is released exclusively as either oxides of nitrogen or molecular nitrogen. The relative concentrations of these products appear to be dependent on the concentration of cyanides in the flames and over the range of concentrations used in this report the NO_x varies from about 0.3 to 2.5 times the concentration of molecular nitrogen.

From the work of this report it is recommended that the concentrations of oxides of nitrogen should be monitored in real fire tests involving the combustion of polyurethane foams and other fuels which release cyanides because of the real possibility of the generation of high concentrations of these gases from the combustion of cyanides.

5. CONCLUSIONS

1. A hydrogen diffusion flame burning in an atmosphere of argon and oxygen with a means of injecting separate fuels is a versatile and convenient system for studies of combustion reactions and end-products.

2. Experiments involving the combustion of C_1 to C_6 saturated hydrocarbons demonstrate that the combustion of the fuel is complete and that the overall flow to and from the burner and the injection rate of fuel can be used for mass-balance experiments.

3. The combustion processes of hydrogen cyanide and acetonitrile are similar and the nitrogen content of each cyanide is released only as oxides of nitrogen or molecular nitrogen.

4. The relative concentrations of oxides of nitrogen and molecular nitrogen are dependent on the concentration of cyanide in the flame. The concentration of oxides of nitrogen measured as NO_x varies between about 0.3 and 2.5 times the concentration of molecular nitrogen over the range of cyanide injection rates used in this report. A low concentration of cyanide favours the production of oxides of nitrogen.

5. Studies with a vitiated diffusion flame indicate that the yields of oxides of nitrogen and molecular nitrogen are largely independent of flame temperature.

6. The nitrogen content of cyanide fuels can produce significant yields of oxides of nitrogen during combustion. In comparison the yields of oxides of nitrogen by nitrogen fixation routes tend to be insignificant.

6. ACKNOWLEDGMENTS

The authors wish to thank Mr T Hersey for his help during the initial considerations of experimental procedures. Mrs A I Pitt assisted with the chromatographic analysis of products.

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8. APPENDIX

Appendix I

Hexane linearity experiments

Oxygen-argon flow to burner (ml/min)	Syringe size (μ l)	Rate of injection* (ml/min)	Carbon dioxide	
			Theoretical (%)	Experimental (%)
170	10	0.341	1.29	1.26 (10)
170	25	0.767	2.91	2.77 (4)
170	50	1.532	5.93	6.17 (6)

*In terms of hexane vapour at room temperature

ϕ Mean value of (x) determinations

Appendix II

Hydrocarbon combustion data

Hydrocarbon	Syringe capacity	Rate of injection (vapour)* (ml/min)	Experimental ϕ carbon dioxide (%)	Rate of production of carbon dioxide (ml/min)	Carbon dioxide to hydrocarbon (mole ratio)
Methane	20 ml	3.40	2.22 (8)	3.456	1.02
Ethane	5 ml	1.22	1.58 (8)	2.507	2.05
Propane	2 ml	0.639	1.20 (5)	1.910	2.99
Butane	5 ml	1.22	3.36 (3)	5.289	4.3
Pentane	10 μ l	0.383	1.21 (7)	1.928	5.06
Hexane	50 μ l	1.53	6.17 (5)	9.572	6.25

*At room temperature

ϕ Mean value of (x) determinations; all based on oxygen argon
flow to burner of 170 ml/min

Appendix III

Acetonitrile combustion data*

Identification number	Injection rate of acetonitrile ^x (ml/min)	Product	Yield of product							
			Experimental (%)						Mean (%)	Theoretical (%)
1	0.844	Carbon dioxide	1.33	1.16	1.11	-	-	-	1.20	1.11
2	1.90	Carbon dioxide	2.53	2.44	2.46	-	-	-	2.48	2.50
3	2.74	Carbon dioxide	3.66	3.62	3.67	-	-	-	3.65	3.61
4	3.79	Carbon dioxide	5.02	5.27	5.14	5.09	5.00	-	5.03	5.00
1	0.844	Nitrogen	0.17	0.21	0.20	-	-	-	0.193	0.27 ^g
2	1.90	Nitrogen	0.50	0.43	0.50	-	-	-	0.48	0.64
3	2.74	Nitrogen	0.49	0.71	-	-	-	-	0.60	0.90
4	3.79	Nitrogen	1.06	1.04	1.03	1.15	1.01	1.08	1.06	1.25
1	0.844	Oxides of nitrogen	0.27	0.24	0.22	-	-	-	0.24	0.54 ^g
2	1.90	Oxides of nitrogen	0.25	0.30	0.33	-	-	-	0.29	1.28
3	2.74	Oxides of nitrogen	0.36	6.35	0.38	-	-	-	0.36	1.80
4	3.79	Oxides of nitrogen	0.37	0.35	0.38	0.38	0.36	0.40	0.37	2.50

*Based on oxygen (21%)-argon flow to burner if 160 ml/min

^gAssuming complete conversion to nitrogen or oxides of nitrogen respectively

^xAs vapour

Appendix IV

Hydrogen cyanide combustion data*

Identification number	Injection rate ^x of hydrogen cyanide (ml/min)	Experimental yields			Theoretical yields	
		Carbon dioxide (%)	Nitrogen (%)	Oxides of nitrogen (%)	Carbon dioxide (%)	Nitrogen ^y (%)
5	0.609	0.40	0.15	0.18	0.40	0.20
6	1.01	0.60	0.19	0.20	0.66	0.33
7	1.08	0.62	0.20	0.20	0.71	0.35
8	1.14	0.74	0.27	0.21	0.74	0.37
9	1.41	0.91	0.34	0.24	0.92	0.46
10	1.71	1.08	0.41	0.27	1.12	0.56
11	2.17	1.45	0.57	0.31	1.42	0.71
12	2.63	1.81	0.72	0.32	1.72	0.86

*Based on an oxygen (21%)-argon flow to burner of 160 ml/min

^yAssuming complete conversion to nitrogen

^xAs vapour

Appendix V

Flame experiments with a vitiated atmosphere
involving acetonitrile and hydrogen cyanide

Identification number	Cyanide ^x	Injection* rate (ml/min)	Experimental yields			Theoretical yields	
			Carbon dioxide (%)	Nitrogen (%)	Oxides of nitrogen (%)	Carbon dioxide (%)	Nitrogen ^y (%)
13	AN	0.844	0.55	-	0.13	0.54	0.13
14	AN	1.90	1.16	0.27	0.18	1.21	0.30
15	AN	2.74	1.81	0.35	0.18	1.75	0.44
16	AN	3.79	2.40	0.48	0.20	2.41	0.60
17	HC	0.654	0.18	0.057	0.087	0.21	0.10
18	HC	1.01	0.36	0.086	0.11	0.32	0.16
19	HC	1.57	0.46	0.18	0.120	0.50	0.25

^xHC - Hydrogen cyanide; AN - acetonitrile

*As vapour

^yAssuming complete conversion to nitrogen

Appendix VI

Values of N_2/NO_x and $N_2 + \frac{1}{2}(NO_x)$ for combustion experiments² calculated from Appendix III, IV and V

Identification number	N_2/NO_x	$N_2 + \frac{1}{2}(NO_x)$ (%)	N_2 theoretical (%)
1*	.80	0.31	0.27
2*	1.66	0.63	0.64
3*	1.67	0.78	0.90
4*	2.87	1.25	1.25
5	0.83	0.24	0.20
6	0.95	0.29	0.33
7	1.00	0.30	0.35
8	1.29	0.38	0.37
9	1.42	0.46	0.46
10	1.52	0.55	0.56
11	1.84	0.73	0.71
12	2.25	0.88	0.86
13	-	-	
14	1.49	0.36	0.30
15	1.94	0.44	0.44
16	2.40	0.58	0.60
17	0.66	0.10	0.10
18	0.82	0.14	0.16
19	1.51	0.24	0.25

