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GAS EXPLOSIONS IN BUILDINGS PART III

A RAPID, MULTI-CHANNEL, AUTOMATIC CHROMATOGRAPHIC
GAS ANALYSIS SYSTEM

by

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SUMMARY

An apparatus is described which has been developed for high-speed analysis of gas samples taken from different positions in an experimental chamber used for large-scale gas explosions. The equipment is automatic (with manual override), can be controlled remotely, gives a quantitative output and is sufficiently versatile to have many other applications.

Department of the Environment and Fire Offices' Committee
Joint Fire Research Organization

GAS EXPLOSIONS IN BUILDINGS

FOREWORD

Following the Ronan Point disaster and the report of the Investigating Tribunal, it was decided that the Fire Research Station of the Building Research Establishment would undertake a study of gas explosions in large compartments. In particular, the study would cover the factors affecting the development and severity of the explosions and the extent to which the pressures obtained could be relieved by venting.

In the context of the problem as a whole, the study is intended to provide the basic data on the form and magnitude of the transient stresses likely to be experienced by buildings, in the event of gas explosions involving one or more compartments. This information is required as a guide for safe structural design and for any reappraisal of the relevent parts of the Building Regulations 1972, Part D, England, or Building Standards (Scotland) (Consolidation) Regulations, 1971.

The study has begun with explosions in a single compartment of realistic dimensions (1000 ft^3, 28 m^3) provided with a single opening of simple configuration, the size of which can be varied and which can be closed with panels having a range of bursting pressures.

In view of the progressive change to natural gas, which is lighter than air, and the probable circumstances of the Ronan Point explosion, special emphasis is placed on the explosion of layered gas/air mixtures and the effects of layer depth, composition and point of ignition.

The principal measurements consist of high-resolution pressure-time records at points both inside and outside the compartment. In general, these pressure records are complex, including both positive and negative pressures, and attention is given to the exclusion of spurious effects due to mechanical vibration and transient heat pulses accompanying the explosion.

The study is to be extended to gas explosions in multiple compartments communicating by door openings and corridors. Here, particular attention will be given to the effects of turbulence generated at openings, bends and obstacles and the possibility of pressures increasing as explosion propagates from one compartment to another.

This series of notes comprises detailed accounts of phases of the work as it proceeds. A project of this magnitude necessarily involves a considerable

amount of preliminary work in the development of equipment and procedures all of which needs to be placed on record, but, in isolation, may sometimes appear somewhat remote from the objectives. This foreword is intended to facilitate the presentation of the detailed material with a minimum of introductory matter - no more than is needed to indicate the place of the particular work reported in the project as a whole. Reports of results and conclusions from this study will be included in the series at appropriate stages as the work proceeds and, correspondingly, these will need to contain a minimum of experimental detail.

Reports preceding the present one in the-series are:

FR Note 984. Part I Experimental explosion chamber. P S Tonkin and C F J Berlemont.

FR Note 985. Part II Measurement of gas explosion pressures. S A Ames.

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INTRODUCTION

In a current research programme at the Fire Research Station concerned
with the venting of gas explosions on a realistic scale, there was an immediate
requirement for a system of gas analysis which would enable the monitoring of
either neat natural gas or natural gas-air mixtures at different positions
during metering of gas into an experimental chamber, initially to form layers.
The approximate dimensions of the present chamber are 3 m x 2.4 m x 3.7 m
(10 ft x 8 ft x 12 ft) and the geometrical requirements for the sampling and
analysis system were that it should be able to analyse samples from different
positions over the whole of the area and initially up to a depth of 4 ft, but
with the additional requirement of occasionally sampling at points right down
to the base of the chamber. The specification for such a system will be listed
at a later stage, but in general the system devised for the analysis had to be
extremely flexible in terms of the number of positions within an experimental
chamber at which analysis could be performed, as the long-term requirement in
the programme was to be for larger chambers with several interconnecting
compartments which would result in a considerable increase in the demands on
the analyser.

The possible methods of analysis are now to be discussed followed by a
statement of the detailed requirements of the system. Then, after establishment
of the general basis of the chosen system, the development work leading to the
final version of the apparatus and the sampling, analysis and control sections
of the system are described in detail. Future possible developments are then
discussed.

In this note reference is made, for convenience, to the trade names of
various components. This does not imply general preference for these products
but simply reflects the availability and compatibility of the various components
at the time they were required.

ANALYTICAL SYSTEM – GENERAL CONSIDERATION

Possible methods of analysis

Currently the methods of analysing gas mixtures are numerous, but as in the present research programme extensive facilities were not available for the complete development of a custom-built system starting from first principles it was necessary to choose a method where the 'building blocks' of the basic apparatus were available commercially (preferably with reasonable choice of components). The following are some of the principal methods available:

(a)   Non-dispersive infra-red methods

(b)   Dispersive spectroscopic methods (including molecular correlation spectroscopy)

(c)   Gas chromatography (using either conventional or capillary columns)

(d)   Use of light absorption from monochromatic sources (for example, a helium-neon gas laser emitting at 3300 nm could be used for methane analysis based on the Lambert-Beer law)

(e)   Mass spectroscopy

(f)   Methods based on chemical analysis of the burnt gases after combustion of the sample (Orsat etc).

(g)   Stimulated laser Raman emission spectroscopy.

Method (a) had the advantages of being continuous and reasonably well commercially developed, but had the disadvantage that a different analyser would be required for each constituent gas and would be limited to those gases absorbing in the infra-red region of the spectrum. Problems could also arise from interference of one constituent gas with another. Methods (b), (d) and (g) had some advantages but were not commercially well developed, method (f) was somewhat dated and certainly time-consuming and (e) was not economically justifiable for this project nor was it particularly suited for automatic analysis. Gas chromatography was very well developed commercially, could be conveniently used for gas mixture analysis, was eminently adaptable for automatic control and had a useful precedent in having been used previously in a similar programme[1]. Its main disadvantage was that it was inherently a discontinuous process requiring separate injection of samples, but the other advantages were deemed to outweigh this. The system of analysis was based therefore on gas chromatography.

Requirements for the gas-chromatographic analyser

The general requirements were that the system should be:

(i) Reproducible, reliable, capable of continuous operation for periods up to one hour, and quantitative.

(ii) Automatic, (remotely controlled where possible) with manual override facilities, cyclic or repetitive based on a given number of samples in a given time.

(iii) Rapid.

(iv) Capable of analysing simple mixtures using small sample volumes (i.e. sensitive) to facilitate rapid analysis and also to reduce the effects of sampling on the layer in the explosion chamber.

(v) Flexible in terms of the number of channels, sample injection time, timing between injections and with order selection of sample points.

The system should also:

(vi) Have an output in such a form as to be accurate and not requiring excessive processing of information (i.e. digital, preferably with simultaneous analogue equivalent).

(vii) Incorporate facilities for automatic and/or manual injection of standard gas samples for calibration purposes.

Having decided what the operational principles were to be, more detailed thinking was necessary on which to base the short-term development programme necessary before the final system was complete.

Basis for the development of the analytical system

It was decided that the system would incorporate the following features:

(a) Component separation The separation of components in a gas mixture would be by conventional gas chromatography. Although capillary column chromatography had some advantages in terms of speed, it was felt that this technique was not sufficiently developed. Temperature programming facilities were not required for the chromatographic separation involved.

(b) Detection of constituents Although flame ionisation detection has the advantage of very high sensitivity it was not considered safe to incorporate any device containing a flame as a component of the system which of necessity had to be placed near to the explosion chamber. Instead a sensitive katharometer detector operating at about $160^{\circ}C$ in a very small volume with helium continually flowing, intended for use with very small volumes of

sample gas, was used in conjunction with an injection device to be described later.

(c) <u>Sequential sampling</u> Previous experience[1] showed that the time for an analysis may be determined by that required to aspirate the previous sample from a long line. To minimise this problem it was decided to use a system of separate lines, sampling continuously, and the gas flows were diverted in turn through a manifold to the sampling and injection valve. In this way only a single short length of pipe between the manifold and the sampling valve has to be flushed out with fresh gas sample before analysis with gas flows maintained by 2 vacuum pumps (see Fig. 2).

(d) <u>Equalisation of pressure before injection</u> Each sample of gas to be analysed was taken from a line which had been allowed to reach atmospheric pressure, to prevent variation in pressure arising from differences in sample line length, configuration etc.which would alter the density of samples being analysed. Pressure was equalised by disconnecting the line from the vacuum pump for a short interval prior to sampling with the other end remaining open in the gas mixture in the chamber.

(e) <u>Main analysis component</u> The analysis was based on the methane concentration as this is a component of both natural and manufactured gas.

QUANTITATIVE CHROMATOGRAPHIC ANALYSIS OF NATURAL GAS/AIR MIXTURES

It was required that natural gas/air and town gas/air mixtures, being fed into the steel chamber[2] measuring 3.0 m x 2.4 m x 3.7 m (10 ft wide x 8 ft high x 12 ft deep) (Fig. 1), be analysed continuously during the period of filling, and at any time between completing the filling and ignition of the mixtures. Due to the hazardous nature of the experiments the analysis would necessarily be controlled from a remote point.

Having chosen gas chromatography, preliminary work was directed towards selecting suitable equipment which would give accurate results for gas mixtures f1.owing in a single stream. Having established a basic analytical unit, further work was carried out to enlarge its capabilities, so that one unit could analyse six gas streams both remotely and automatically, with little attention. The general arrangement for six sampling lines is drawn in Fig. 2.

Basic analytical unit

The equipment which comprised this unit consisted of an O-ring type sampling and injection valve (Loenco type L-208-8) connected to one end of a chromatographic

column, the other end of which was connected directly to a thermal conductivity detector (Servomex Micro Katharometer type Mk.158) by suitable compression fittings, thereby minimising the length of gas lines. Having small internal volume (2.6 /ul) the detector gave fast response, and good sensitivity to small gas samples.

