He points out that it is usual to replot the results of D.T.A. thermograms in order to obtain differential temperature against sample temperature. The temperature-measuring couple is usually positioned in the inert sample, in which case it forms part of the differential thermocouple, alternate readings of the differential and furnace temperature being obtained by some switching device. Alternatively, the temperature-measuring couple is positioned in a separate container filled with an inert material.

This couple has most often been constructed from platinum versus platinum - 13% rhodium wire since the small e.m.f. of this material is no disadvantage for temperature measurement and it is very durable. Where proportional control is used for the rate of temperature change of the furnace, this couple is used as the detector.

(c) Heating Programme Controller :

Many workers have stressed the importance of a uniform rate of heating for accurate D.T.A. work, although Pask and Warner(42) state:-

"The heating rate is critical only in the sense that it has to be the same from run to run in a given laboratory.......A straight line heating curve is preferred for it is easier to report, although actually this is not a requirement for good results providing whatever heating pattern is used is always repetitive." (Page 170).

Mackenzie(32) and Webb(52) agree with the above statement, and this seems to apply especially when we are interested in only a limited temperature range.

/Methods ...

Methods of regulating the heating rate have varied from manual, to semi-automatic to fully automatic. The most simple method is to adjust the power input into the furnace from time to time, but this is not very satisfactory. A more common method is to use a motor driven variable transformer which increases the voltage applied to the furnace windings at a predetermined rate. This is fairly satisfactory up to about 900°C. if the voltage supply is stabilized and the heating element is not of platinum, whose resistance does not increase linearly with temperature. The best method is that which employs the actual furnace temperature to control the heating rate. This is achieved either by a system of proportionally controlling the average power input to the furnace, or else by applying a fixed voltage to the windings for gradually increasing periods. The danger with these systems is that they will cause A.C. pickup by the differential thermo-couple to interfere with thermograms in certain types of recording equipment. Special precautions must be adopted to avoid such pickup.

Programme controlling equipment of the motor driven variable transformer type was used by Berkelhamer[1], Merjenberg and van Santen[35], Grim[17] and Pask and Warner[46], whereas fully automatic proportional control systems were used by Gruver[23], Kerr and Kulp[26], Webb[52] and Wilburn[53]. Grimshaw and Roberts[21], in their reply to discussion on this paper state (page 66):-

> "Our own views are that even proportional-controllers tend to produce a step-wise heating-rate. This ever-changing heating rate can

/seriously ...

seriously affect the quantitive determination of minerals. A second important consideration is that even if a true linear rate of the furnace temperature could be assured, the heating rate of the specimen can never be linear, by virtue of the endothermic or exorthermic reactions taking place. The essential requirement is a smooth reproducible rate of rise in the inert reference material."

They achieved this by keeping the power input into the furnace constant, and in their work on quartz, used the natural cooling rate of the furnace, which they found to be very reproducible after heating the furnace to 700°C.

(d) <u>Differential Temperature Recorder</u> :

There are only three common methods of observing the very small potential developed by the differential thermo-couple during a thermal change in the dust sample. Manual observation of the deflection obtained on a sensitive galvanometer has been used by Berkelhamer[1]. Grimshaw and Roberts[19] and [20], and Nagasawa[37]. It is noteworthy that all these workers were making observations on the very small thermal effect produced by the α-β quartz inversion. Berkelhamer obtained a deflection sensitivity of about 100 mm. for a pure quartz sample of 0.5 grams, while Grimshaw and Roberts claim that a sensitivity of ± 0.01°C is attainable.

A second and much more satisfactory method for routine work is that which involves the photographic recording of the deflections of a spot galvanometer. This method is cheap and sensitive, it requires no attention and several traces may be obtained simultaneously on the same chart. Disadvantages are that it

/is very ...

is very cumbersome as it requires a fairly large light-tight box and the records have to be processed before they can be assessed. It has been extensively used, Faust[14], Grim[17] and Grimshaw and Roberts[21] being some workers who employed the method.

