

PROPORTIONAL COUNTING TECHNIQUE  
FOR LOW LEVEL C<sup>14</sup> ACTIVITIES\*

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RESUMEN

*En este trabajo se presenta la información técnica preliminar para modificar la instalación actual del Laboratorio de Carbono 14 del Instituto de Física de la UNAM, a la que se requiere para determinar actividades Betas de baja energía usando contadores proporcionales de bajo nivel.*

*Dicha información fué obtenida durante la permanencia del autor en el Laboratorio de Investigación del Museo Británico durante 1963.*

I. INTRODUCTION

In the radio-chemistry Division of the Institute of Physics of the Universi-

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\* Report presented to the O.I.E.A. by physicist Augusto Moreno y Moreno, in relation with his training in counting of C-14 at low level using proportional counters, at the Research Laboratory of the British Museum (England) under Dr. H. Barker's direction.

dad Nacional Autónoma de México, a laboratory has been installed to date archaeological samples and determine the contents of  $^{14}\text{C}$  at low level following Libby's method. However, in 1962 it was found convenient to change the techniques used to that of proportional counting.

This report is the preliminary work which is being done for the mentioned purpose.

The technical data was obtained during the writer's permanence at the  $^{14}\text{C}$  laboratory of the British Museum's Research Laboratory, working under Dr. Barker's direction

## II. DESCRIPTION OF THE ACETYLENE METHOD

### 2.1 Preparation of the sample

Before combustion, it is necessary to make a careful inspection, in order to detect probable contamination of the sample with organic material not corresponding to the sample's nature, for example: radicals of recent origin on charcoal samples, etc.

All organic samples are tested for the presence of  $(\text{CO}_3)^{2-}$ . If it is present, the sample is washed with HCl in excess and subsequently with distilled  $\text{H}_2\text{O}$  until neutral.

It is dried at  $\sim 100^\circ$  before combustion (Fig. 1) the latter is done in the silica tube for such purpose (T). This tube has two oxygen inlets: one directly to the inner tube where the sample is deposited, and the other to the outer tube in which the products of combustion are mixed with excess oxygen and passed through a packing of silica wool which is heated to about  $800^\circ\text{C}$ . In this way, the sample is completely burned to carbon dioxide combustion products. Part of the water produced in this combustion is deposited in trap (2) and the rest in trap (4) (cooled by means of acetone + solid  $\text{CO}_2$ ). The  $\text{CO}_2$  produced is condensed in (6) which is cooled by liquid oxygen.

Through the combustion process, stopcock (7) remains open so that the residual  $\text{O}_2$  may go out through a guard tube, filled with soda-lime to prevent back

diffusion of atmospheric  $\text{CO}_2$ . During the combustion the oxygen flow rates are regulated by means of simple Venturi type flow meters, the flow in the outer tube being in the range of 200–500 c/min and that in the centre tube somewhat lower depending on the nature of the sample.

With the  $\text{CO}_2$  condensed at (6), it is pumped for 30 minutes to eliminate as far as possible, contaminating gases from the  $\text{CO}_2$ . This is then condensed at (11) and expanded to flask (10) where its pressure is measured so that the amount of  $\text{CO}_2$  produced by combustion can be calculated.

## 2.2 Reaction of $\text{CO}_2$ with metallic lithium.

The reduction of  $\text{CO}_2$  to  $\text{C}_2\text{Li}_2$  is made at high temperature according to reaction:



from which it is inferred that each liter of  $\text{CO}_2$  at NTP requires approx. 1.5 gr. of lithium.

However, using this theoretical amount the conversion is not complete and the production of  $\text{C}_2\text{H}_2$  is very low; thus, an excess of 200% lithium is used and in this way the efficiency of conversion of  $\text{CO}_2$  to  $\text{C}_2\text{H}_2$  is raised to about 96% 97%.

It has also been shown that despite the fact that the conversion is not 100%, M-isotopic fractionation effects are negligible (private report from Dr. H. Barker et al.).

Depending on the amount of  $\text{CO}_2$  derived from the sample, an estimation is made of the lithium required. In most cases the amount used is about 22 gr. The lithium is washed with petroleum ether, and the layer of  $\text{Li}_2\text{O}$  which may have been formed on its surface is removed. The clean lithium is then introduced into the furnace, which has been connected to the main vacuum system through connection (21). The furnace is pumped during one hour whilst the temperature is raised to  $450^\circ\text{C}$  and pumping is continued until gas evolution has ceased (The

lithium contains much dissolved hydrogen) when the pressure has fallen to a few microns the temperature is raised to about 650°C.

With the CO<sub>2</sub> already expanded in flask (10) and with the lithium at a temperature of c.a. 650°C, reaction is initiated in the furnace. The visual inspection of the lithium's color at the temperature (dull-red) is possible by observing the bottom of the furnace through its projecting pyrex tube (Fig. 2b).

CO<sub>2</sub> is introduced by means of stop-cock (9) so that pressure in the furnace measured with M2 does not exceed 10cm, but watching that the color of the reaction is kept as indicated above - the temperature then being approx. 650°C.

When the reaction ends, the residual pressure is negligible. The furnace is pumped out and kept at 650°C for about 2 hours. During this period, any radon in the sample is eliminated. The factors regulating the production of Li<sub>2</sub>C<sub>2</sub> are:

Temperature of the liquid lithium, pressure of the CO<sub>2</sub>, and the free area of lithium, pressure of the CO<sub>2</sub>, and the free area of lithium in the furnace.

### 2.3 Conversion of Li<sub>2</sub>C<sub>2</sub> into acetylene.

Once the Li<sub>2</sub>C<sub>2</sub> is cooled, the furnace and flasks 15.....19 are emptied, and distilled H<sub>2</sub>O is slowly added to the furnace (2 or 3 drops/second). Trap (24) is cooled with acetone and solid CO<sub>2</sub>; when the pressure increases in M2 to 65cm S.C. (25) is opened, condensing the C<sub>2</sub>H<sub>2</sub> in (26) by means of liquid oxygen. With S.C. (29) closed, S.C. (28) is opened, controlling -with (25). So that the outgoing pressure of the residual gasses in trap 26 (H<sub>2</sub>, etc) be 1.5cm in M<sub>3</sub>; thus, the pressure in M<sub>2</sub> slowly decreases as the C<sub>2</sub>H<sub>2</sub> condenses in (26).