Control of the katharometer was effected by a Servomex type GC.197 katharometer bridge control unit. The voltage control was set between 6-8 volts according to the requirements of the analysis. In the earlier stages of development the output from the bridge control unit was connected directly to a high sensitivity galvanometer installed in an S.E. Laboratories model 3006 U.V. recorder. The integrator shown in Fig. 2 was introduced subsequently (see below).

Helium was selected as carrier gas, being the most suitable for the required analysis under the hazardous conditions. The supply was branched before the sample valve (with a pressure gauge in the line) and a valve inserted in the line through the reference side of the katharometer. To the two katharometer outlets flowmeters were connected, so that the flow of carrier gas through each arm of the katharometer could be monitored and balanced.

The various columns which were used were of 3.2 mm ($\frac{1}{8}$ in) O.D. stainless steel tube. Porapak Q was the first column packing material employed, but later Porapak R, which at room temperature gave more convenient retention times for air and methane. It was not found necessary to place the column in an oven (since temperature programming could not practicably be used with the fast repetitive cycle required for continuous analysis), and was simply kept at ambient temperature.

Prepared gas mixtures of up to 10 per cent CH_4 in N_2 were obtained from B.O.C. Ltd., as well as cylinders of pure CH_4 and N_2. By the method of partial pressures various mixtures of CH_4 (0-100 per cent) in N_2 were made up in a steel pressure vessel and injected, at just above atmospheric pressure, into the system in single shots of 15 /ul volume. The column length was initially 0.3 m (12 in), but because separation of the air and methane peaks was poor the length was increased to 0.8 m (30 in). Carrier gas pressures up to 207 kN/m^{-2} (30 lb/in^{-2}) were tried, but eventually 97 kN/m^{-2} (14 lb/in^{-2}) was found quite adequate for a 0.8 m (30 in) column, the retention time for the CH_4 peak being about 9 s. From a measurement of peak areas it was observed that there was a fairly good correlation between % CH_4 and peak area, for the conditions under which the katharometer was being used. However, noticeably tailed peaks were occurring, and it was suspected that the nature of 'sweep out' of the gas sample in the

O-ring type valve was the cause. The sample valve was therefore replaced by a Servomex SV 220 slide sample and switching valve (Fig. 3) operated from compressed air at 310 kN/m^{-2} (45 lb/in^{-2}) by an RGS Electro Pneumatics EP.255/20SB 4-way valve. This sample valve, being of the sliding plate type, was able to inject a discrete 'plug' of gas into the carrier gas stream. The sample valve was aspirated continuously with gas mixture by a vacuum pump, and by the operation of a 2-way solenoid valve the vacuum was shut off 1-2 s prior to injection, to allow the sample mixture to reach atmospheric pressure. The whole analysis apparatus was mounted on a metal panel (Fig. 4) in a cabinet. 10 μl samples were taken, and a significant improvement in peak shape was noticed, giving better resolution of peaks.

The sample valve was next linked to a cam timer to give a 1-2 s injection period every 10 s, with peak areas being measured by a simply constructed electronic integrator, giving visual digital display only. This did not prove adequate for continuous work at such a speed for which a fully automatic peak area and retention time 'printout' was required. For this purpose an Electronic Instruments Chromalog 2 digital electronic integrator was used. The signal from the katharometer bridge control unit was fed directly to the integrator input, and from the integrator output to the U.V. recorder. The volume of injected sample was subsequently increased to 25 μl, because it was found that the peak area counts from the integrator were relatively small, and the injection cycle changed to once every 20 s. This, however, had the effect of overloading the integrator for a fraction of time in its integration (an audible alarm signal being sounded). It was overcome by inserting a 76 mm (3 in) length of 4.8 mm (3/16 in) O.D. empty stainless steel tube between the chromatographic column and katharometer, which broadened the peaks slightly. The same result was obtained by increasing the column length to 1.1 m (42 in) and the carrier gas pressure to 124 kN/m^{-2} (18 lb/in^{-2}), which also gave better peak resolution.

Since the operation of the sampling and injection valve momentarily interrupted the helium flow the bridge balance was also momentarily upset. This was detected by the integrator as a 'spurious' peak when the bridge control attenuator was set at X1 or X2. This effect was eliminated by incorporating a packed chromatographic column identical to that used for gas separation, into the line to the reference part of the detector. This sufficiently damped the pressure pulse in the reference line to remove the out of balance signal resulting from the transient mechanical effects of the sampling and injection valve.

The natural gas used had a nominal composition as shown in Table 1. This is compared with accurate analyses performed at FRS on a nearly empty cylinder 690 kN/m^{-2} (100 lb/in^{-2}) pressure and a full cylinder, employing mass spectrometry and gas chromatography. These results indicated some fractionation of the gas as a cylinder was emptied and, on the advice of the suppliers, it was decided that for filling the steel chamber with gas/air mixtures the gas cylinders would not be allowed to fall below 690 kN/m^{-2} (100 lb/in^{-2}) in pressure.

Table 1

Natural gas analyses

Gas	Air Products Ltd % (Vol.)	FRS (Cylinder 100 psi) % (Vol.)	FRS (Full cylinder) % (Vol.)
CH_4	93.9	91.2	93.6
C_2H_6	3.0	3.1	2.6
C_3H_8	0.6	1.4	0.4
iso C_4H_{10}	0.7	0.3	0.1
n C_4H_{10}	0.1	0.3	0.1
C_5H_{12}	0.1	0.2	–
$N_2(+ O_2)$	1.2	3.1	3.1
CO_2	0.4	0.4	0.1

With the bridge control unit attenuator set at X1 and the voltage at 8 V, a single injection of 25 μl natural gas gave detectable peaks for $N_2(+ O_2)$, CH_4 and C_2H_6, the other components of the gas being too small to cause any response by the integrator. With the attenuator at X4 only $N_2(+ O_2)$ and CH_4 were detected, giving retention times of approximately 6 and 9 s respectively. During a $\frac{1}{2}$ h test build up of minor components in the column appeared to have no effect on results.

Channel selection unit

Having established a basic analytical unit for the analysis of a single gas stream a second unit was developed, to enable six gas streams to be analysed on a continuous rota basis (Figs 2 and 5).

This consisted of 6 two-way three-port solenoid valves, each linked to a sample probe, a single central sampling manifold and also connected via a common line to an aspirating pump. Selection of the channel requiring to be analysed was made by operating the requisite solenoid. In the 'OFF' position each channel was closed to the analysis unit but open to a vacuum purging system. The electronic aspect of this unit is described later in this report.

The basic unit and the channel selection unit were both housed in a small wooden shed (Fig. 6) which was heated (approx. $20^{\circ}C$) in order to ensure smooth operation of the sample injection valve.

Gas sampling probes

For the purposes of analysis of gas layers in the steel chamber several sets of multiple sample probes (Fig. 7) were constructed, being made up of differing lengths of 7.9 mm ($^5/16$ in) O.D. stainless steel tube silver-soldered into a standard $2\frac{1}{2}$ in BSP plug. These could be screwed into the structure of the chamber, either vertically or horizontally, at a variety of positions as required. Using one set of probes the formation of gas layers in a single vertical plane could be examined by sampling from the roof of the chamber to the floor (Fig. 8). Using five sets of probes, inserted at different positions over the roof of the chamber, but analysing only one channel from each (all at the same depth) the formation of gas layers in a horizontal plane could be examined.

Flame arresters (capable of arresting explosions with stoichiometric town gas/air mixtures) were fixed directly on top of the probes together with solenoid valves (Fig. 9). The valves were kept open during analysis, but closed prior to an explosion. Sampling lines from the probes to the channel selection unit were constructed partly of 7.9 mm ($^5/16$ in) O.D. stainless steel tube and partly of 9.5 mm ($\frac{3}{8}$ in) O.D. butyl rubber tubing, the latter being a flexible material which would not adsorb and desorb gas mixtures resulting in erroneous analysis results.

At the channel selection unit the lines were connected directly to the 3-way solenoid valves, such that they could be continuously aspirated whilst not being analysed. In this way 'fresh' gas/air mixture was made readily available for the analysis unit, with no long waiting period for each line to be purged. The lines were nevertheless kept as short as possible by placing both the analysis and channel selection units together, next to the explosion chamber.

The total rate of aspiration through the five probe lines not connected to the analyser at any given time was approximately 7 l/min^{-1} and the rate of

aspiration through the line connected to the analyser was 6 $1/\text{min}^{-1}$. These
values are approximately 1 per cent of the mean filling rate used in layering
experiments. It is, of course, possible to control these flow rates and the
effect of sampling on layer stability and configuration will be discussed in
a later report.

Control of analysis

Control of the whole analysis procedure was maintained both automatically
and remotely, because of the safety requirements for gas explosions. For this
reason the katharometer bridge control unit, integrator, and U.V. recorder were
housed in an instrument shed approximately 15.2 m (50 ft) from the analysis unit.
In addition, an automatic control unit to select the channel required for analysis
and to initiate the operation of the analysis unit, was constructed and housed
alongside the above equipment. The unit was set to give sample injections
approximately every 20 seconds, so that an analysis of 6 channels could be
completed in about 2 minutes.

Model analyses

For the analysis of gas/air mixtures of unknown composition one of the
6 channels to the analysis unit was reserved for a calibration gas mixture of
known % CH_4 in N_2 (as supplied by B.O.C. Ltd.,). The calibration mixture at
a pressure from the pressurised cylinder was brought to near atmospheric pressure,
entering channel 6 by a system of dreschel bottles, with a minimal head of water
sufficient to effect a seal, as shown in Fig. 10. It was not necessary to purge
this line continuously because the gas composition remained constant, and a
solenoid valve was therefore inserted in the line so that gas only flowed when
that channel was selected for analysis.

Using the calibration mixture, calculation of the unknown mixture is as
shown below:

Consider a 2 component gas mixture of Gas A and Gas B, whose actual peak area
counts as given by an integrator are A and B respectively.