* Based on mean figures

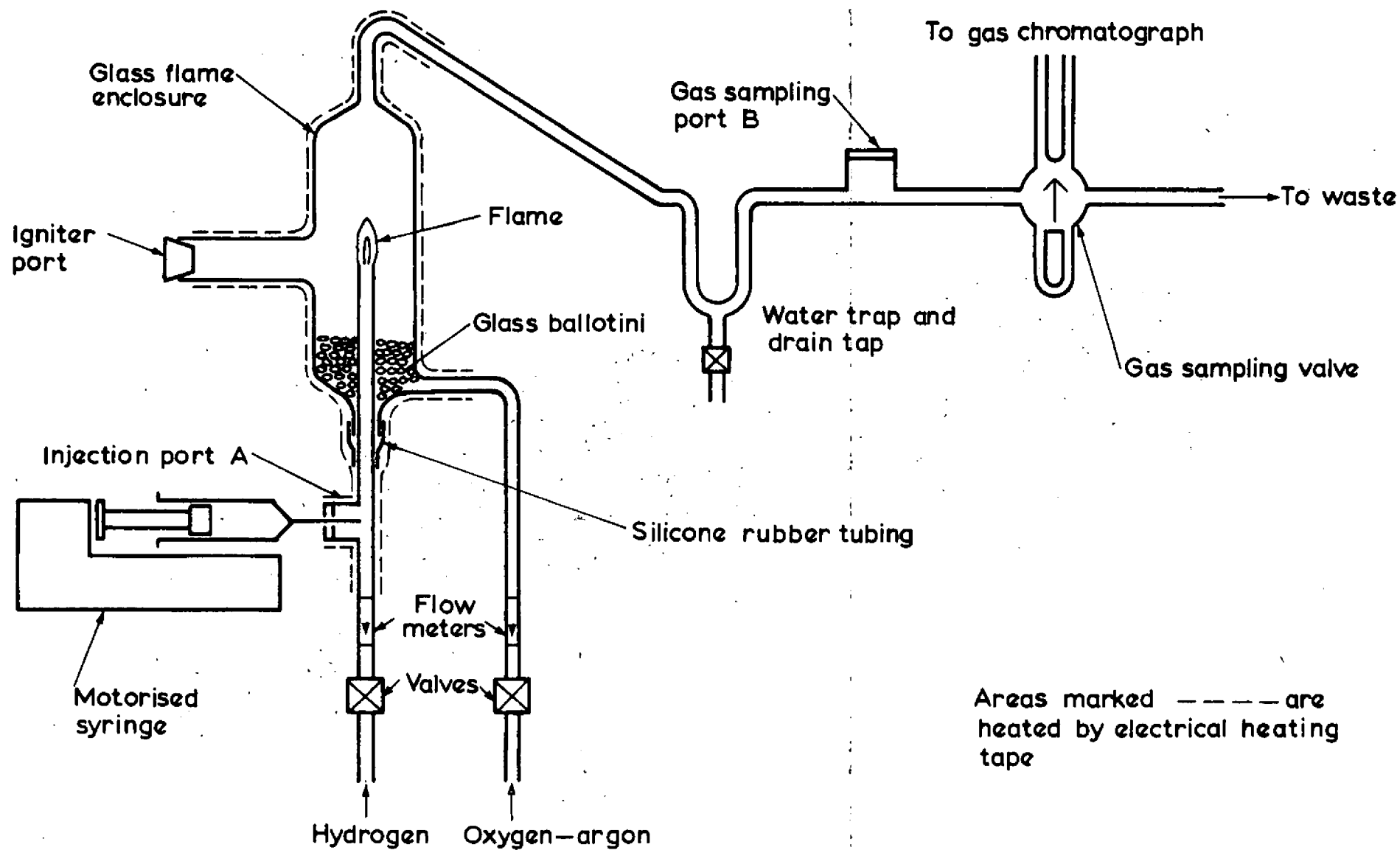


Figure 1 The burner system

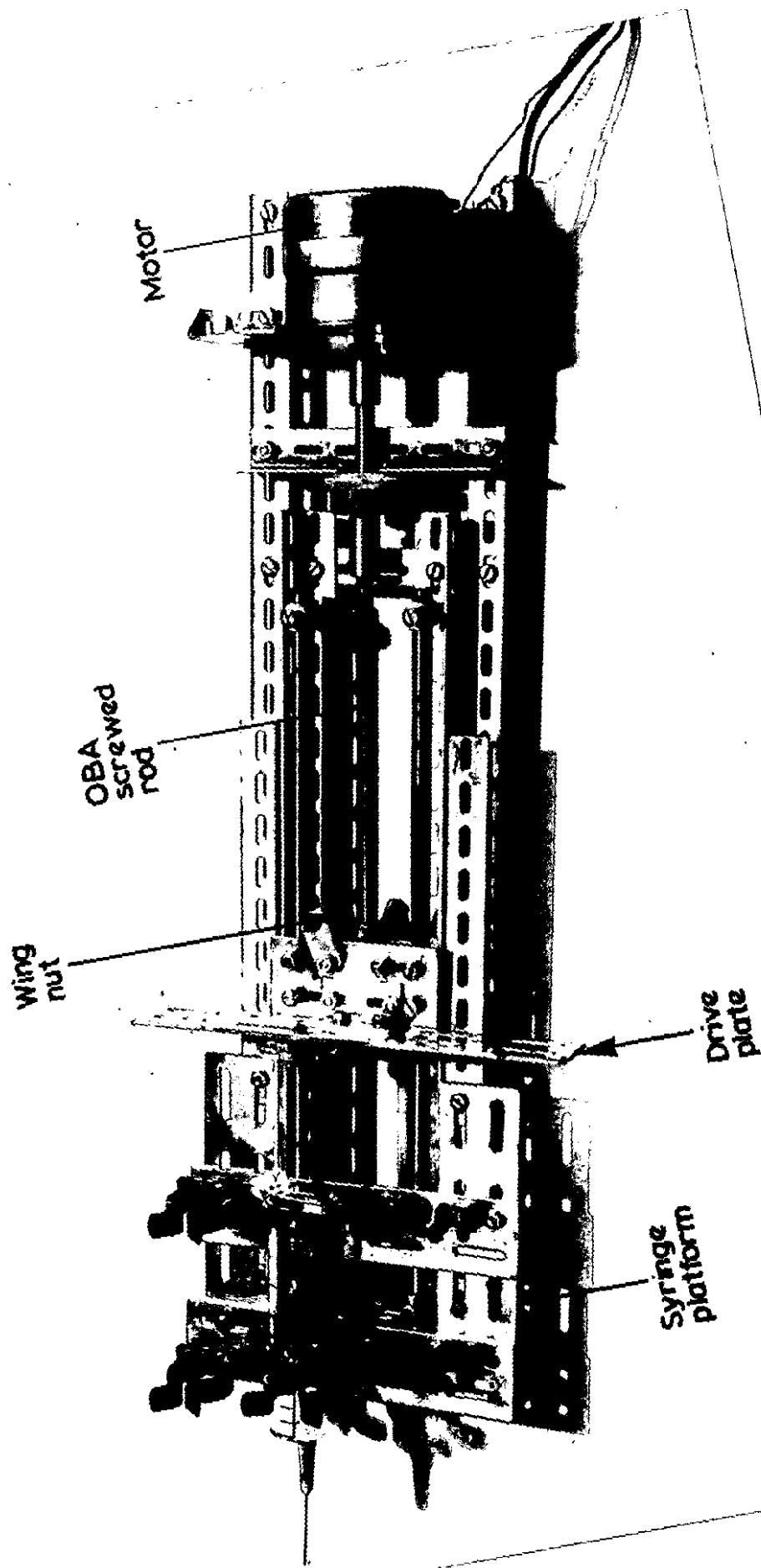


Figure 2 The motorised syringe unit