When this condensation ends, the C<sub>2</sub>H<sub>2</sub> is driven to trap (32) from where it is expanded to Flask (30) to measure the conversion relation of CO<sub>2</sub> → C<sub>2</sub>H<sub>2</sub>. The C<sub>2</sub>H<sub>2</sub> is again condensed in trap (32).

### 2.4 Purification of C<sub>2</sub>H<sub>2</sub>.

As the C<sub>2</sub>H<sub>2</sub> count in the proportional region is perceptibly affected by electronegative impurities (ammonia, H<sub>2</sub>O, CO<sub>2</sub>, O<sub>2</sub> nitrogen oxides) its purification is necessary. This is done by passing the gas successively through 2 columns, (41) and (42) of the U tube shown in the diagram of the vacuum system.

Column (41) contains glass spheres impregnated with  $H_3PO_4$ , and column (42) spheres moistened in 50% NaOH solution. Having emptied the vacuum system from (29 to (49), and with the  $C_2H_2$  condensed in (32) this is driven to trap (38), from where it expands through columns (41) and (42) to bulb 68. It is then frozen back directly to trap 38. This procedure is repeated twice. Then with the gas expanded into bulb 68 the gas is condensed via the De Vrie trap (46) at  $80^\circ C$  to retain  $H_2O$  into trap (48), from where it can be expanded and stored in any of the flasks (54) to (65) before it is introduced into the counter for measurement.

The reagents of columns (41) and (42) are renewed each 10 or 12 samples.

### 2.5 Vacuum system and Furnace.

The diagram of the vacuum system can be seen in the general drawing. The design of the furnace is important. It must be hermetically sealed to vacuum and support consecutive heatings.

The furnace is constructed of stainless steel.

If possible, welding of the base of the furnace to its structure should be avoided, since hot lithium often causes welded joints to link. A furnace body turned from a billet of metal is more satisfactory.

The internal diameter of the furnace must be such that the liquid lithium surface be adequate for easy reaction with the  $CO_2$ . The size of the furnace should be big enough so that the LiOH solution formed in the reaction does not exceed concentrations greater than 5% as  $Li_2C_2$  reacts only very slowly with concentrated solutions of lithium hydroxide.

### 2.6 Yield of conversion of $CO_2$ into $C_2H_2$ .

The volume of Flask (10) and the measured pressure of  $CO_2$ , that the Flask (30) and the final pressure of  $C_2H_2$  permit one to estimate the yield of conversion which - in all determinations made - was better than 97%.

### 2.7 Filling the counter.

The required sample from any one of Flasks (54)...(65) is condensed in its appropriate trap (53) and any residual non-condensable gas (air) is pumped

away. Then the sample is expanded and condensed in trap (65).

S.C. 67 is closed and 64 opened and the sample is allowed to expand until the required filling pressure is registered on manometre M6. Excess acetylene is condensed via 67 to 66 back into its appropriate storage bulb. Normally the counter is operated at a filling pressure of 140 cm. Hg.

### III. ELECTRONIC EQUIPMENT.

This consists of two channels. The first one, for the proportional counter, consists of the following electronic blocks: preamplifier, main amplifier, pulse discriminator, 2 E.H.T. units, A.C. circuit and count system. The preamplifier is a modified type 1251 A (gain 26 db) but a type 1430A can be used and has the advantage of being commercially available.

The main amplifier is a Dynatron model 1430A set to a gain of 66 db. (The discriminator will be described when mention is made of the anticoincidence circuit).

Two E.H.T. units of 5000 V., of positive or negative polarity, are used to apply the required potential difference between the central wire (+) and the cathode (-). This potential difference in the counter used is about 6000 V., and is a function of the counter's diameter, of the diameter of the central wire, and of the nature and pressure of the filling gas.

The second channel consists of 17 Geiger counters (type 5.84 cosmic ray counters) which act as a cosmic ray screen followed by the following blocks: Quenching unit, E.H.T. power supply, anti-coincidence unit and count system.

A brief description follows each of the electronic blocks and of their main characteristics. As the pulses coming from the counter are of only a few millivolts, they must be amplified before they can be counted. The first step of amplification is given by the head, with a gain factor of 20. The primary tube of the preamplifier must be chosen to give the least possible thermionic noise. The pulses coming from the preamplifier are now fed into the main amplifier. This has two selectors of integration and differentiation constants. If these time constants



are conveniently chosen it is possible to obtain an adequate noise signal ratio for a given detector and associated circuits.

However, it is not advisable to use particularly large differential and integration constants because counts of the proportional detector could be lost.

### 3.1 Pulses shape in different parts of the circuits.

output Geiger tubes - 1.5 v, 20  $\mu$  sec

output Q.U., + 100 v, 1 m sec.

output proportional counter: 1 to 5 mv, < 1  $\mu$  sec

output main amplifier:

output of A.C. channel:  -4 v, 20  $\mu$  sec. (10  $\mu$  sec)

output of the A.C. Geiger counters channel:  -4 v, 20  $\mu$  sec

### 3.2 The quench unit.

The operation of this unit is as follows. The potential on the grid of V3B is such that the valve is biased almost to cut off by the cathode potential developed across the 25K variable and the 82K resistors in the cathode circuit. The cathode potential of V3B (and the grid potential of V2), is set by the 25K to a low enough value to keep V2 cut off completely. The negative input pulse from the Geiger counters is passed via C1, C2 + C3 and R5 to the grid of V4. The positive overshoot of the Geiger pulse is by-passed by V1B. The positive pulse developed across R7 is passed via C4 to the cathode follower V5 and the output of this is used as the anticoincidence gate pulse. The positive pulse from V4 is also fed to V3B causing the current through this valve to rise sharply. The voltage developed across R7 and R8 rises, therefore the grid and screen potentials of V2 to become fully conducting and a large negative pulse (200V) is developed across R2 and R3. This is used as the Geiger quench pulse. Part of this pulse is tapped off at the junction of R2 and R3 and this is fed via C4 to the cathode of V1A, the anode of which is at earth potential. The negative pulse is therefore bypassed to earth leaving only the positive overshoot which is used to provide a scaler pulse via the A/C unit. C2, C3 and R6 are chosen to give a time constant of 1 milli-

second so that the gate pulse is one millisecond in length.

The pulses of the A.C. counters formed in the quenching unit are directly applied to grid V3B (A.C. unit Fig.4) via cathode V5 (quenching unit); at the same time, such pulses are counted, directly from that unit, via cathode V1A (Q.U.) and V1a, V1b, and V4a of the A.C. unit Geiger counters channel.