By far the most frequently favoured method is by means of an electronic potentiometric pen recorder. It has the very big advantage that the record can be watched while the thermal reaction is taking place, and adjustments can be made if necessary. However, multiple pen recorders are very expensive, and commercially available instruments of sufficient sensitivity for small reactions are unattainable. It is necessary to use some sort of pre-amplication of the differential thermal voltage in such cases, and it is only recently that D.C. microvolt amplifiers of sufficient stability have become available. This method of recording D.T.A. thermograms has been used by Boersma[4], Grim[17], Gruver[23], Kerr and Kulp [24], Merjenberg and van Santen[35], Pask and Warner[46], Webb[50] and Wilburn[53]. Grim states that his equipment gave a sensitivity of two inches at 600°C for a 10°C temperature difference between crucibles. Kerr and Kulp claim that they achieved a sensitivity of 0.1°C, and indicate a peak deflection of 1 cm. for the $\alpha \rightarrow \beta$ quartz inversion. Merjenberg and van Santen in their studies on quartz obtained a deflection of 2 cm. for 1°C temperature difference.

Pask and Warner[46] mention the use of X - Y type recorders for D.T.A. work. In these instruments the chart speed varies with the rate of temperature change in the furnace, so the trace obtained is a true differential temperature versus temperature curve.

/Kracek ...

Kracek[28] described a special potentiometer system that was sensitive to 0.5μV, and he states that temperature differences of 0.01°C were easily detected.

Final choice of the differential temperature recording equipment must depend on the capital available, but the electronic recorder system seems to be ideal for routine work.[32].

3. DESIGN OF APPARATUS IN THIS LABORATORY

The foregoing discussion indicates that the choice of the apparatus for a particular application depends as much on individual preference as on anything else. Satisfactory results have been reported for widely different types of equipment, and careful control of the experimental techniques employed in obtaining thermograms is probably a much more significant factor in determining the accuracy and reproducibility of the results.

Before giving details of the four parts of the D.T.A. apparatus discussed in the previous section, a brief description will be given of the main features of the equipment assembled for the present work.

(a) Description of Apparatus :

The "Differential Thermal Analysis Apparatus" (see Fig: II, 1) in the Chamber of Mines Research Laboratory was developed solely for making measurements on fairly small dust samples containing unknown amounts of quartz.

The components of the apparatus are:-

(i) Two electrical tube furnaces, one with its axis horizontal and the other vertical. (See Fig: II, 1).

(ii) An A.C. Power supply (220 volts, 50 cycles per second) controlled by a circuit-breaker labelled "Mains" (Fig: II, 2).

/(iii) An ...