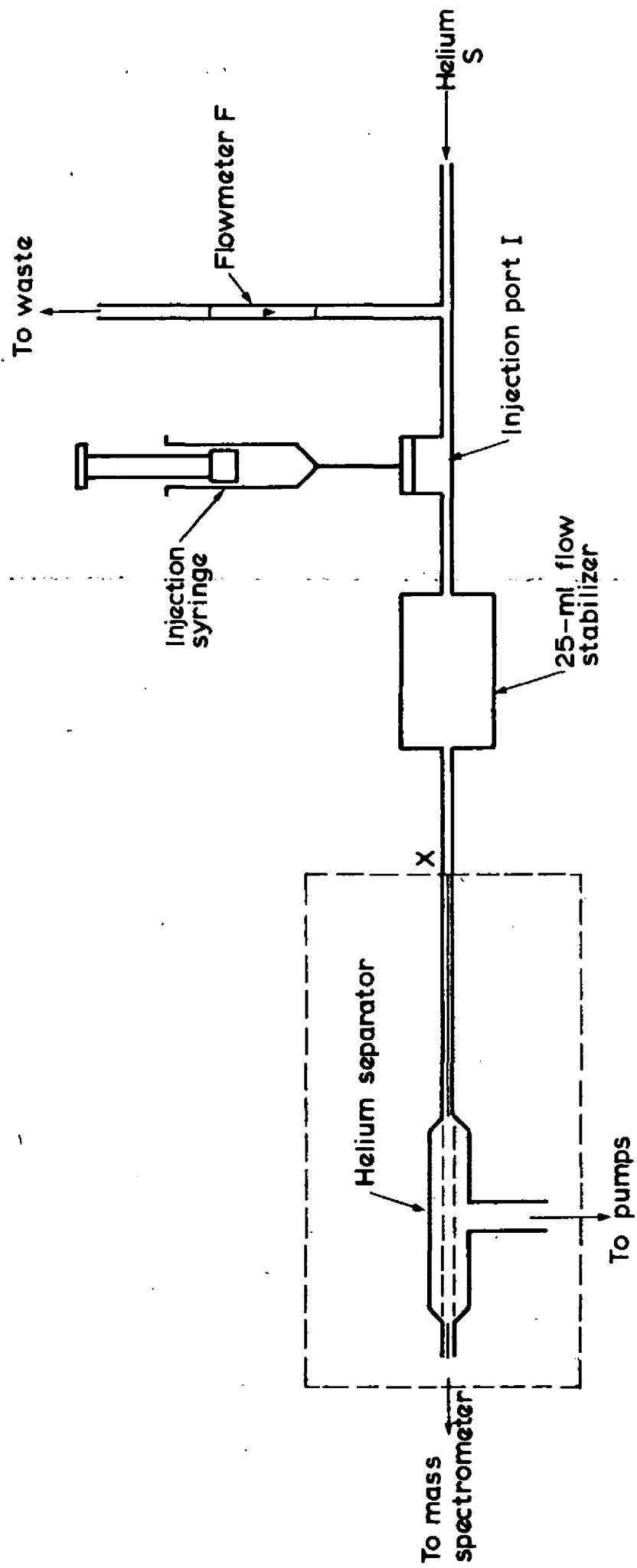


Figure 3 The mass spectrometric analysis system

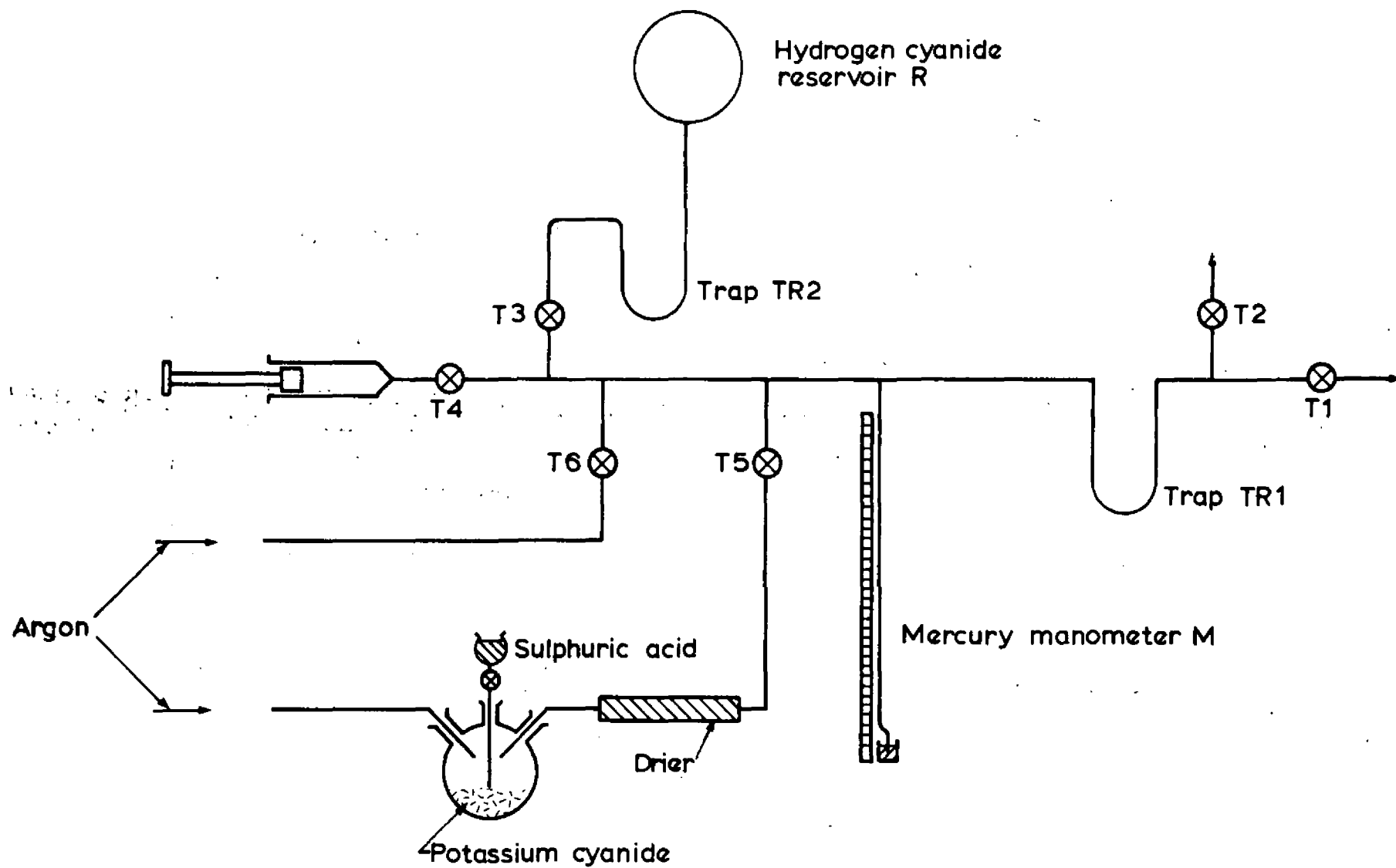
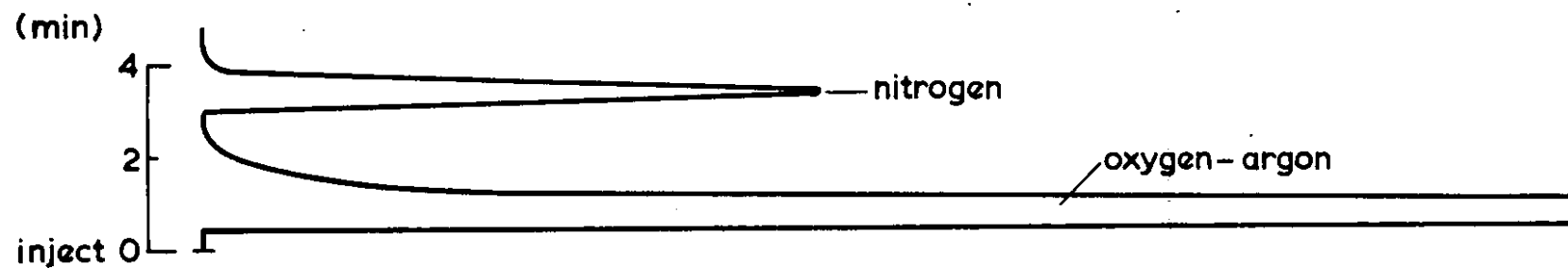
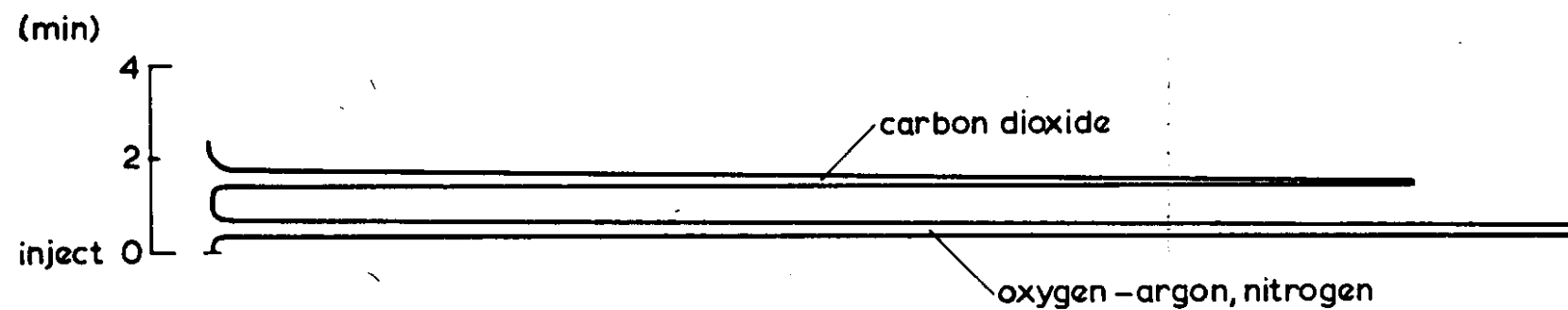