Gas A   Gas B

- 9 -
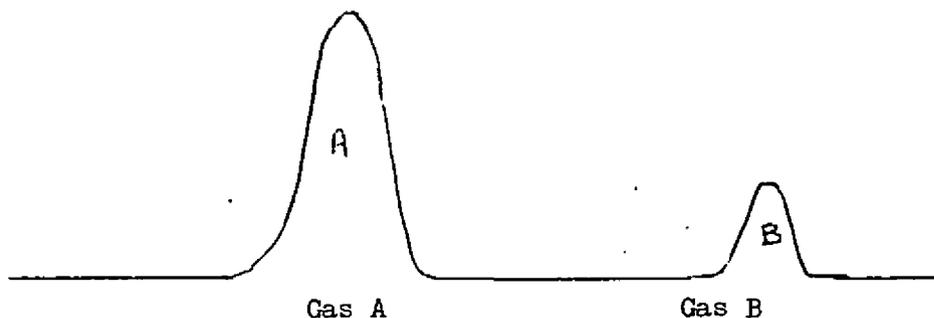
Let b_A and b_B be the thermal response factors for each gas with respect to the katharometer. The true peak areas are then given as Ab_A and Bb_B

$$\therefore \% \text{ Gas } B = \frac{Bb_B}{Ab_A + Bb_B} \times 100 = \frac{B\frac{b_B}{b_A}}{A + B\frac{b_B}{b_A}} \times 100 \qquad \ldots\ldots (1)$$

For a calibrating mixture (of the same two gases) of known composition, let the composition be X per cent gas A and Y per cent gas B. Then, using equation (1):

$$Y = \frac{100\, B\frac{b_B}{b_A}}{A + B\frac{b_B}{b_A}} \qquad \text{for the calibrating mixture}$$

$$Y\left(A + B\frac{b_B}{b_A}\right) = 100\, B\frac{b_B}{b_A}$$

$$YA = B\frac{b_B}{b_A}(100 - Y)$$

$$\therefore \frac{b_B}{b_A} = \frac{YA}{B(100 - Y)} \qquad \text{or} \quad \frac{YA}{BX} \qquad \ldots\ldots (2)$$

As X and Y are known for the calibrating mixture, the value of $\frac{b_B}{b_A}$ can be substituted back in equation (1) to find the composition of the unknown mixture.

In a typical $\frac{1}{2}$ hour period of filling the explosion chamber about 15 sets of figures for N_2 and CH_4 peak areas of the calibrating gas mixture were obtained, and the average ratio of N_2 to CH_4 counts calculated (with standard deviation also given) by using a set programme on a Hewlett Packard 9810A Calculator.

A typical set of readings gave an error of 2 per cent. From these figures the calibration factor $\frac{b_B}{b_A}$ was calculated. Using a second programme the readings for each gas line were calculated.

Confirmation of these results was shown by a normalisation technique using thermal response factors recorded by Dietz[3,4]. The same analysis result calculated by this method is shown in Table 2.

Table 2

Calculation of gas mixtures by
a normalisation technique

Gas	Peak area counts (Integrator)	Dietz factor	P.A.C. D.F.	Per cent Gas
Calibration mixture (10 per cent CH_4 in N_2)				
N_2	3929	42	93.5	90.0
CH_4	371	35.7	10.4	10.0
			103.9	100.0
Unknown mixture (100 per cent natural gas)				
N_2	156	42	3.7	3.6
CH_4	3548	35.7	99.4	96.4
			103.1	100.0

Several experiments were calculated by this method, and since the results obtained were as accurate as those using a calibration gas mixture it was decided to continue using normalisation. It should be noted that these methods of calculation dó not take into account the minor components of natural gas, which are not recorded by the integrator when the katharometer bridge control unit attenuation is set at X4 - they simply show the percentages of N_2 and CH_4 relative to each other. The results from single injections of 100 per cent natural gas with attenuation at X1, showed that the third major component (C_2H_6) could be included in the calculation, with the results shown in Table 3. These give good agreement with accurate analyses performed at FRS (Table 1) on a full cylinder. As the amount of propane was so small it was neglected in all subsequent analysis of natural gas/air mixtures.

Table 3

Analysis of natural gas by single injections
(attenuation X1)

Results of 3 separate analyses

Gas	Per cent (1)	Per cent (2)	Per cent (3)
N_2 ($+O_2$)	3.53	3.43	3.50
CH_4	93.12	93.72	93.66
C_2H_6	3.35	2.85	2.84
	100.00	100.00	100.00

For analysis of town gas/air mixtures it is probable that a different type of chromatographic column or columns would have to be employed because of the larger number of components to be monitored. The basic mechanical design and operation of the apparatus, however, would probably require little alteration.

ELECTRICAL AND ELECTRONIC CONTROL EQUIPMENT

Selection and analysis functions (General)

The selection of one of six sample channels is achieved by diverting its flow through the chromatograph by means of a 3-way solenoid valve. The valves used for this purpose are mains operated but controlled by means of low voltage relays enabling remote operation by a low voltage DC signal, see Figs 2, 5 and 11. An extra solenoid valve is connected in parallel with channel 6 to conserve the standard gas mixture.

When the flow from any channel is diverted, it is delivered to the chromatograph by means of a separate pump. The sample gas must be permitted to pass through the chromatograph sample injection valve until all traces of any previous mixture have been completely displaced from the system.

A vacuum cut valve, situated between the injection valve and the pump, must be closed for a brief period (1 s) before the sample injection valve is actuated to permit the sample gas in the system to equilibrate to asmospheric pressure. The sample injection valve is actuated pneumatically via a double-acting 4-way solenoid valve in the pneumatic line, see Fig. 4. This sample injection valve can be closed after a short period (1-2 s) and the process repeated on the next

selected channel. This sequence of automatic functions is shown in Table 4.

An earlier prototype of automatic control system

The first unit built was based on a bank of cam switches driven by a synchronous motor with an integral gearbox. This device controlled the function of channel selection and the purge delay for each channel, twelve separate cams being required. The disadvantage of this system was that a change in repetition rate was only possible by replacement of the synchronous motor/gearbox unit which could only be obtained in specific speeds 1 rpm, 2 rpm etc.

Automatic channel selection

The primary timing unit consists of a cyling timer (solid state controls 'Cycloset' type) which can be adjusted to produce $\frac{1}{2}$ second pulses at intervals of 5-20 s. The frequency of these pulses is controlled by a potentiometer mounted on the front panel of the instrument.

These $\frac{1}{2}$ second pulses are fed into a stepping or counting relay (Rodene type 794 - an alternative type would be Radiation type ELMA B4) fitted with a resetting coil wired to give a switched output to each of the six channels in turn and on the seventh pulse resetting the relay back to the first channel to repeat the sequence over again.

The six output channels from the relay are fed into a Matrix board (Oxley Developments two deck miniature type 10 x 10) which permits permutation of any of the six inputs to any of the six outputs so that any require sequence may be produced.

The outputs from the matrix board are fed to the output socket. A set of six 12 volt indicator lamps are connected to the output socket to indicate which channel has been selected and in series with these indicators is a set of six interlocked push button switches so that the sample channels can be selected manually if required (see Fig. 12).

Automatic analysis control

When a sample channel has been selected, a short sequence of operations is necessary to inject a sample of the mixture into the chromatograph.

Table 4

Sequence of automatic functions

(a)   Select channel - divert to analysis unit.

(b)   Wait t_1 s for gas to sweep through the analysis unit   (15 s)

(c)   Switch off vacuum pump valve.

(d)   Wait t_2 s for pressure in line to equalise   (1 s)

(e)   Open sample injection valve.

(f)   Wait t_3 s for sample to be swept into chromatograph column (1 s)

(g)   Return sample injection valve.

(h)   Go back to (a) select next channel.

Typical values for t_1, t_2 and t_3 are given in parentheses.

In the present arrangement an analysis can be carried out every 20 s.
The cycling timer controlling the selector relay uses a set of changeover contacts
to produce the series of $\frac{1}{2}$ second pulses, by using the normally closed contacts
a series of $t - \frac{1}{2}$ second pulses can be obtained, where t is the repetition
rate (see Fig. 13).

These long pulses are fed to a chain of time delay modules (solid state
controls plug-in types). Each module triggers the next when its delay time
has expired, thus producing the necessary aspiration delay, pressure equalisation
delay and sample injection valve 'on' period. The delay times of these modules
are controlled by potentiometers mounted on the modules, or in the case of the
aspiration delay mounted on the front panel of the instrument (see Figs 14, 15).

When the cycling timer produces its next short pulse to change the channel
the signal to the delay modules is momentarily interrupted. This interruption
resets them ready for the next cycle of operations.

Manual override systems and indicators

Each of the functions of the automatic equipment can be operated by a
manual control. These manual controls consist of illuminated push buttons with
the indicator lamps wired so that the lights will come on when (a) the function
is selected automatically, or (b) when the push button is operated manually.

This system was chosen so that the operator can see at a glance the exact
state of the equipment and can assume manual control of any or all of the functions
should any malfunction occur in the automatic equipment.

Each of the solenoid valves, controlling the selection and analysis function, has a neon-indicator connector in series so that the operator has visual confirmation that the remote part of the equipment is functioning correctly (see Fig. 11). -

Replacement of timing modules and relays

The timing modules used are all plug-in types so that spare units may be kept available and replaced quickly should failure occur.

The cycle timer unit contains a plug-in module which contains the active timing device, this can also be replaced quickly.

The relays used are also plug-in types.

The stepping relay used is not a plug-in type but a similar type of relay is available which uses a printed circuit edge connector which would facilitate quick removal and replacement.

DISCUSSION

The preceding sections have shown in detail the development of an analytical system in which samples can be taken at different points from flammable natural gas/air mixtures in a combustion chamber, the major components separated chromatographically and the concentration of natural gas determined quantitatively, based on the amount of methane present in any given sample. The sampling sequence, the rate at which samples are analysed, the time intervals between samples are all controlled automatically and can be varied when necessary. Rapidity of analysis has been achieved with the system and the system is capable of considerable extension to the analysis of other fuel gases and also a form in which it could handle larger number of sample inlets. The presentation of the quantitative results is presently as a digital printout of integrated areas for the major components (air, methane) from which the actual percentages are obtained using simple mathematical formulae and a desk calculator. It is possible at present for one person to translate the digital output (say for one or two samples out of every cycle of six) into percentage gas terms for accurate control over the input concentration and to obtain some accurate information regarding the concentration versus time profiles at different depths in the experimental chamber. The full concentration-time profiles for six channels over a period of, say, 30 min, necessitates subsequent calculations on the digital printout data using a programable desk calculator. As the intention with the current research programme is to increase the complexity of the experimental chamber with respect to the

number of compartments, and with the increased number of sampling channels which will be used a completely automatic on-line calculating and plotting facility will be required. This possibility is presently under active consideration.