The pulses of the proportional counter's channel - after pre and amplification are applied to the grid of V3a, via VR97, V7a by anode of V7b.

### 3.3 Discriminator.

With the purpose of eliminating the noise of the pre and main amplifier, and to discriminate them from the intelligence signal of the proportional counter, diode VR97 is used. Changing its plate polarity, the desired effect is obtained by adjusting the 25K potentiometer.

The main amplitude of the noise is  $\sim 2$  volts, measured at the output of the main amplifier whereas the intelligence signal is of the order of 45V. The discrimination potential is adjusted to 20 volts., thus giving a high margin of security.

### 3.4 Anticoincidence circuits.

This circuit is based on the so called "Three triode gate" comprised of V3a, V3b and V2a which are cathode coupled. They are biased at + 70V, + 40V and + 55V respectively. Thus V3a is normally conducting and the other two valves are cut off. The positive output pulses from the main amplifier (proportional channel) are fed to V7 (a or b) which is an univibrator with a time constant of  $20\mu$  sec. The output of this feeds to V2b (to provide a pulse for the proportional channel scaler) and part of it also goes to the grid of V3a. Since it is a positive pulse it has no immediate action on V3a which is already conducting. However, it is a square pulse  $20\mu$  sec in length with a negative overshoot of about - 30v and this overshoot reduces the bias of V3a and cuts it off. When this happens the potential across R24 falls until the valve with the next lowest bias (V2a) conducts and develops a pulse across R28. This is shaped by the univibrator V5 and fed via the cathode follower V4b to the A/C output. However, when a coincidence



occurs, the  $20\mu$  sec delay before the negative part of the pulse from V7b arrives at V3a allows time for the gate pulse ( $100v +$ ) from the quench unit to arrive at V3b and cause it to conduct, thus cutting off V3a and preventing V2a from passing on a pulse to the A/C output.

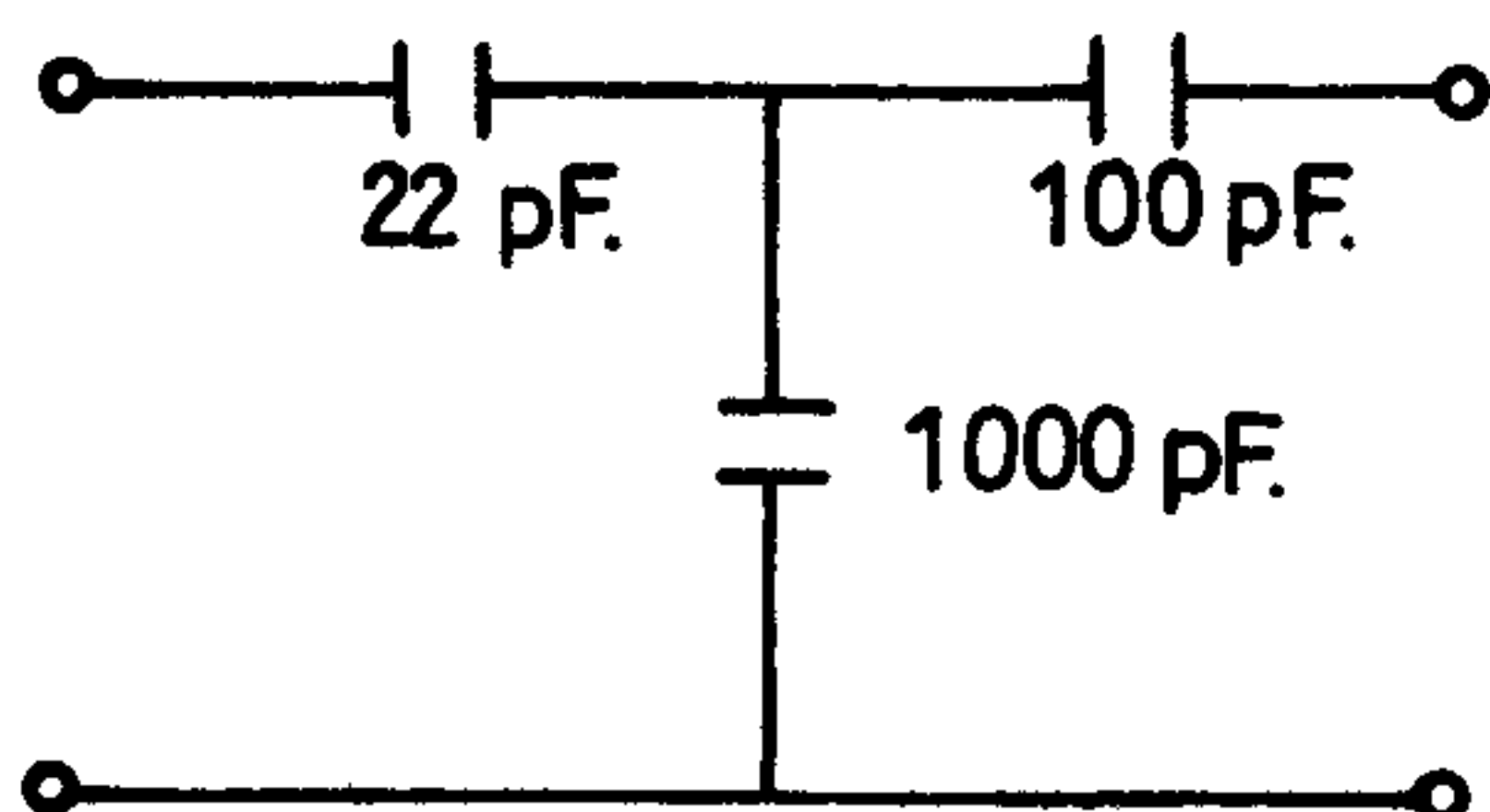
### 3.5 Counting scalers.

Three scalers connected to the points PLB, PLC, and PLF (A.C. unit) give the proportional, the A.C. proportional and the Geiger counts. An electronic timing unit is used to connect the output of the scalers to a bank of P.O. registers in succession each 1, 5, 10, 50, 100 or 500 min. periods. Usually 50 minutes period are chosen so that the overnight count is split into 30 sub-period. In this way the results can be subjected to statistical analysis. Thus always a check to be made on the stability of the equipment.