Figure 4 The preparation and gas handling system for hydrogen cyanide



(a) Molecular sieve column



(b) Porapak Q column

Figure 5 Chromatographic analysis of nitrogen and carbon dioxide

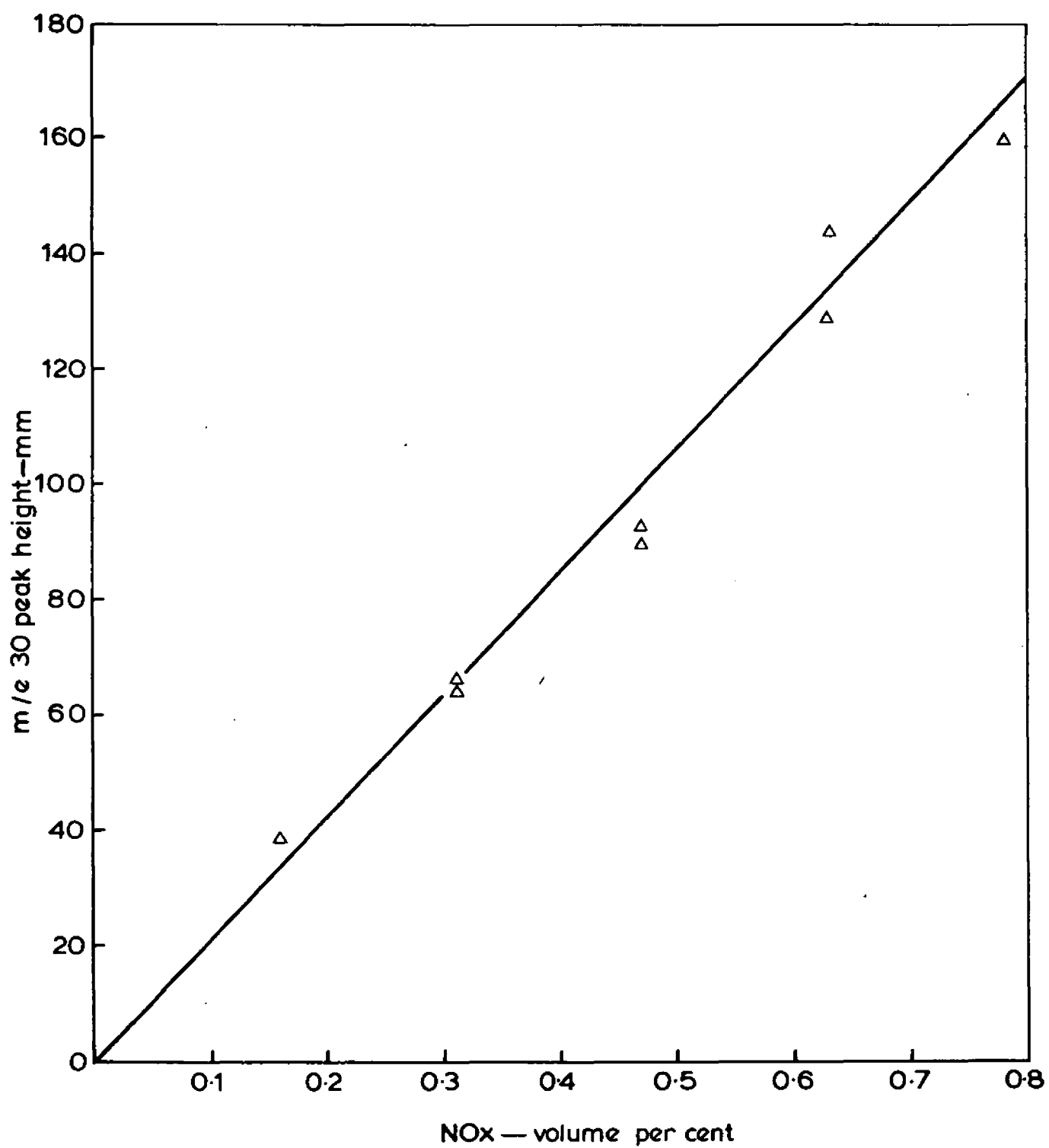


Figure 6 Calibration curve for NOx by mass spectrometry