The sampling probe system used on the chamber is simple and works adequately. There are two drawbacks to this system in that

(i)   the probe positions have to be fixed before an experiment
       and cannot be changed (safely) during an experiment;

(ii) when the chamber has the requisite gas/air mixture in it the
       probe system cannot be removed before ignition. The presence
       of the probes could give rise to turbulence in the explosion
       which might not otherwise be present.

To overcome these two problems a hydraulic/pneumatic control system has been designed (and is currently approaching the final stages of completion) in which movement of the probe system to enable variation of the sampling position position during an experiment will be possible by remote control as will the withdrawal of the probe system immediately prior to ignition. The details of this device will be reported elsewhere.

The necessity for introducing a calibrating gas mixture is diminished by the use of the Dietz method of computation. Nevertheless the system described in this note is not entirely adequate and for the occasions when samples of calibrating gas mixtures are introduced into the system as an extra check on accuracy, a better method of introducing the gas from a high pressure cylinder needs to be developed.

The analytical system described in this report has been operated virtually trouble-free for about 12 months.

CONCLUSIONS

1.   A six-channel automatic, rapid analysis system has been developed and has
      proved to operate satisfactorily and reproducibly under large-scale
      experimental conditions. Small samples are used (25 μl) and analyses
      are presently achieved at a rate of about 1 sample every 20 s. This rate
      is satisfactory for present needs but is not a limit value. The system
      is presently used solely for natural gas.

2.   Only minor modifications should be necessary for the analysis of mixtures
      of manufactured gas or lower hydrocarbon gases with air (the analysis of
      the former may necessitate removal of interfering constituents before
      analysing the major components to stop the slowing down of the sequence).

3. The system is capable of extension to many more channels either by the use of manifolds or by using extra modules.

4. The flexibility of the system would be increased by the use of a more versatile sampling system. This is presently being constructed.

5. The method of supplying a constant pressure of calibration gas where necessary could be improved (probably using constant pressure switches on a large reservoir of gas, itself fed from a cylinder of gas).

6. One major improvement would be to incorporate on-line processing and plotting facilities to the system. This is under active consideration.

ACKNOWLEDGMENT

Dr W D Woolley and Mr P J Fardell carried out the analyses of natural gas.