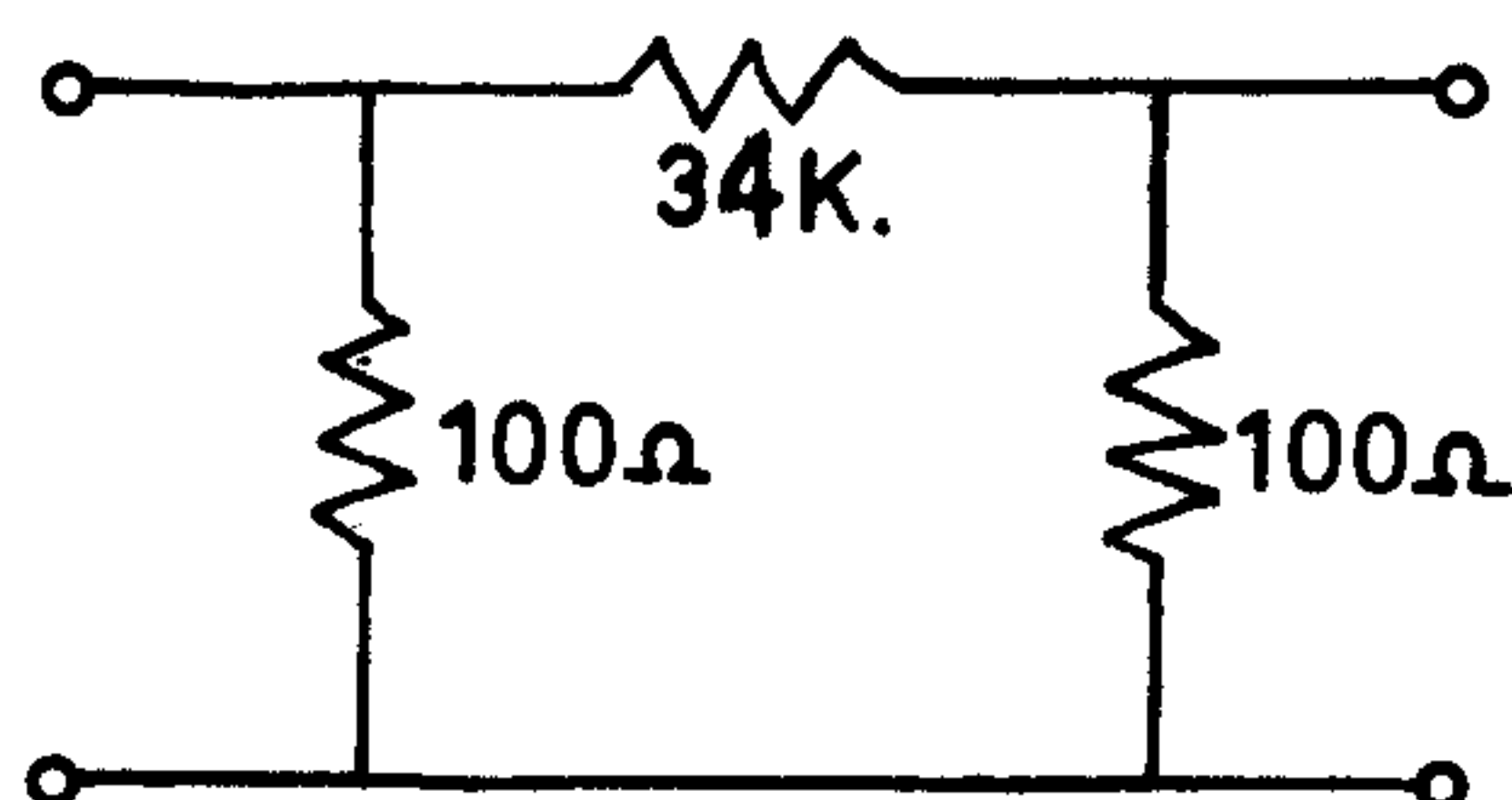
## IV. CHECKING OF THE ELECTRONIC EQUIPMENT.

A pulse generator type 1013C is used to simulate proportional and Geiger counter pulses in order to test the electronic equipment. It is set to its minimum rise and decay times ( $1\mu$  sec and  $10\mu$  sec) and the 50v output is fed via filter (1) to the quenching unit whilst, the 1v output is fed via filter (2) to the head amplifier filter (2).

FILTER. (1)



FILTER. (2)



The following characteristics of the pulse should then be obtained in the input proportional channel: 50 volts, duration

$7\mu$  sec to 1/2 height, output proportional channel: - 4 volt, duration

$10\mu$  sec to 1/2 height, output A/CO channel: - 4 volt, duration

$10\mu$  sec to 1/2 height.

The most common failures of the electronic equipment are valves with poor working characteristics due to long operation.

## V. COUNTER

The counter is made of a mild steel tube (0.10 to 0.25% carbon content) 31.5cm long and 5.5cm internal diameter (Fig. 5). However the sensitive counter volume is smaller due to the guard tubes.

The gas inlet from the vacuum system to the counter is made through the side wall.

The center wire is made of Inconel alloy with a diameter of 0.002", which is insulated from the counter body by means of a specially made ceramic to metal seal (Ferrant Ltd).

Positive voltage is applied to the center wire and guard ring, and the negative voltage to the counter body. Since the counter body is at high voltage it must be insulated from the steel shield.

Both, positive and negative voltages are fed through filter units to prevent spurious pulses arising in the power units or cables being applied to the counter.

The same positive voltage is fed to the guard tube and center wire and to the guard ring, which are separated from each other by a small insulator. This arrangement ensures that if electrical breakdown occurs in the main insulator, this spurious pulse will be considerably attenuated. On the other hand, the intelligence signal will be fed directly to the preamplifier via the 150 pf condenser..

A mercury shielding tank 1 inch in thickness is integral with the counter body and helps to decrease the background count. The background counting rate

is 4.23 c/m, when the filling gas is  $C_2H_2$  at a pressure of 140 cm of Hg. and at 22°C.

Recent modern counting rate (Oxalic ac. Standard) in identical condition a before is 11.45 c/m.

The voltage working point is found by running a plateau curve using cobalt-60 source at fixed distance from the counter. Since this curve is similar to the one obtained with  $C_2H_2$  if two points are found in the  $\gamma$  curve, the working point for Carbon-14 is easily determined once the relationship between the two curves has been determined accurately.

When the  $C_2H_2$  sample contains electronegative impurities such as water, vapour or air even in minute amounts e.g. 20 or 30 microns, the  $\gamma$  curve shows a peculiar dip in the plateau region. This provides a sensitive indication that the sample requires further purification.