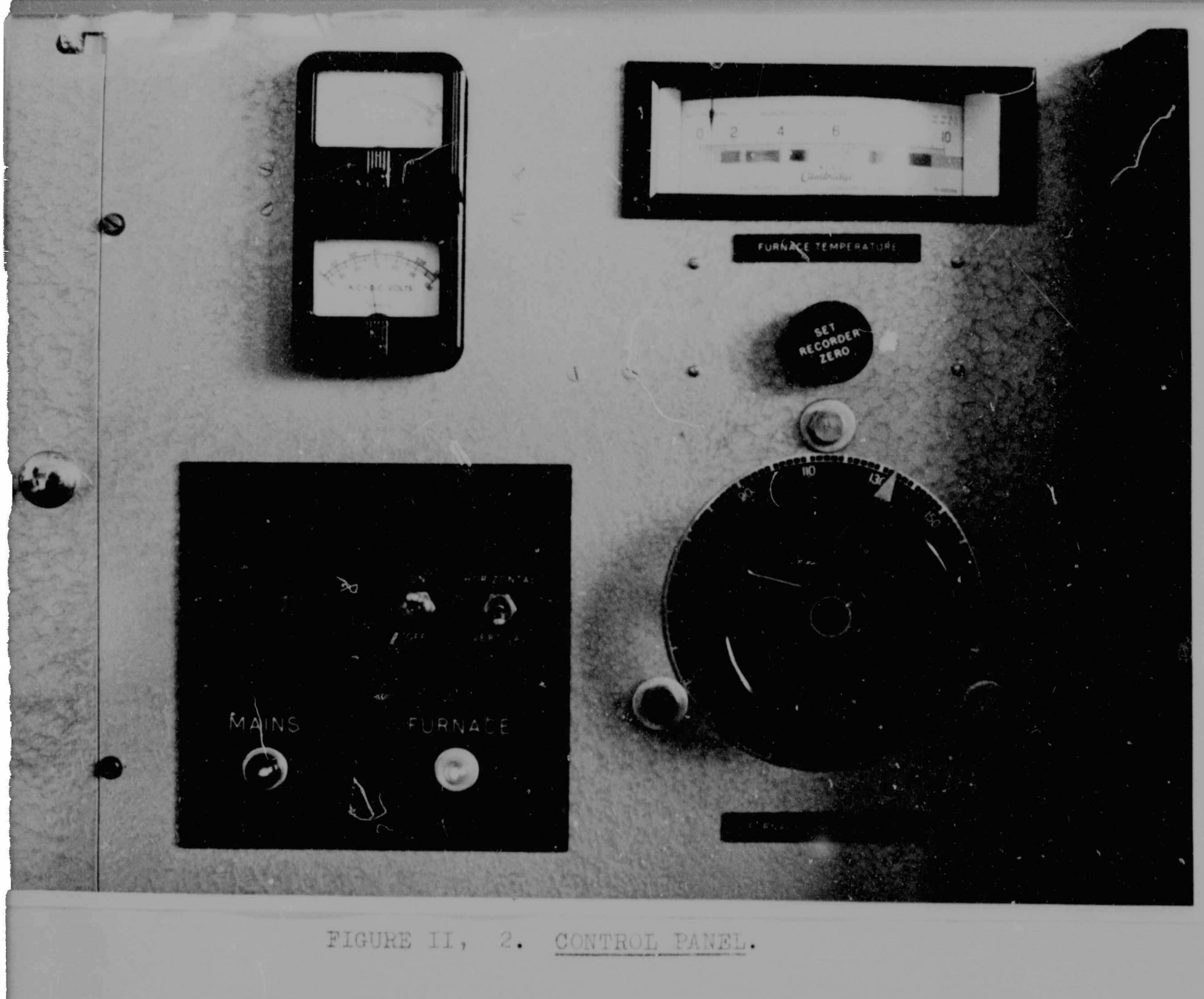


FIGURE II, 2. CONTROL PANEL.

(iii) An "on-off" switch for controlling the power supply to the furnaces, and a furnace selector switch which directs the power to either the horizontal or the vertical furnace. (Fig: II, 2).

(iv) A twin-dial Wattmeter-Voltmeter. (Fig. II, 2).

(v) A "Furnace Power Control" variac by means of which the power to each furnace can be set at a predetermined value using the above Wattmeter. (Fig: II, 2).

(vi) Sample holders for each furnace. There are two pairs of leads, a red and black one of fairly thin (0.3 mm. diameter) wire, and a red and black one whose protruding ends consist of strips of platinum foil from each furnace. The respective sample holders will be described in a later section. (Figs: II, 3, 4, 5 and 6).

(vii) A wide necked thermos flask containing water at room temperature. The cork top has four identical U-tubes let into it. These are filled with mercury. Two of these mercury-filled U-tubes form the contacts for the differential thermocouple leads (the thin wire), and the other two contacts for the temperature-measuring thermocouple. (Figs: II, 7 and 8).

(viii) A "Furnace Temperature" meter, graduated in degrees Centigrade. This instrument is designed for a platinum versus platinum - 13% rhodium thermocouple of 30 ohms. resistance. The contacts at the back of this meter lead to the U-tubes in the thermos flask. (Fig: II, 2).

(ix) A "Leeds and Northrup" stabilized D.C. microvolt

/amplifier ...