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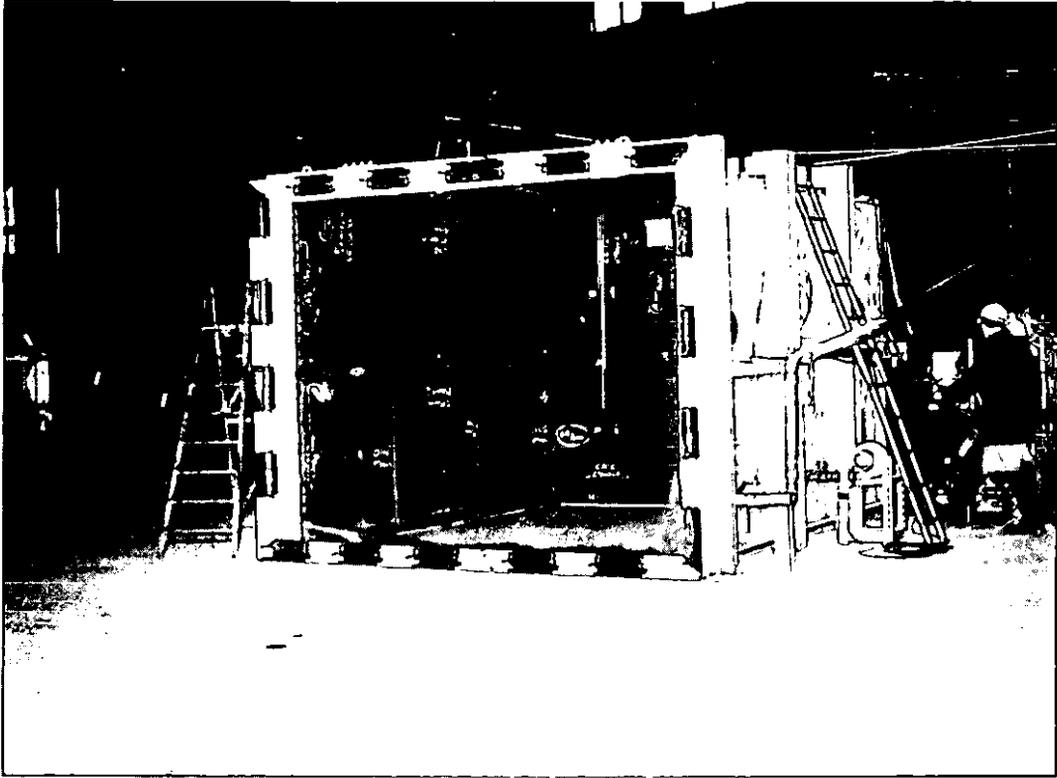
FIG. 1. GENERAL VIEW OF EXPLOSION CHAMBER
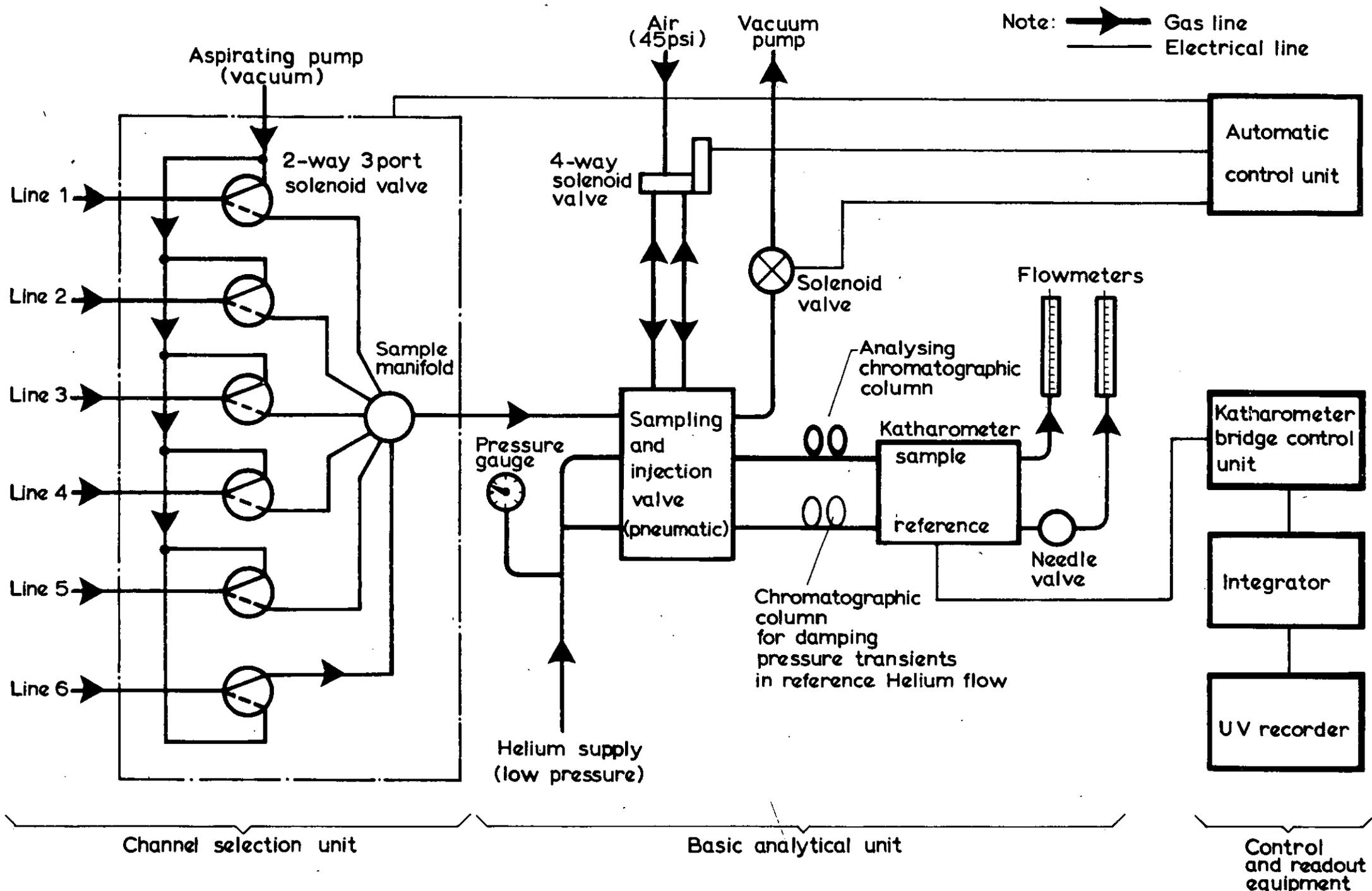
Figure 2   Automatic gas sampling unit (6-channel)
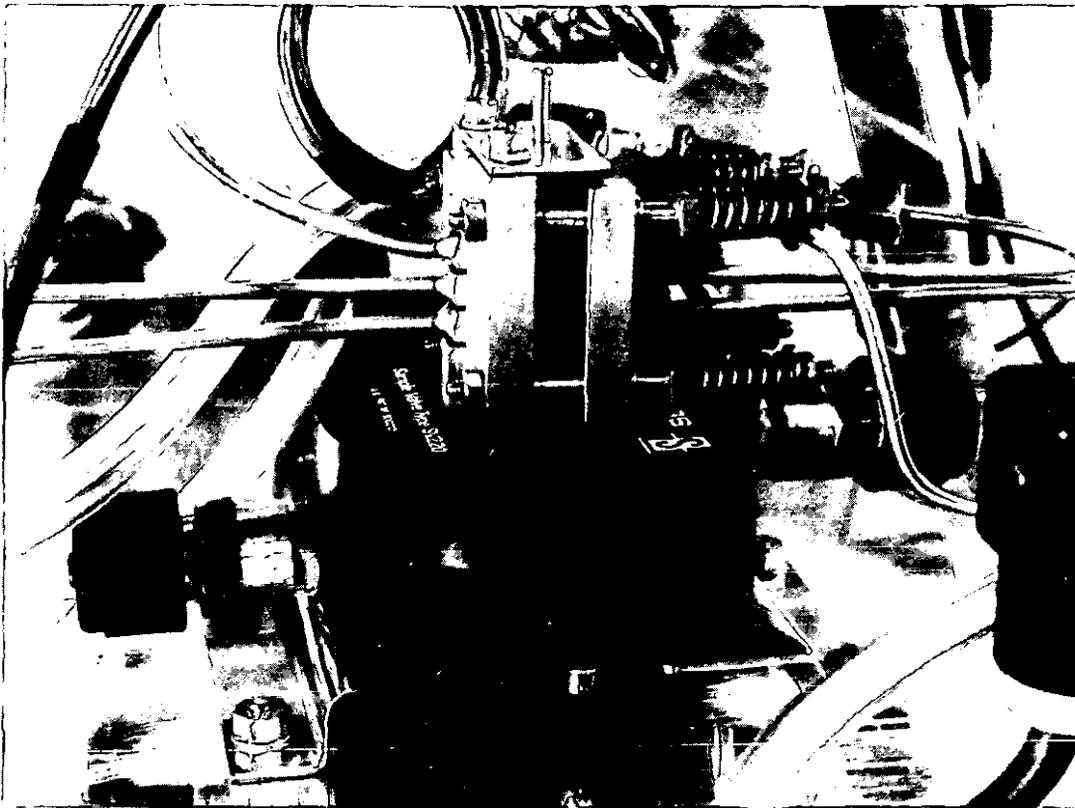
FIG.3. SLIDE SAMPLE VALVE
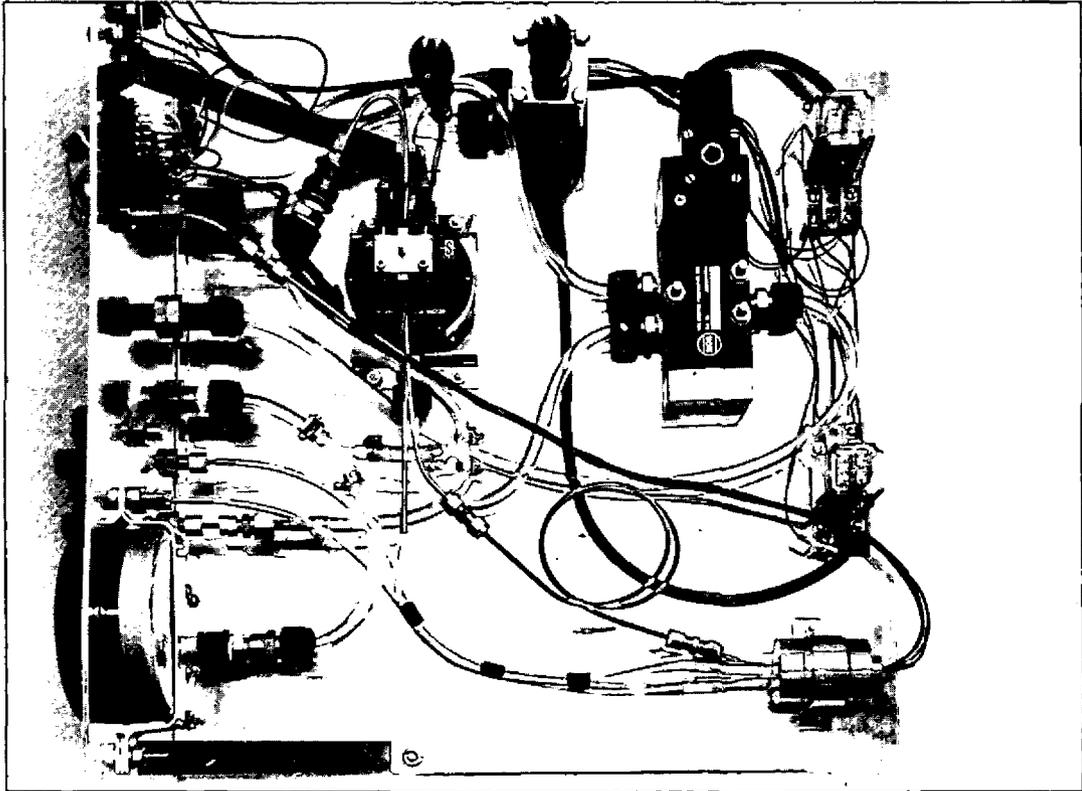
FIG. 4. GAS ANALYSIS UNIT
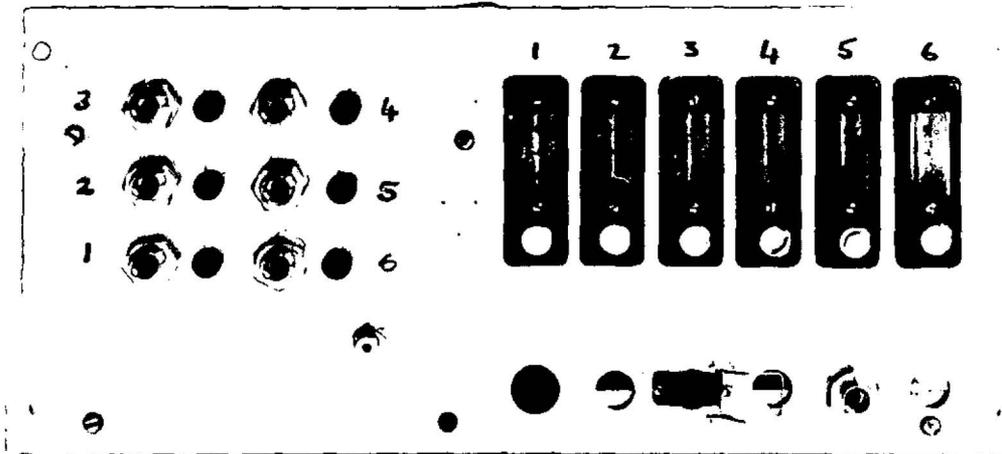
FRONT PANEL
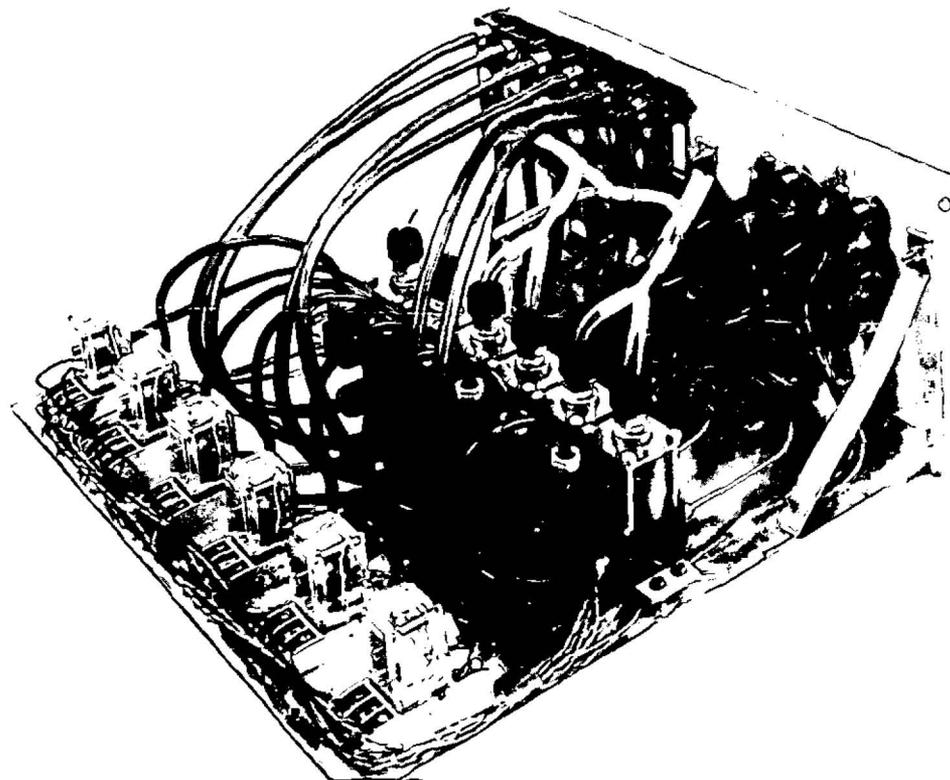
BEHIND FRONT PANEL