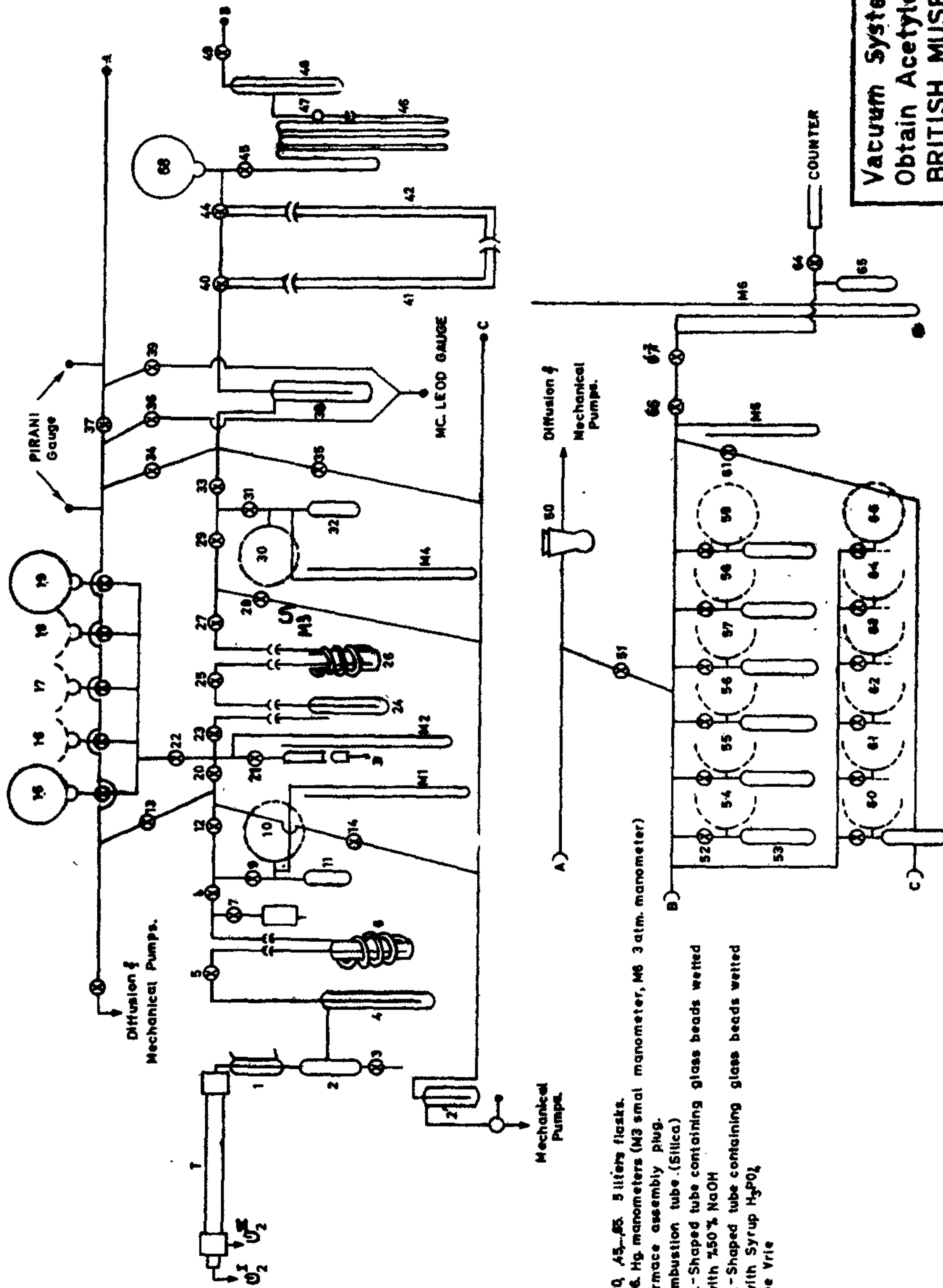
## VI. BREAKDOWN TEST

The purpose of this test is to check the actual insulator condition and is done applying + 4000 V to the counter center wire cathode grounded, and reversing the polarity in the second test. In a satisfactory test spurious pulses must be absent.

## ACKNOWLEDGMENTS

I am happy to acknowledge the valuable help of Dr. H. Barker, Head of the Research Laboratory of the British Museum, in the accomplishment of the present paper. I am also grateful for permission by the authorities of the Atomic Energy Research Establishment, Harwell, England, to draw the electronic circuit diagrams used at the above mentioned laboratories.

Figure 1



Vacuum System to Obtain Acetylene. BRITISH MUSEUM

- 10, ..., 20, 45, ..., 65. 5 liters flasks.
- M1, ..., M6. Hg. manometers (M3 small manometer, M6 3 atm. manometer)
- D. Furnace assembly plug.
- T. Combustion tube (Silica)
- 41 L-Shaped tube containing glass beads wetted with 750% NaOH
- 42 L-Shaped tube containing glass beads wetted with Syrup  $H_3PO_4$
- 46 De Vrie