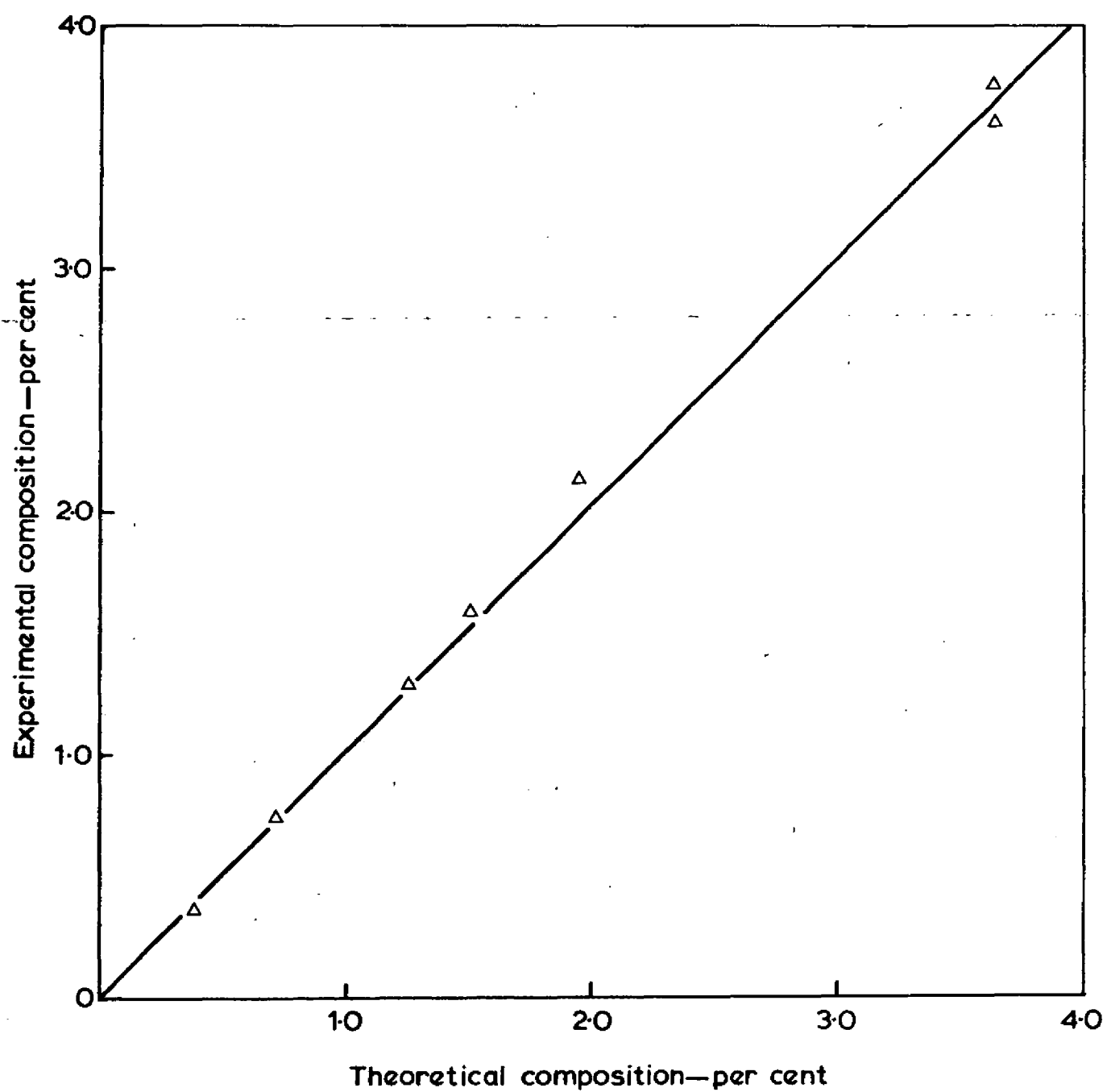


Figure 7 Flame calibration for carbon dioxide

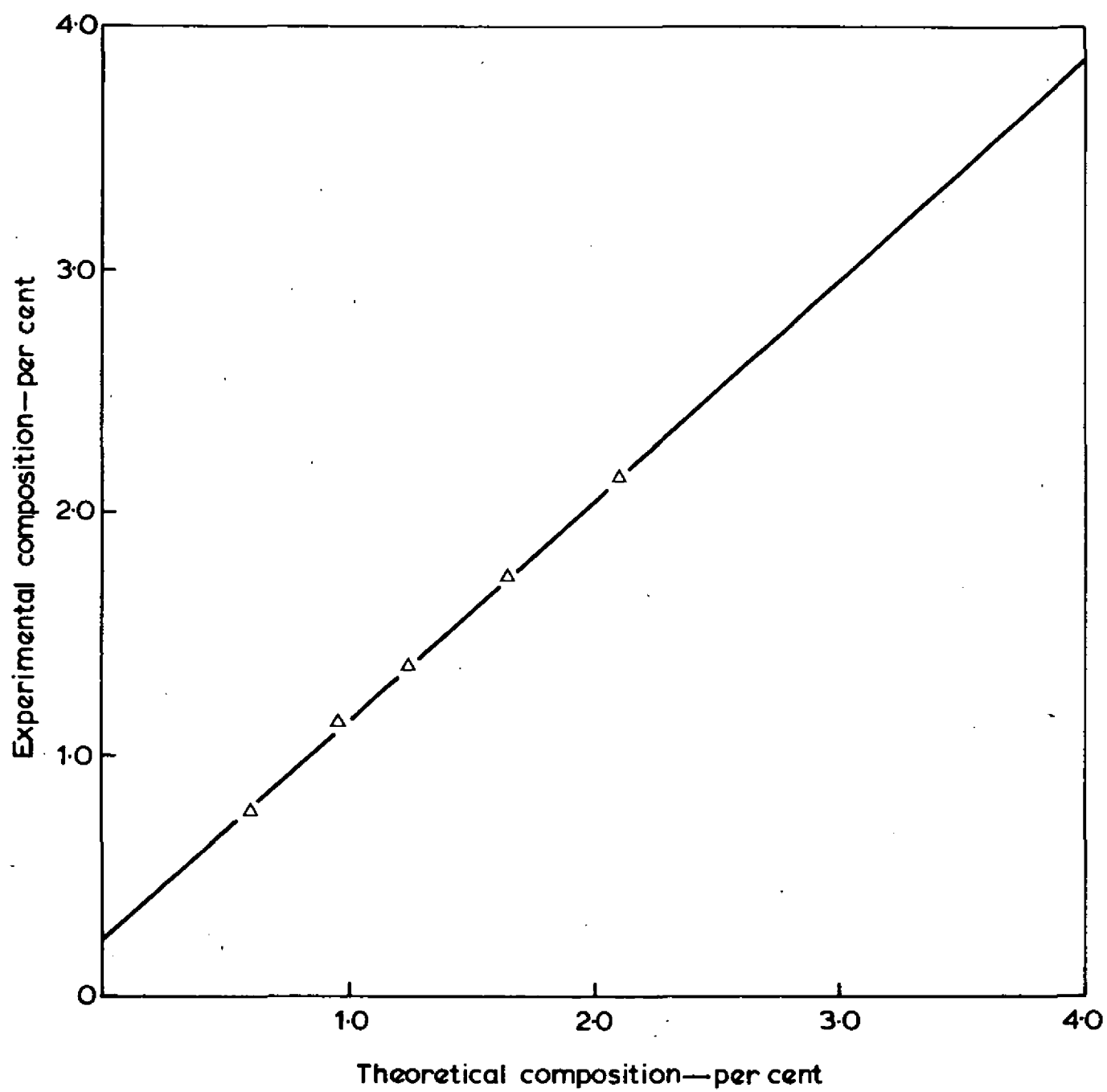


Figure 8 Flame calibration for nitrogen

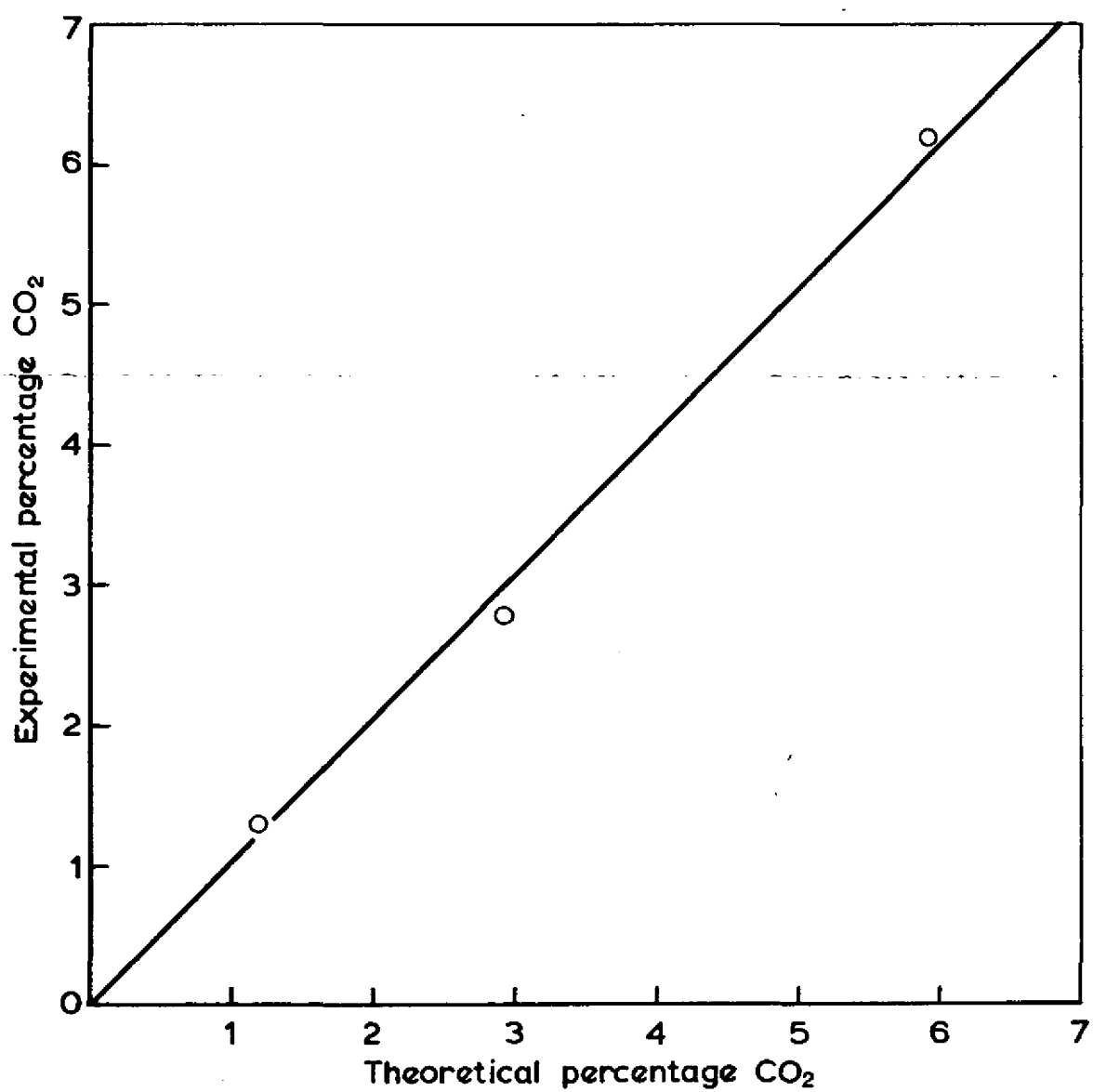


Figure 9 Linearity check using n-Hexane

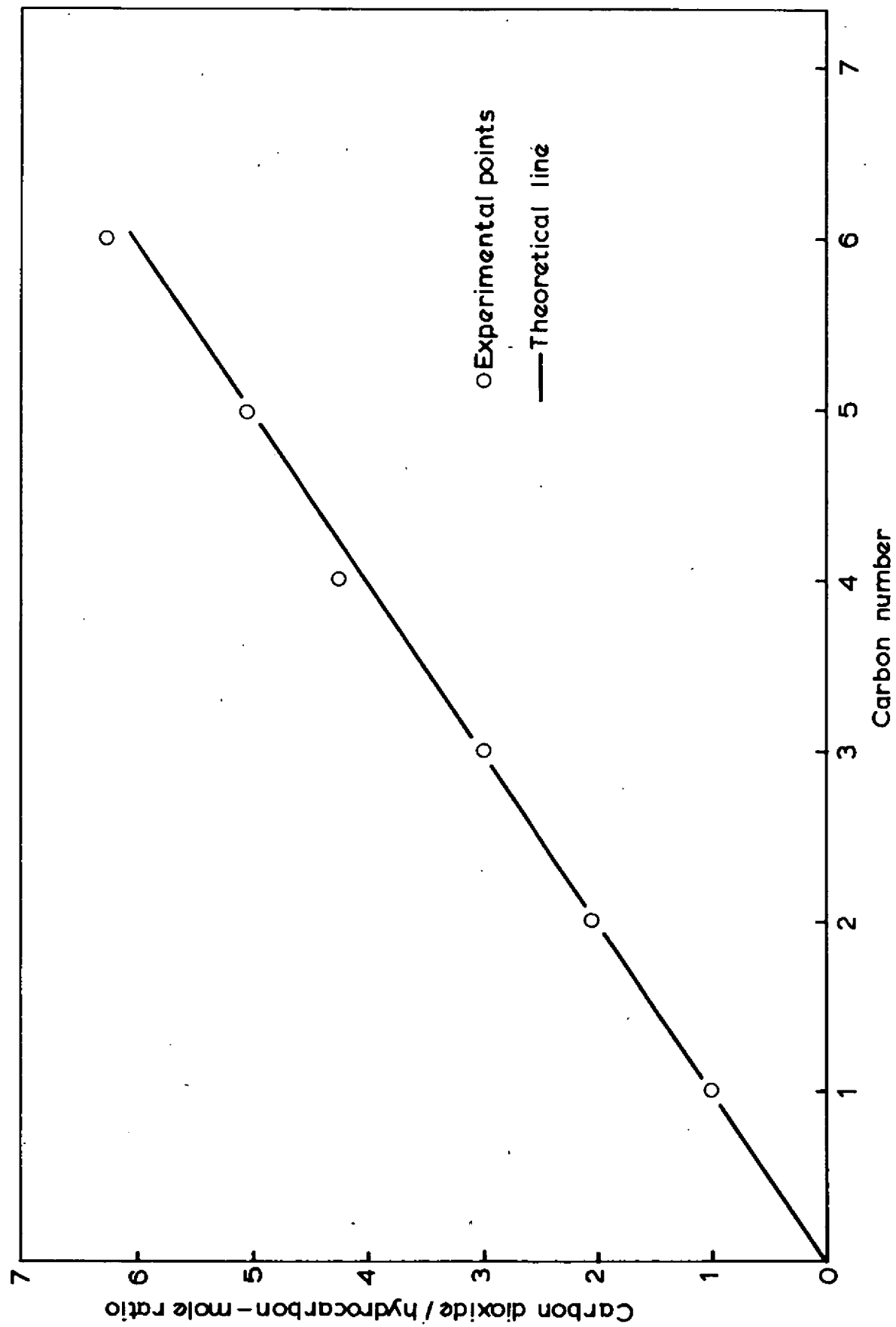