FIG. 5. CHANNEL SELECTION UNIT
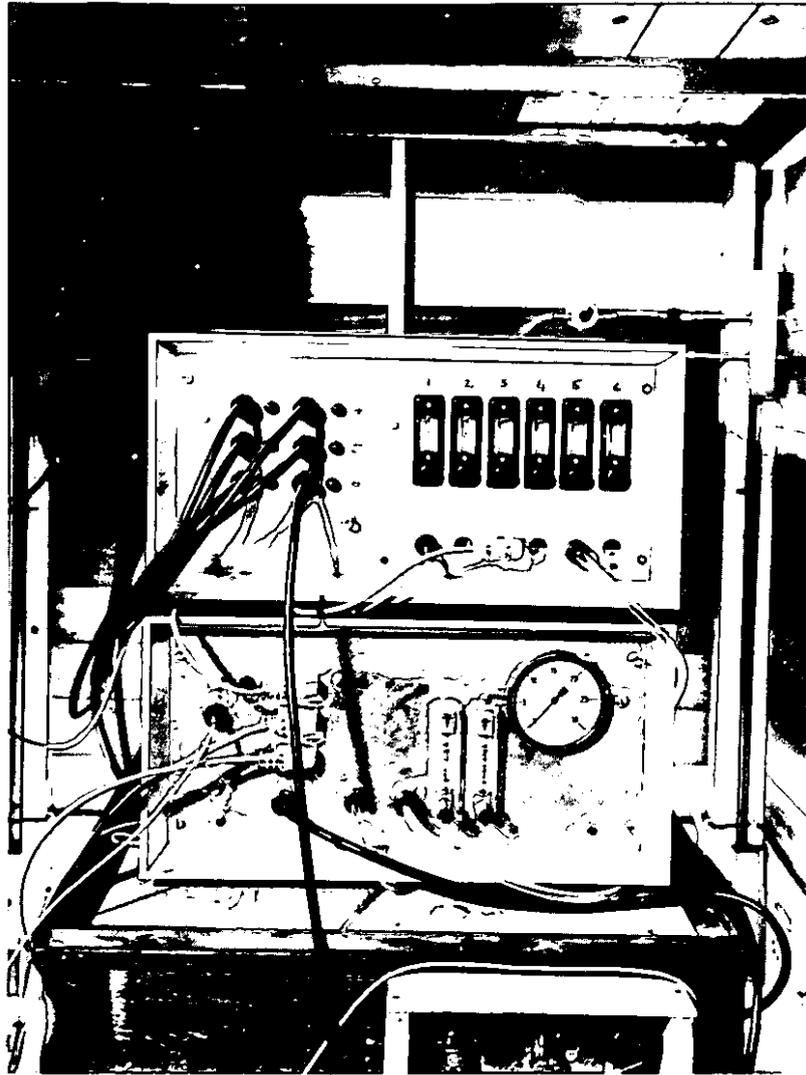
FIG. 6. CHANNEL SELECTION UNIT (TOP)

WITH BASIC ANALYSIS UNIT (BOTTOM)
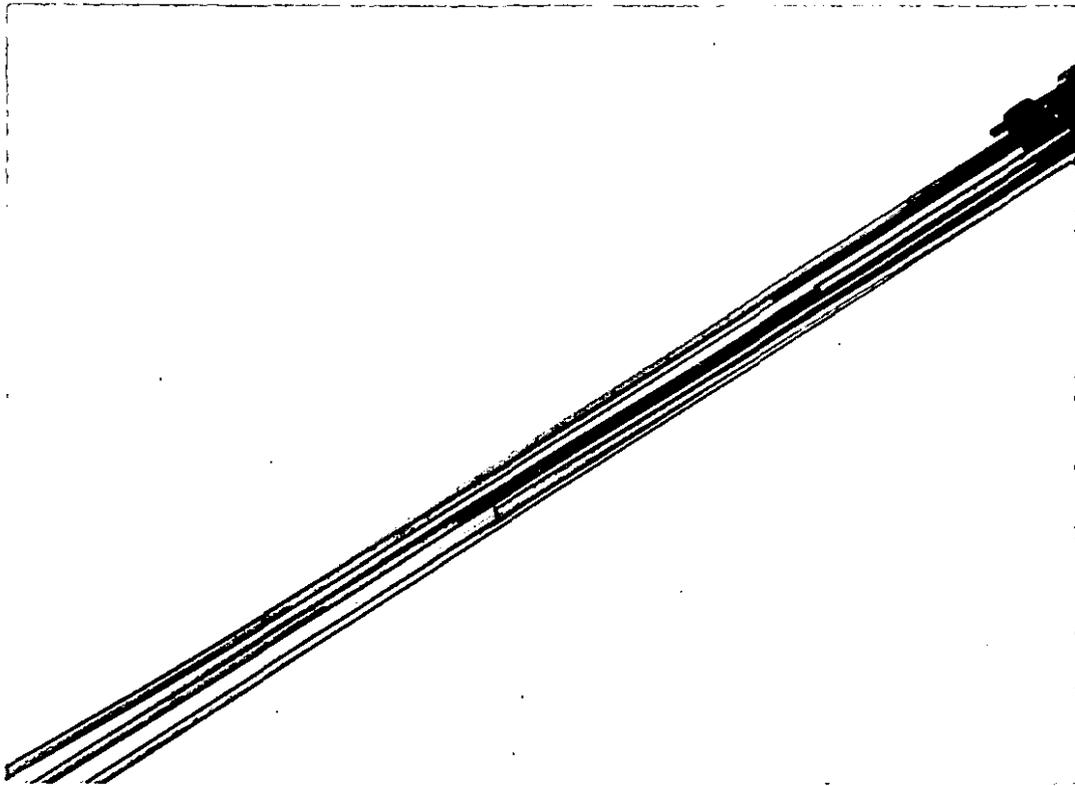
FIG.7. MULTIPLE SAMPLE PROBE, SHOWING
STEEL TUBES CUT TO 300 mm INTERVALS
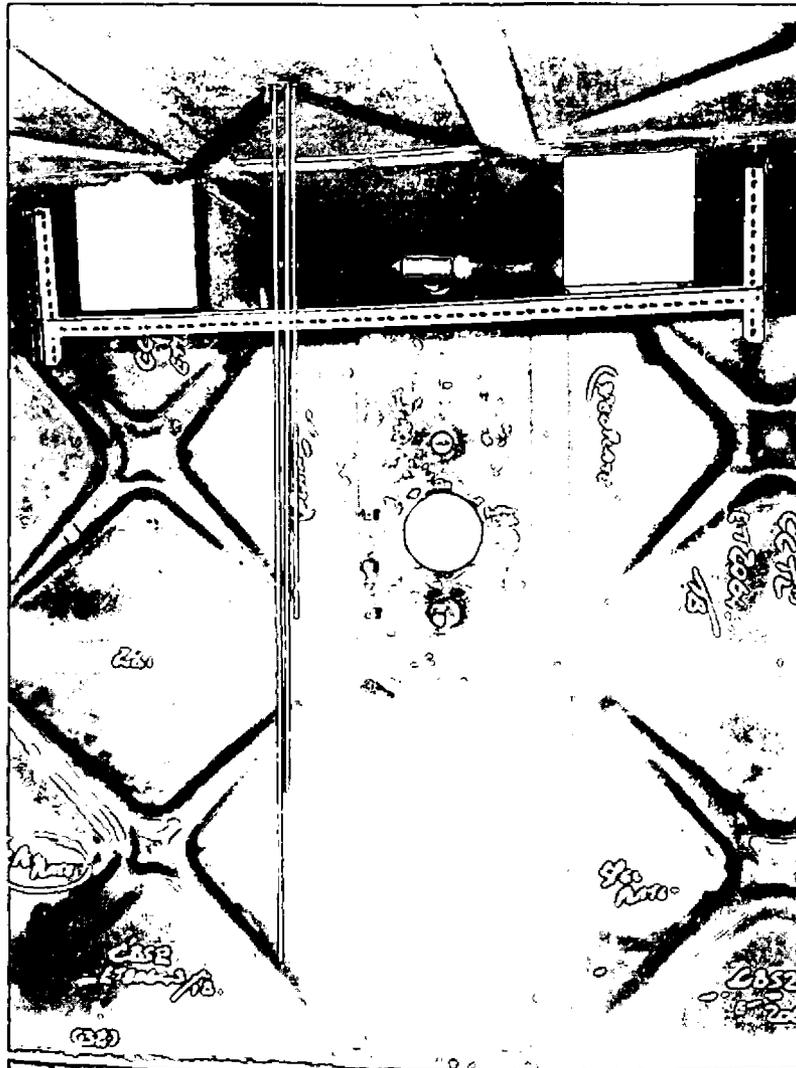
FIG. 8. SINGLE SET OF SAMPLE PROBES

SCREWED INTO STRUCTURE
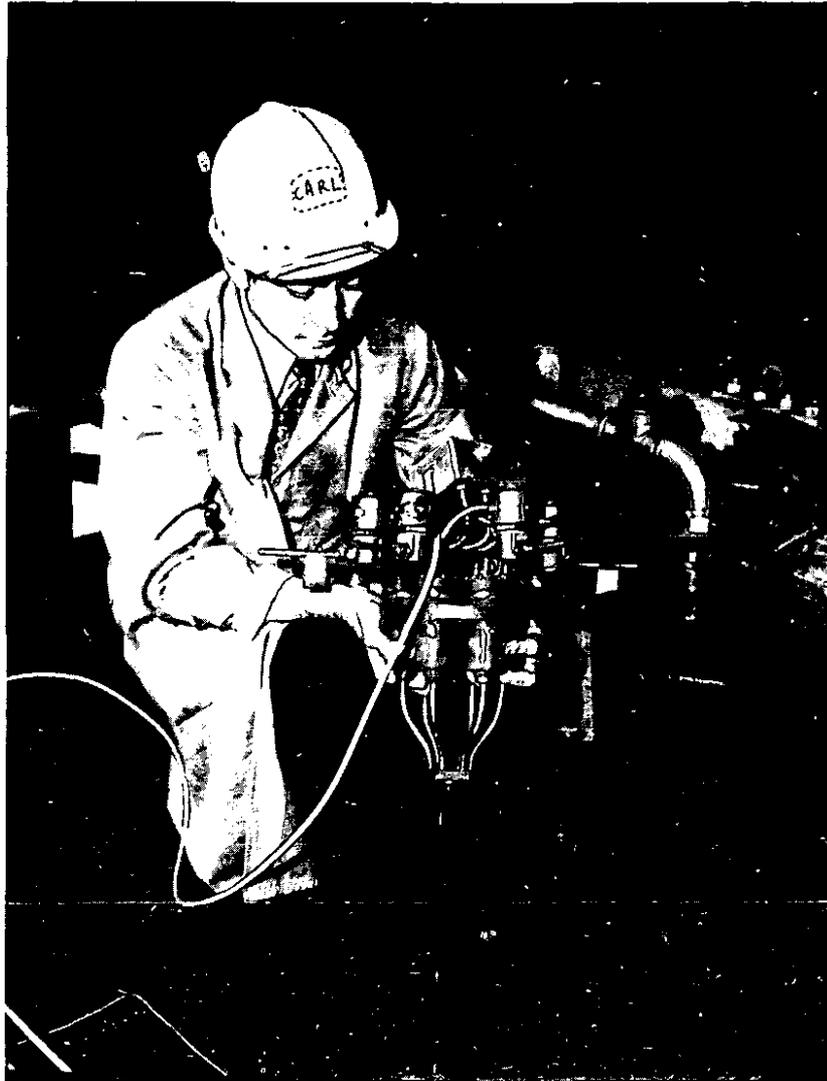
FIG. 9. FLAME ARRESTERS AND SOLENOID VALVES