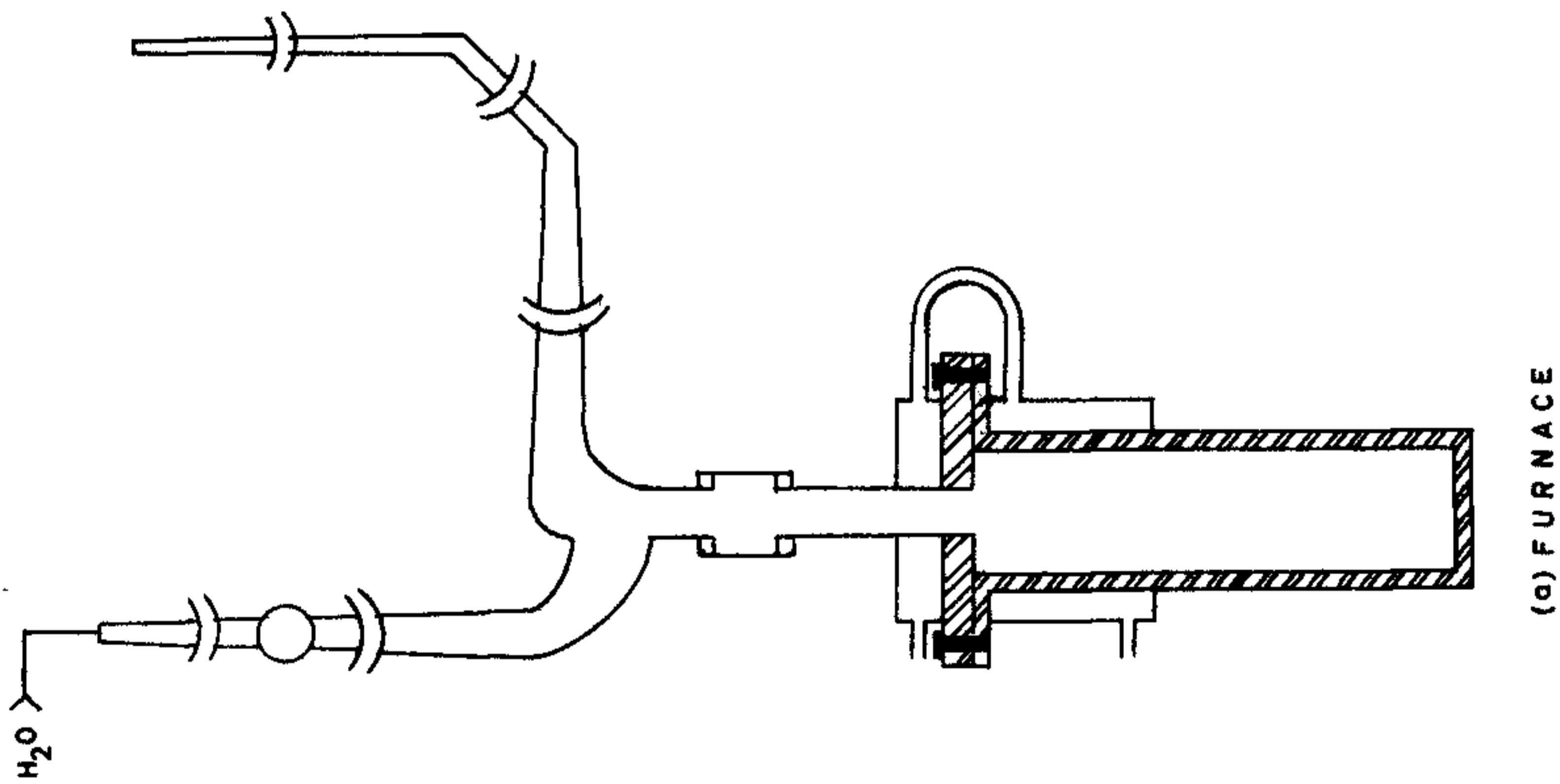
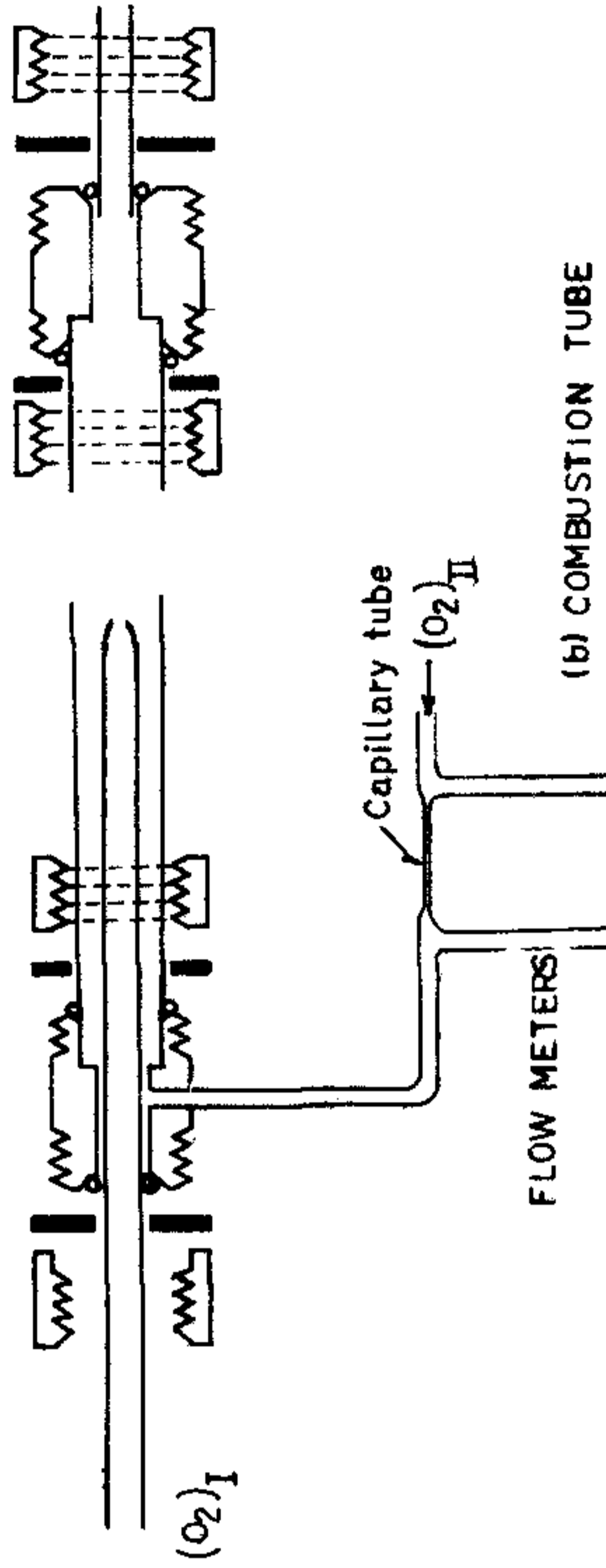
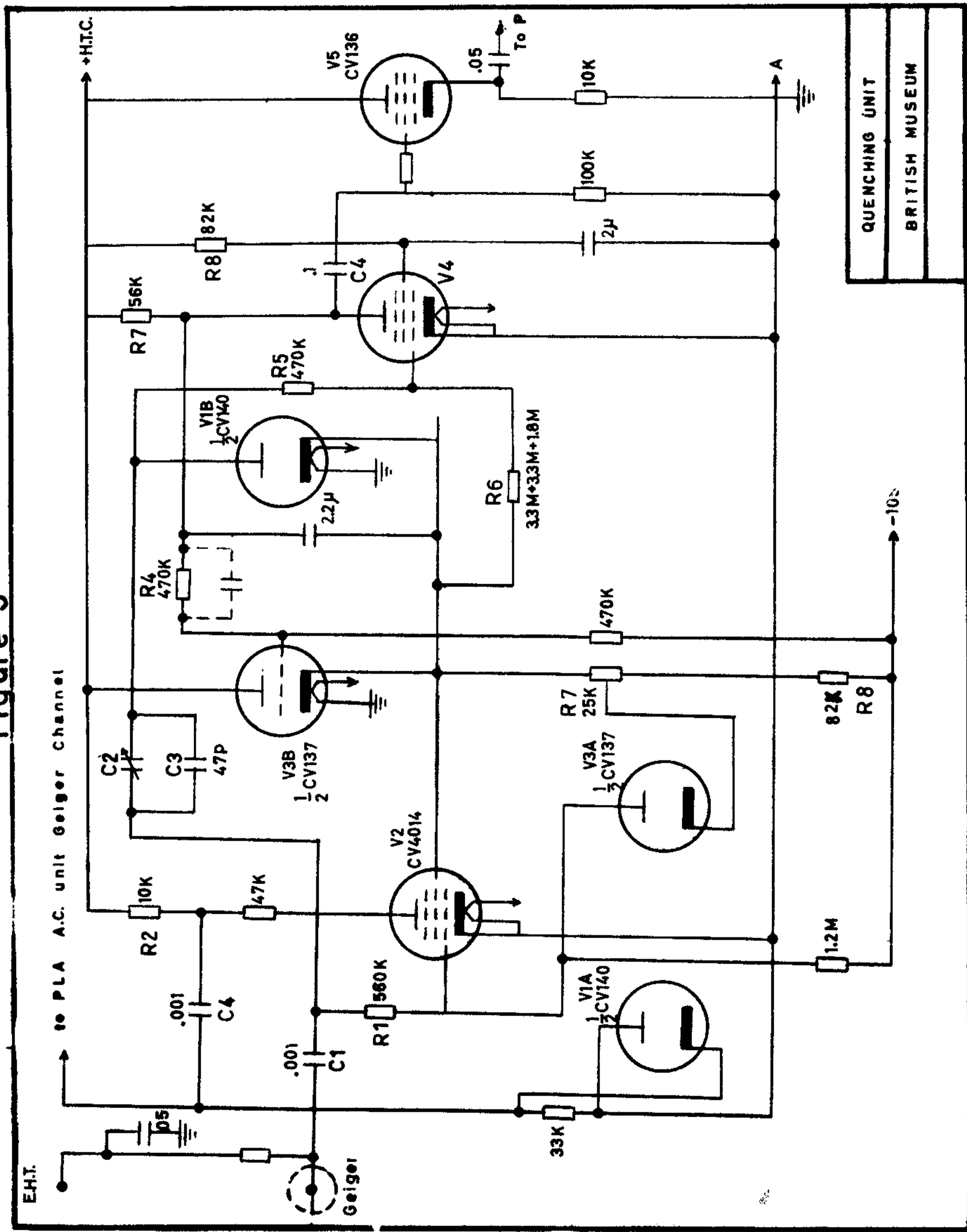