Figure 10 Hydrocarbon combustion data

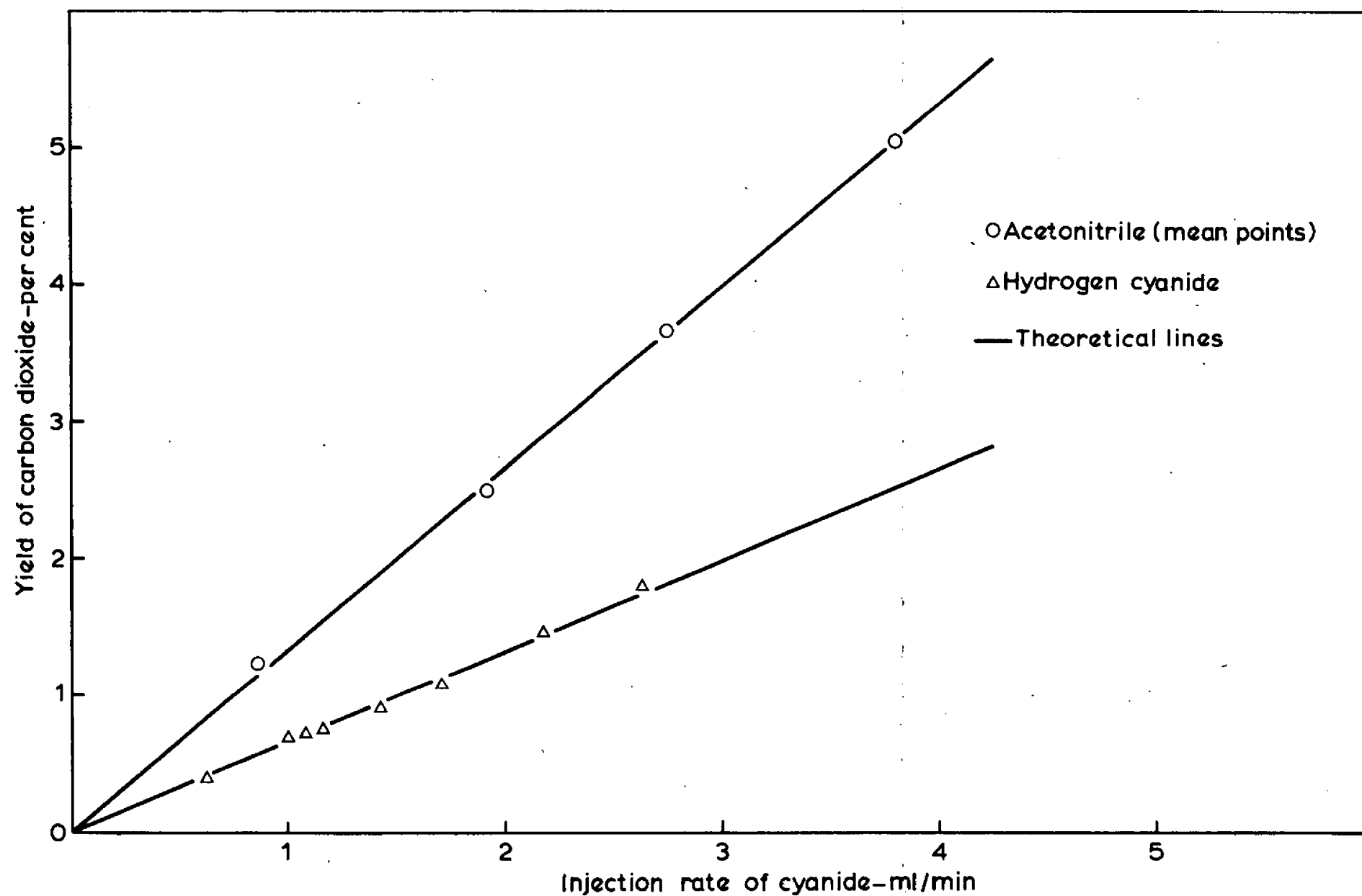


Figure 11 Yields of carbon dioxide during cyanide combustion

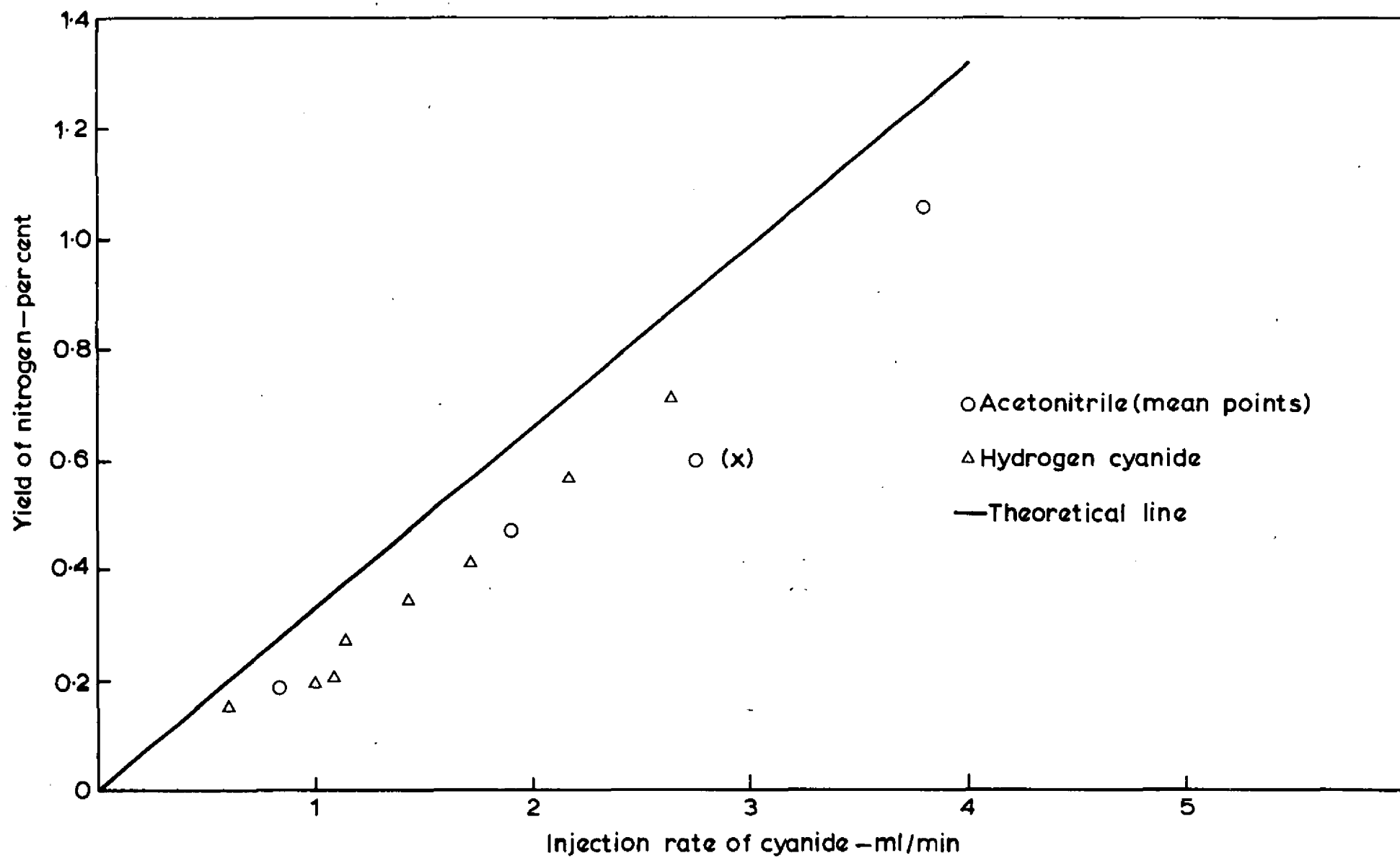


Figure 12 Yields of nitrogen during cyanide combustion

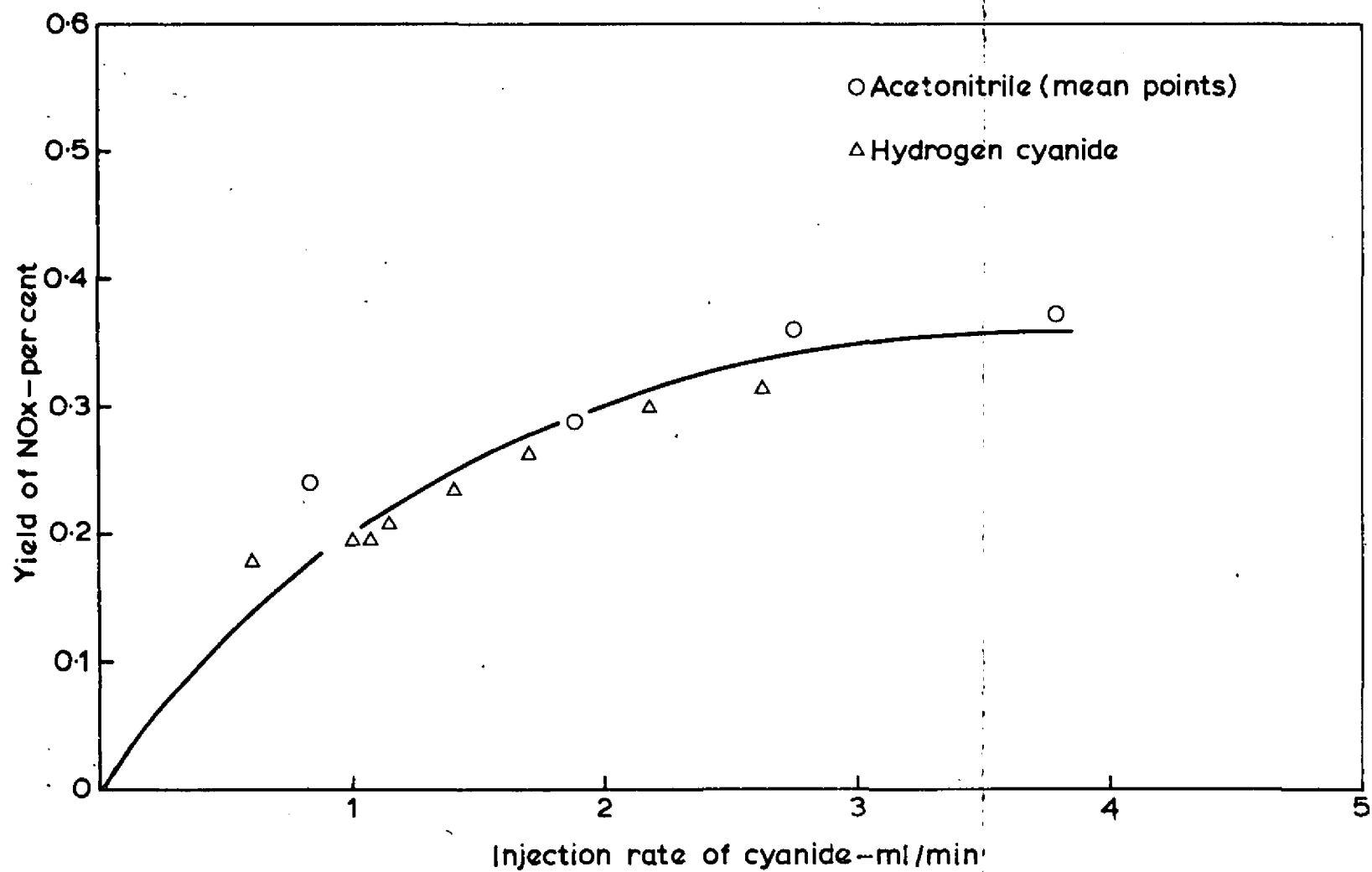


Figure 13 Yields of oxides of nitrogen during cyanide combustion