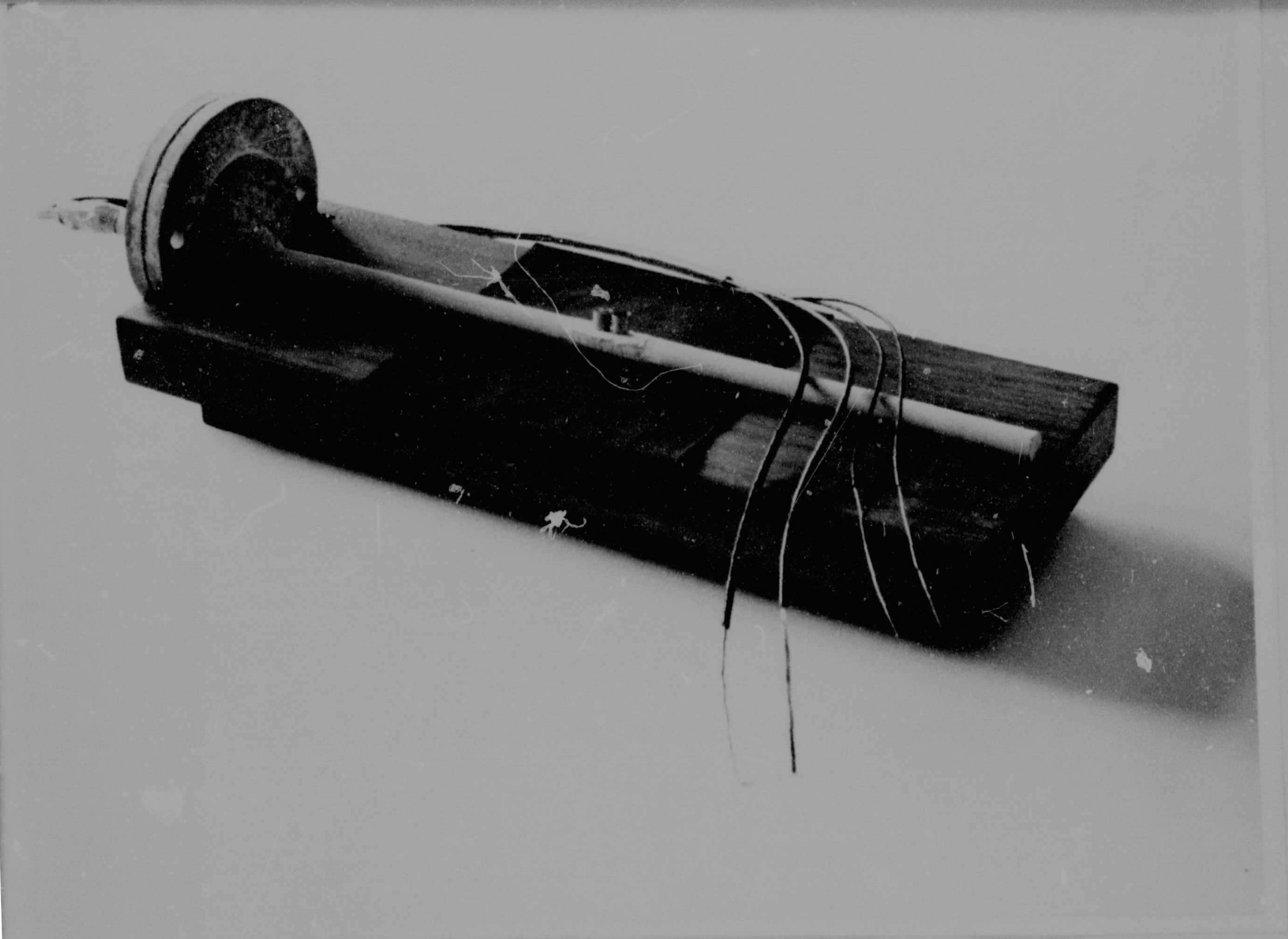


FIGURE II, 3. HORIZONTAL FURNACE SAMPLE HOLDER, PLATINUM CRUCIBLES MOUNTED.