Figure 2



BRITISH MUSEUM  
Furnace & Combustion Tube

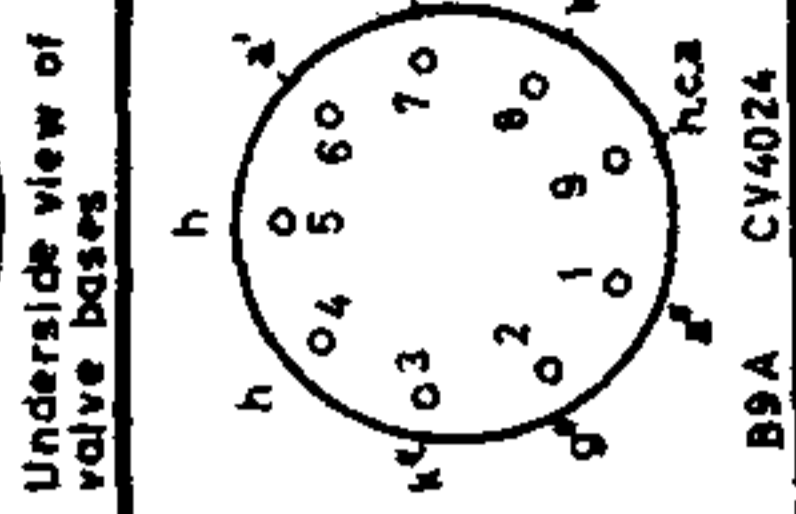
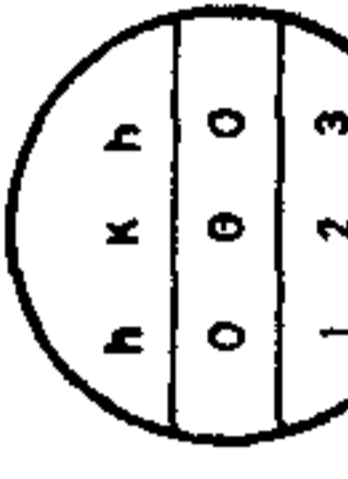
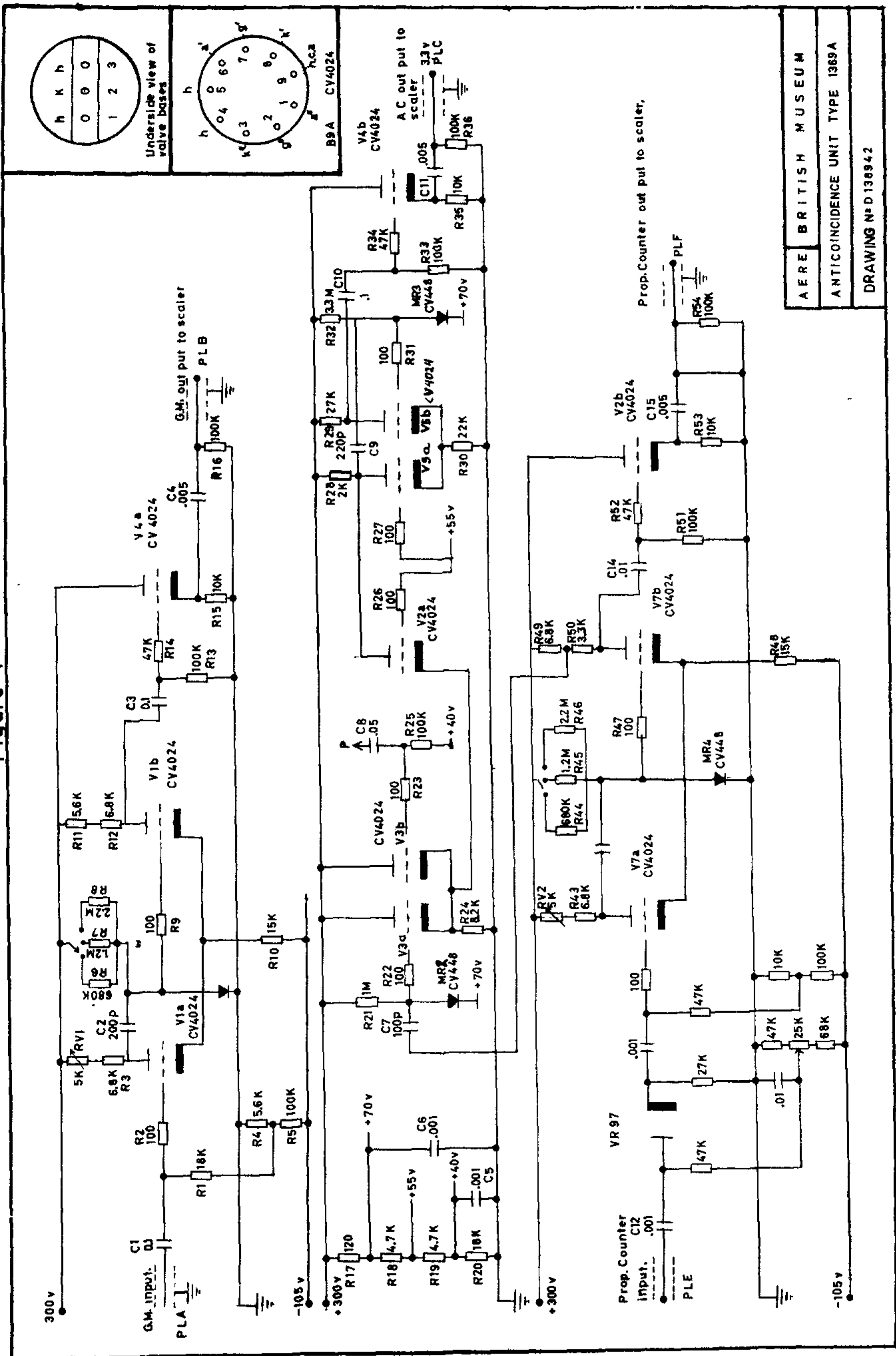
Figure 3