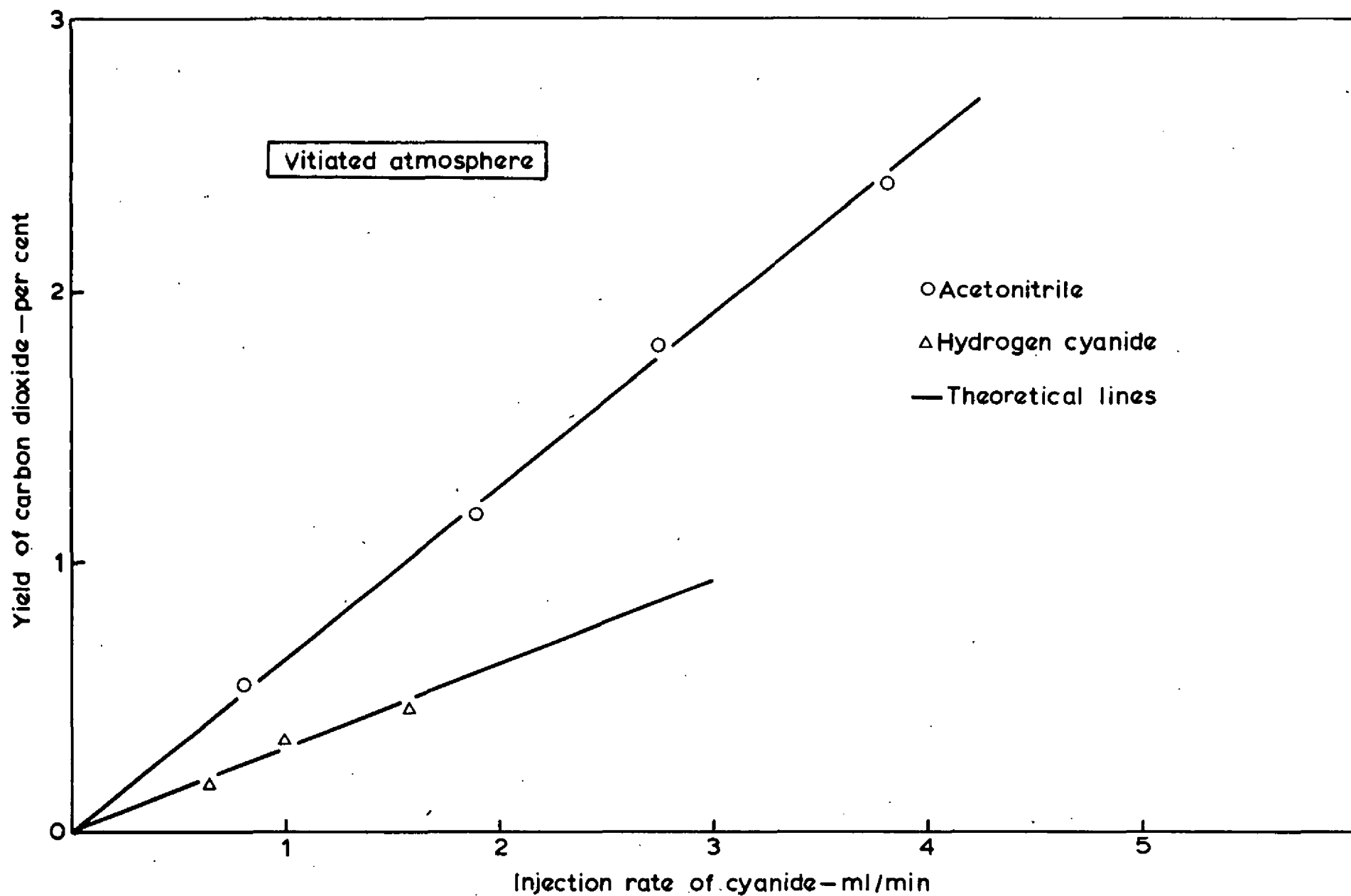


Figure 14 Yields of carbon dioxide during cyanide combustion in vitiated atmosphere

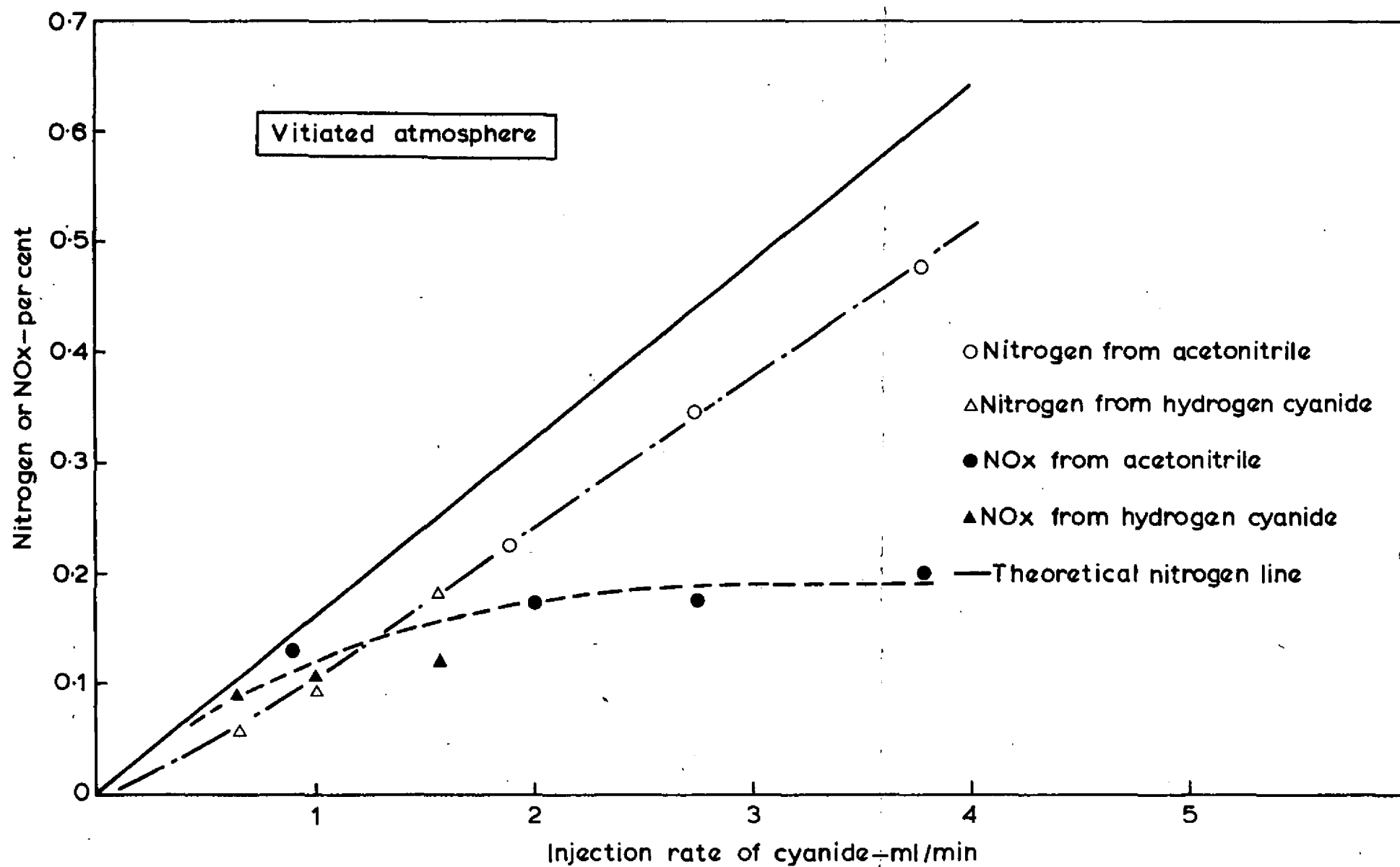


Figure 15 Yields of nitrogen and oxides of nitrogen during cyanide combustion in vitiated atmosphere