ON A SET OF SAMPLE PROBES

To channel 6 of
Channel selection unit

From
pressurised
cylinder
(calibration
gas)

Gas flow

To
atmosphere

Solenoid
valve

Drechsel bottles

Water
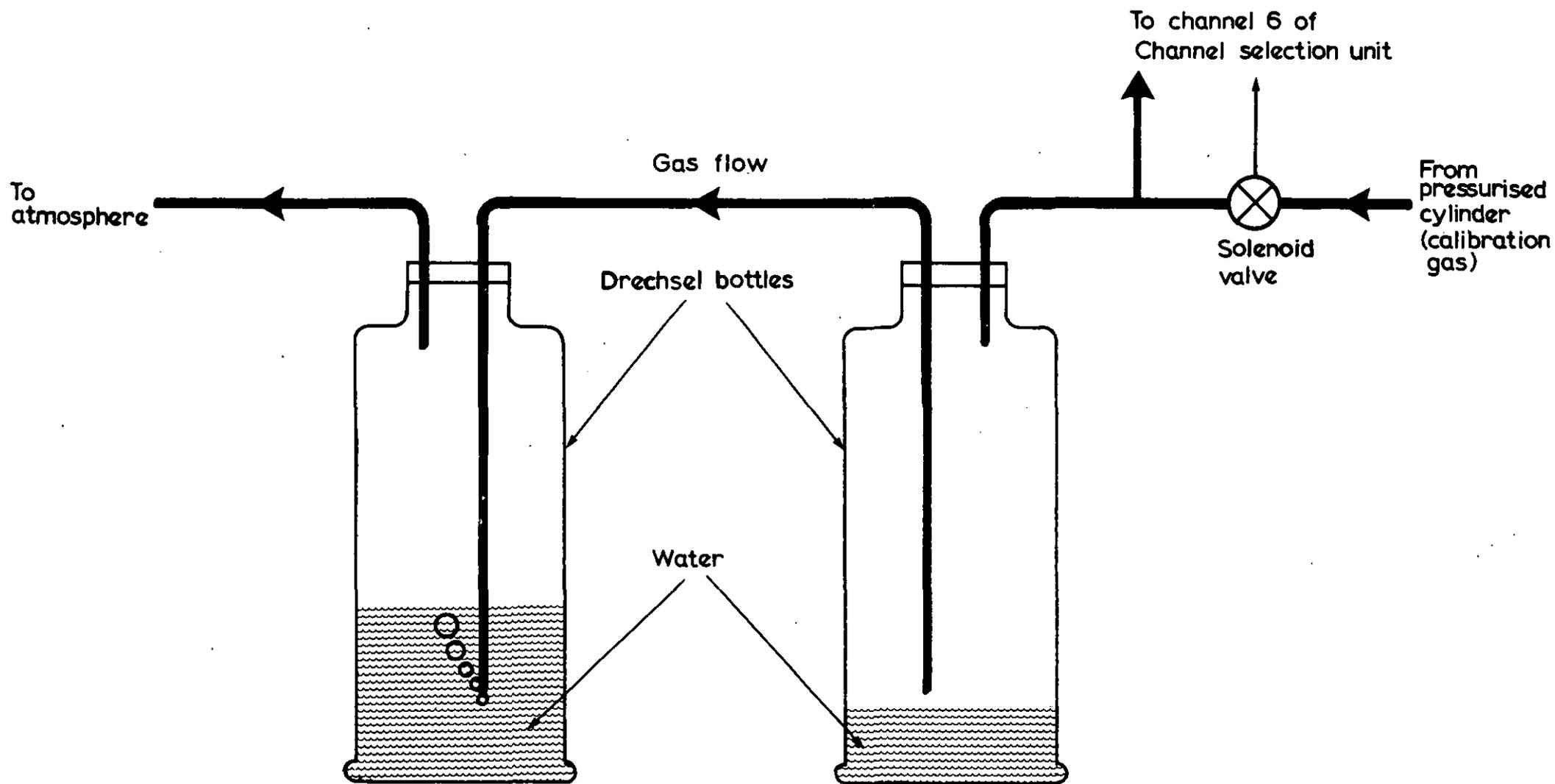
Note:

Gas line

Electrical line

Figure 10   Apparatus for equilibrating calibration gas mixture to atmospheric pressure
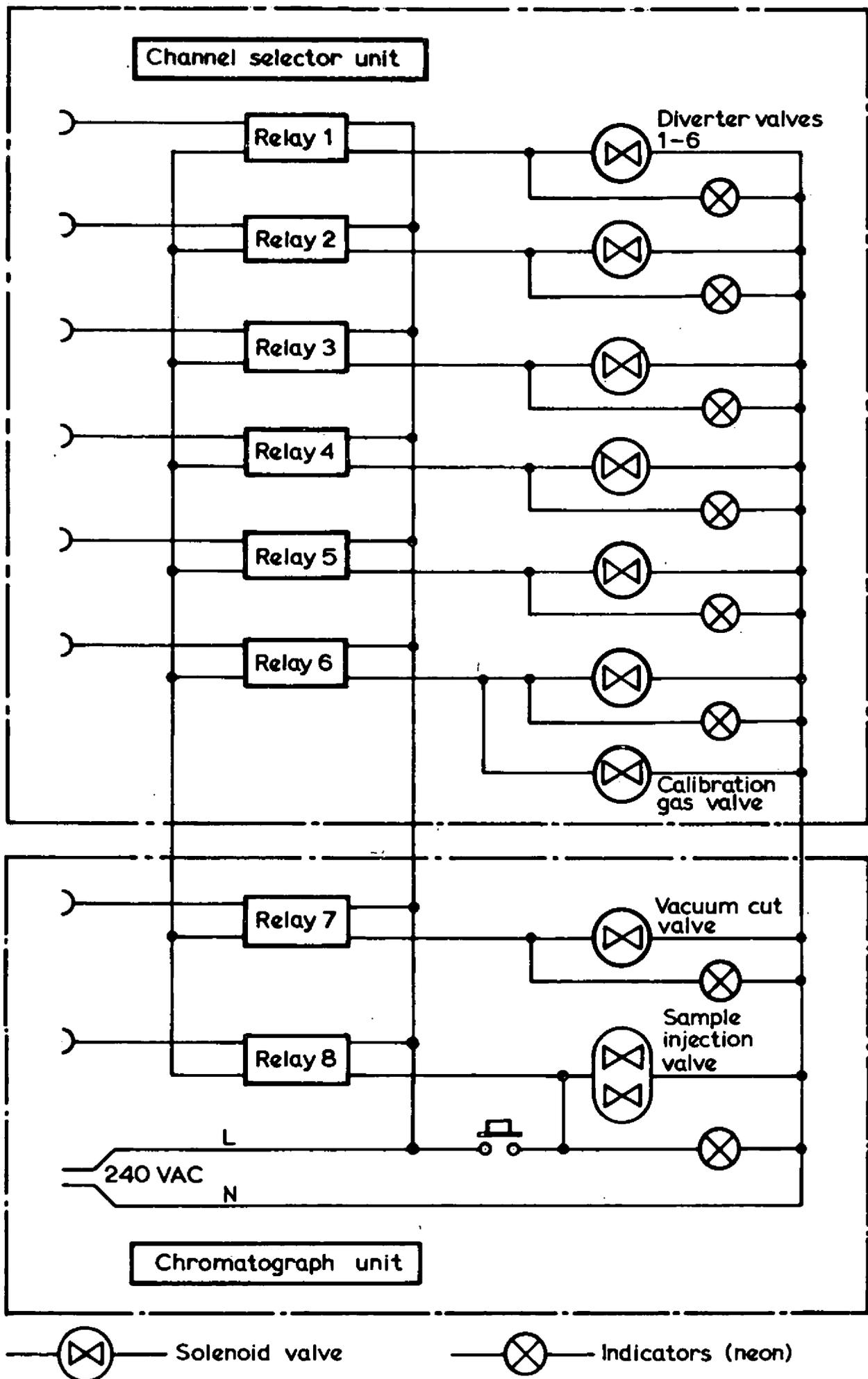
Figure 11 Control circuits contained within the selector
and chromatograph units
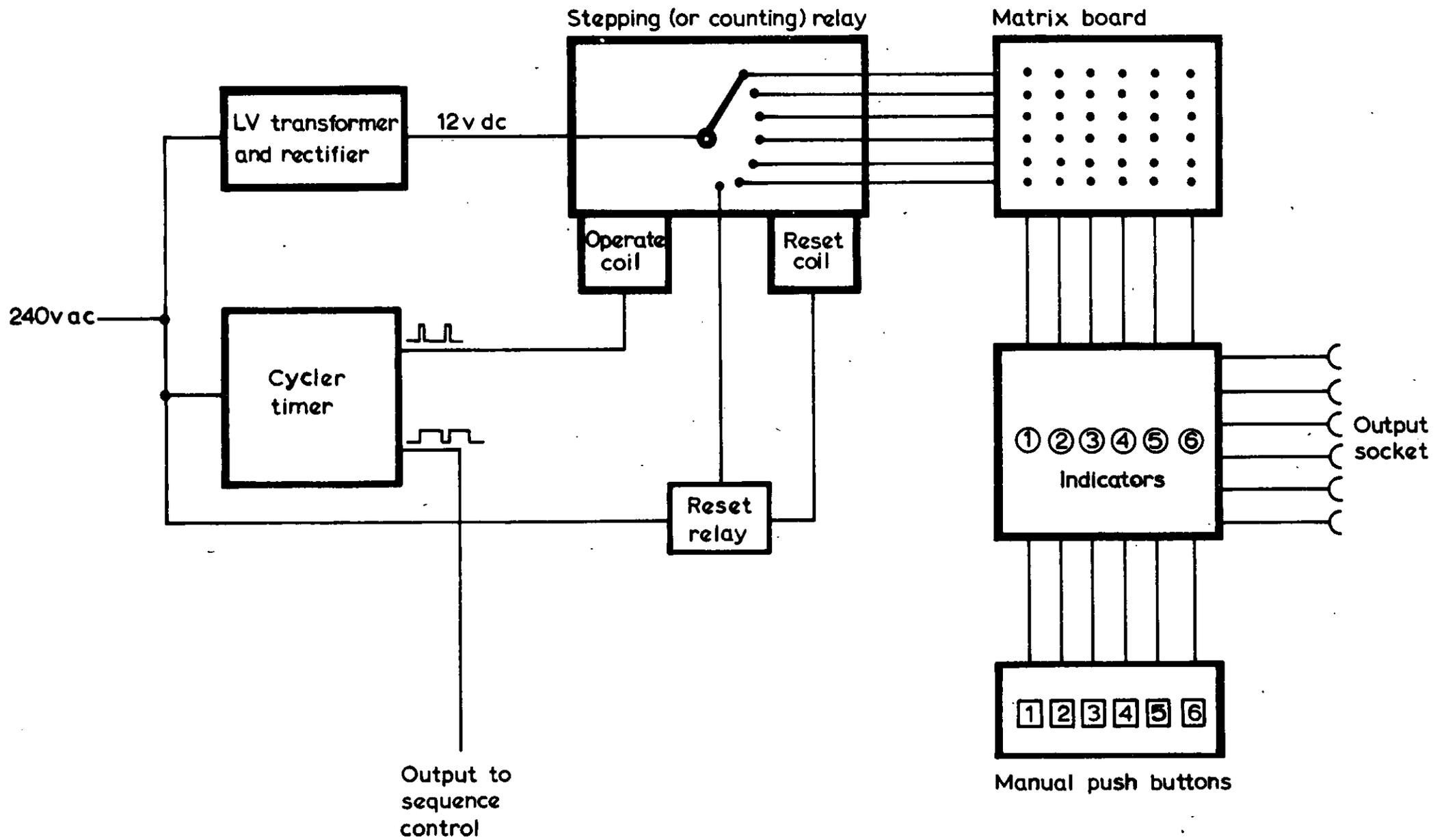
Figure 12   Automatic channel selection system
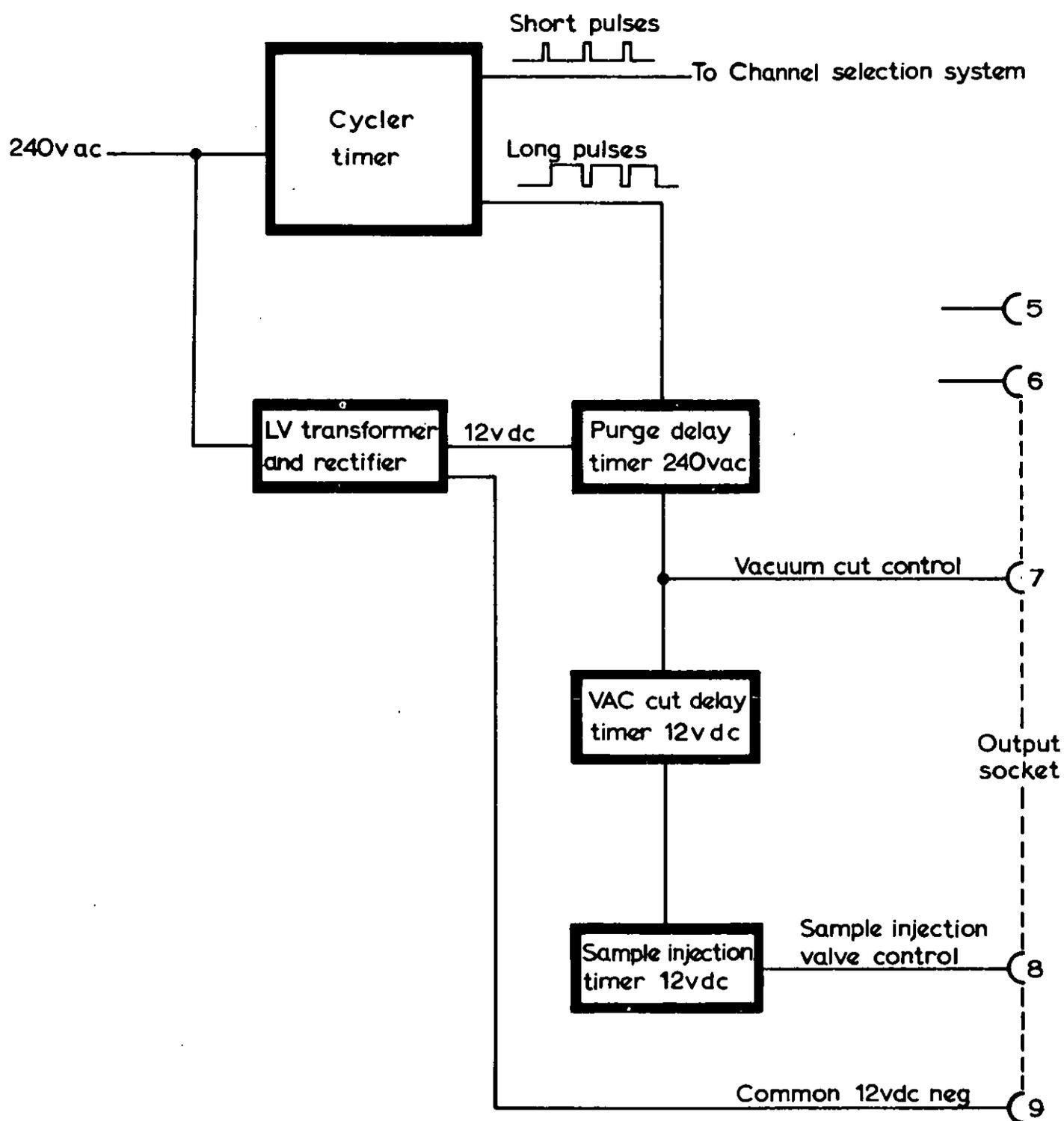
Figure 13 Automatic sample sequence control system
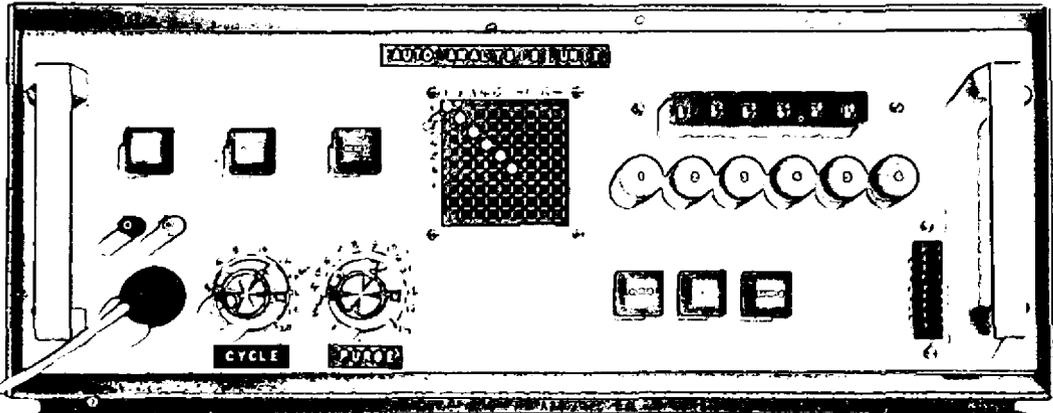
FIG. 14.   THE AUTOMATIC CONTROL UNIT, FRONT PANEL
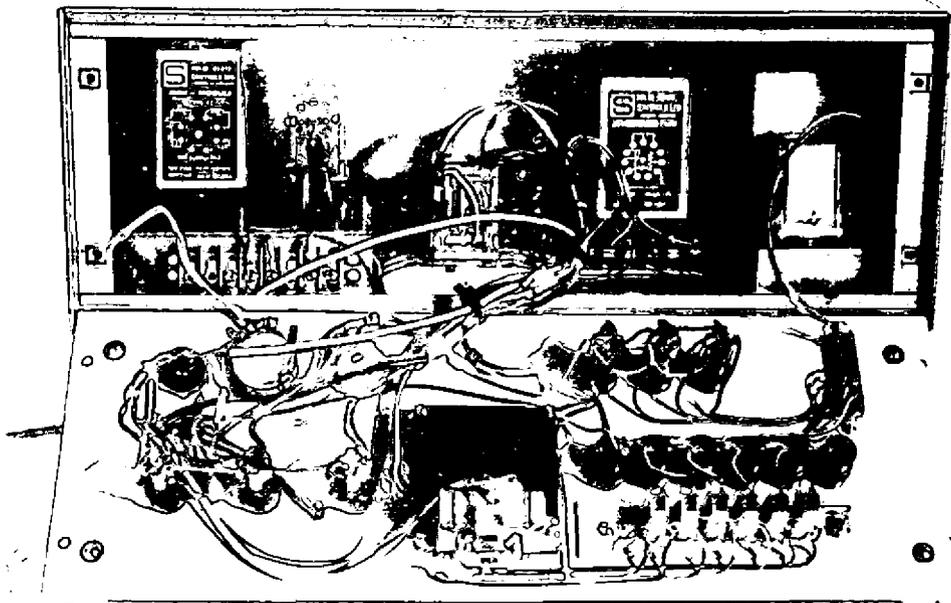
FIG. 15.   CONTROL UNIT SHOWING TIMING MODULES, ETC.