QUENCHING UNIT  
BRITISH MUSEUM

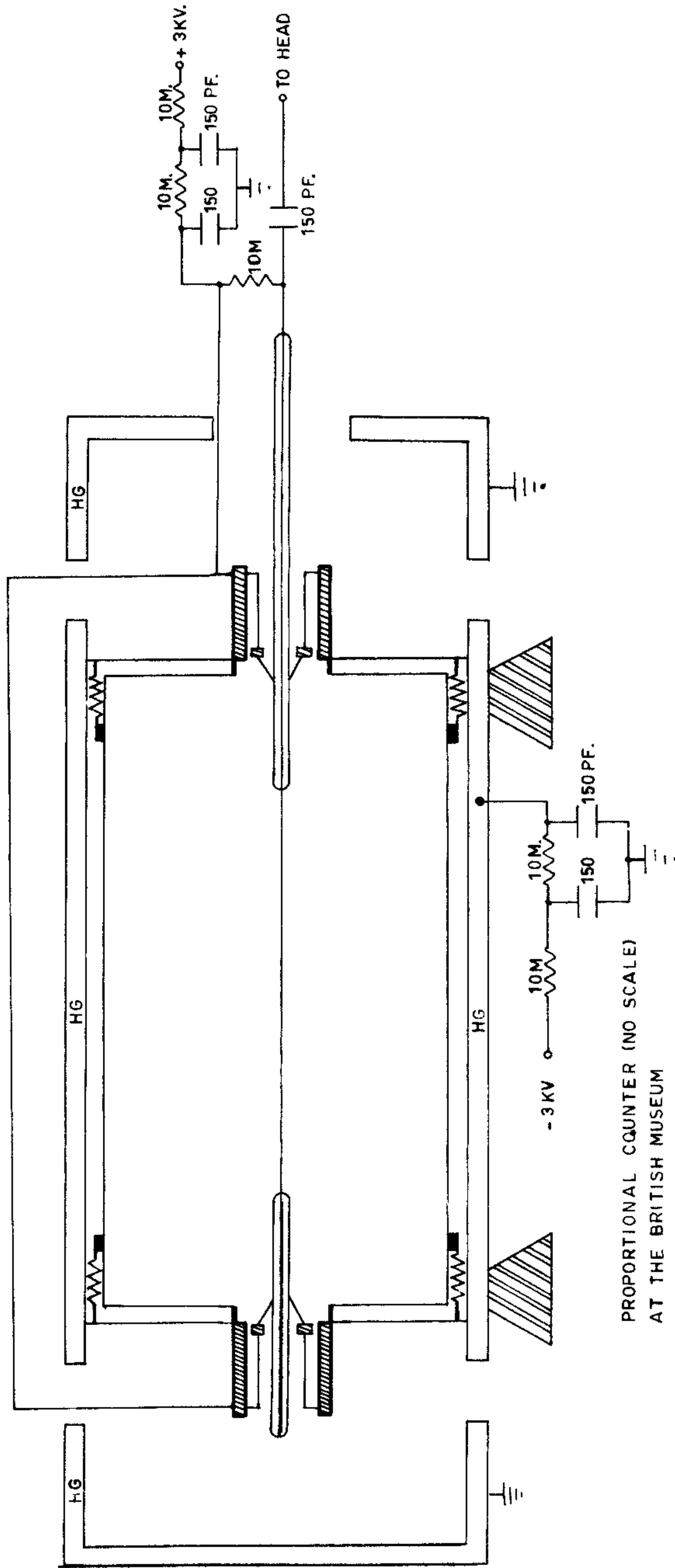


Figure 4



AERE BRITISH MUSEUM  
 ANTICOINCIDENCE UNIT TYPE 1369A  
 DRAWING N° D 136942

Figure 5



PROPORTIONAL COUNTER (NO SCALE)  
 AT THE BRITISH MUSEUM  
 RESEARCH LABORATORY.

BRITISH MUSEUM.