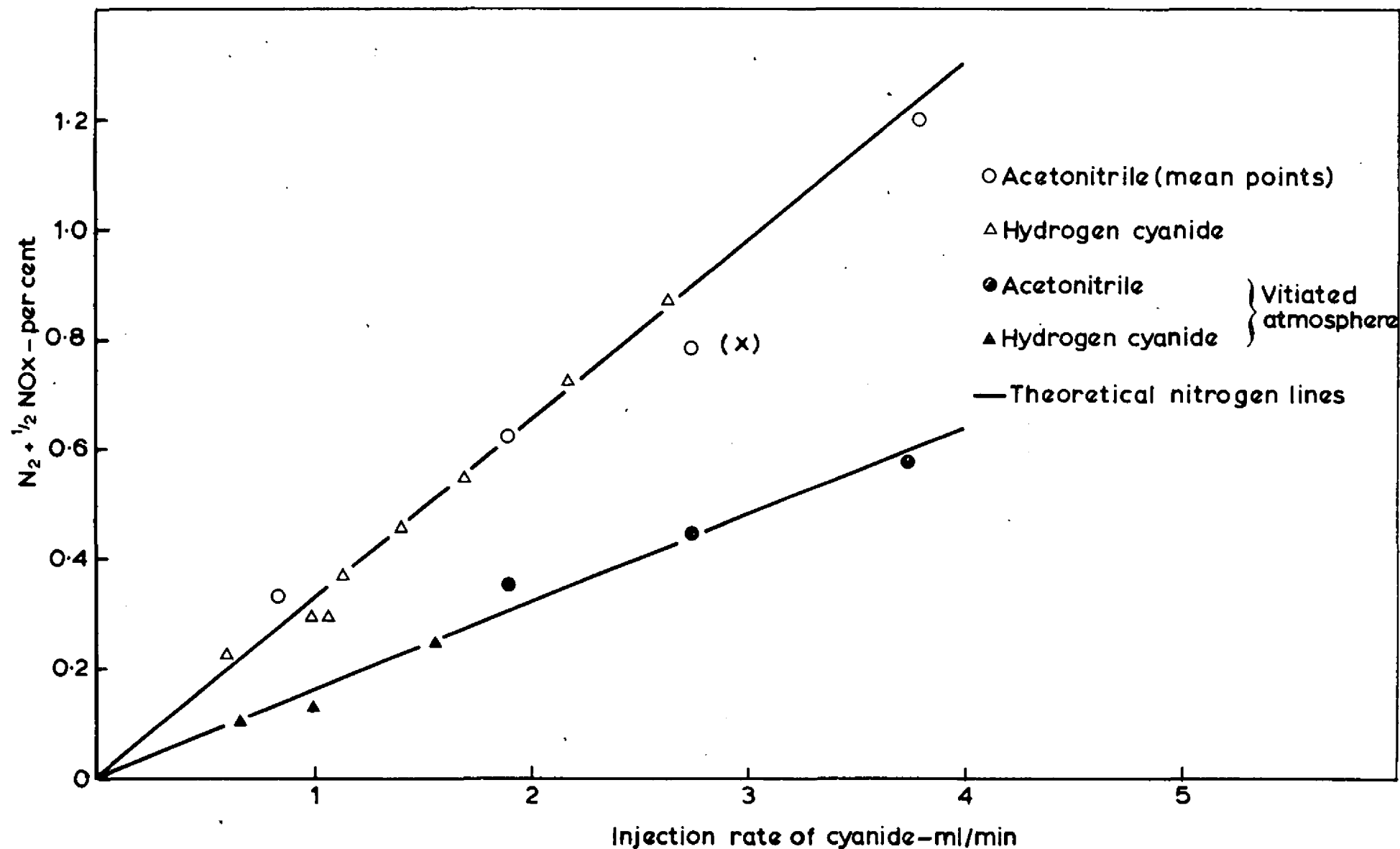


Figure 16 Comparisons between $(N_2 + \frac{1}{2} NO_x)$ and the theoretical yields of nitrogen for cyanide combustion

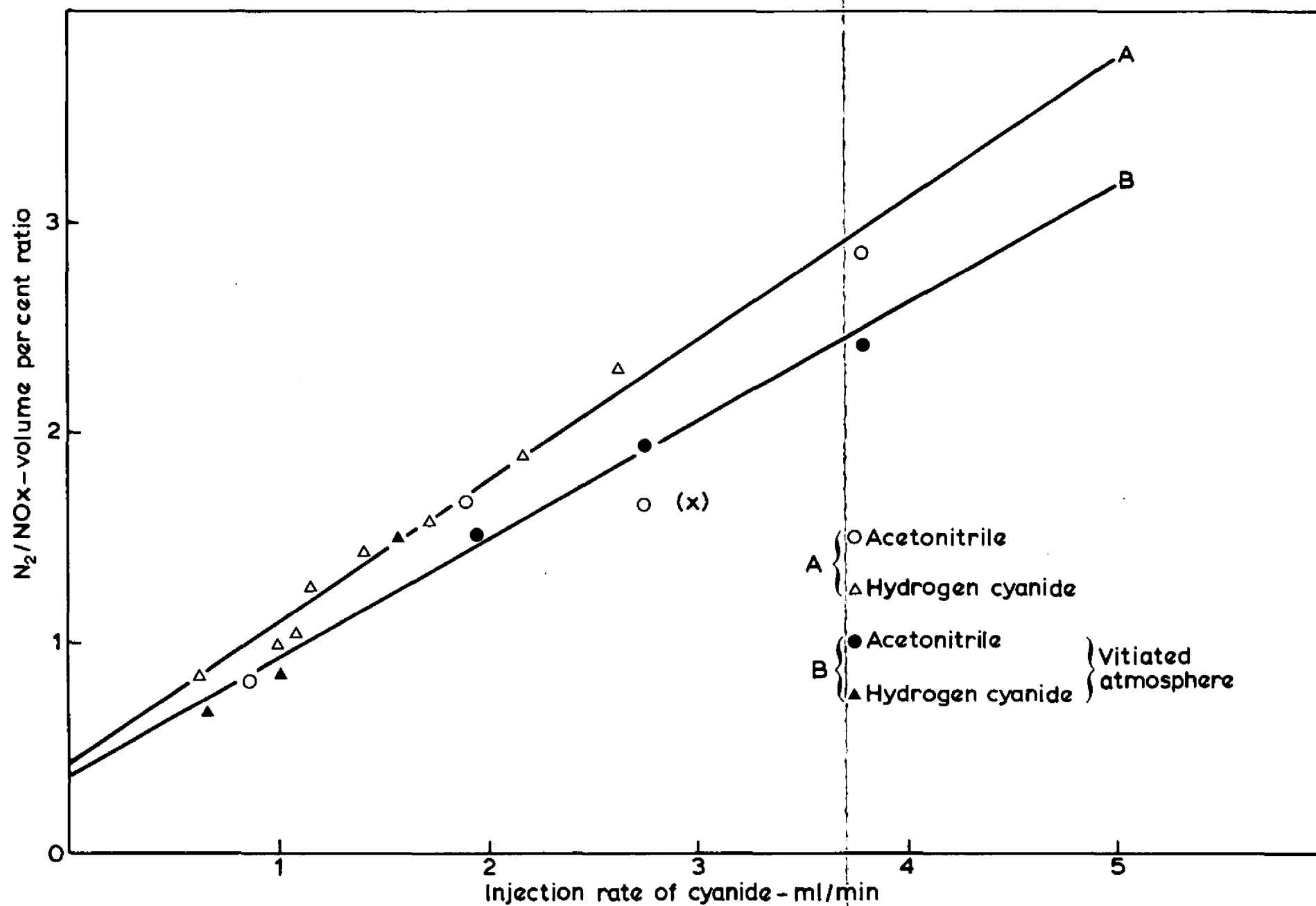


Figure 17 N_2/NO_x as a function of injection rate for cyanide combustion