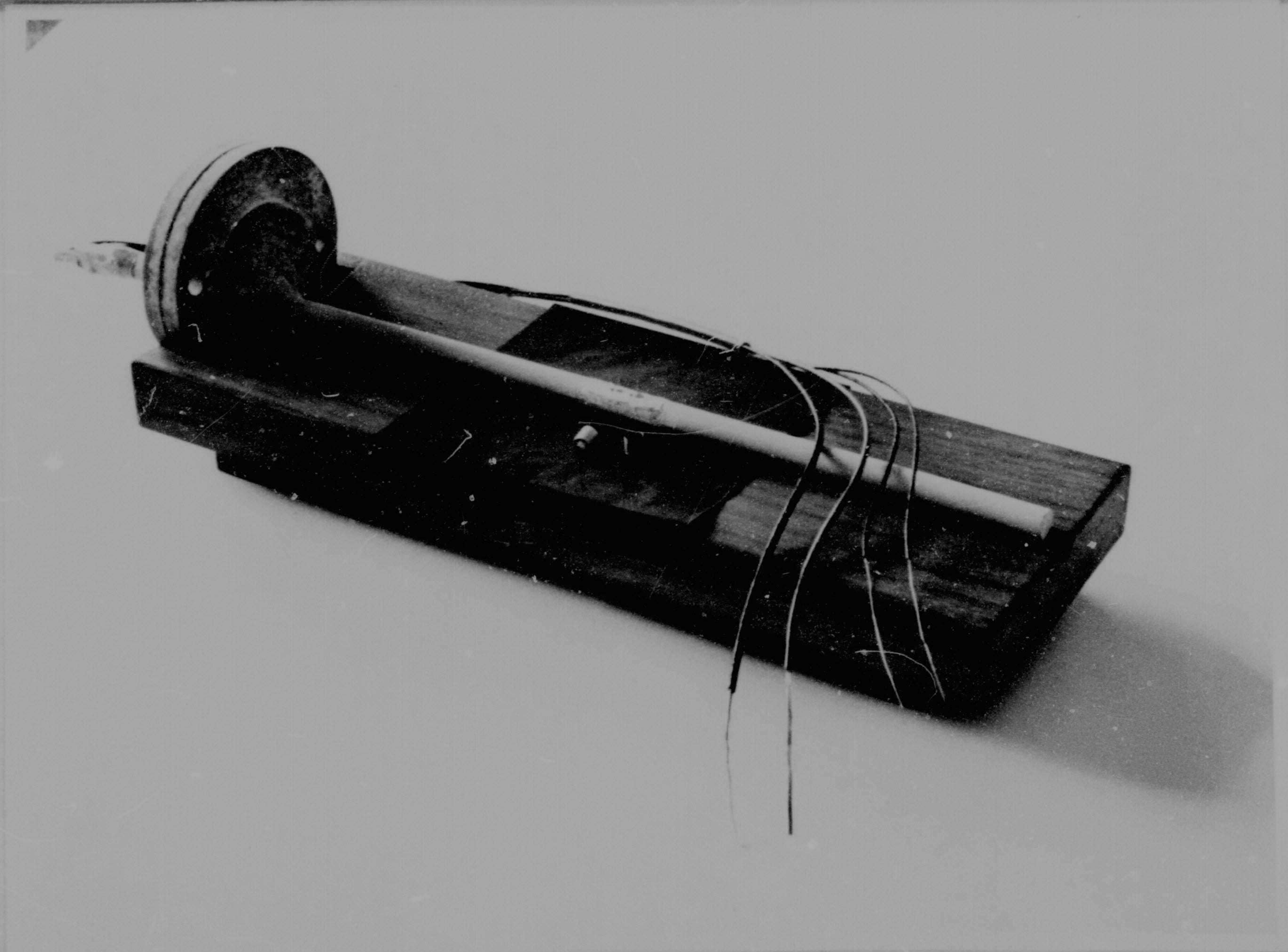


FIGURE II, 4. HORIZONTAL FURNACE SAMPLE HOLDER, PLATINUM CRUCIBLES REMOVED.

FIGURE II, 5. VERTICAL FURNACE SAMPLE HOLDER COMPONENTS ASSEMBLED

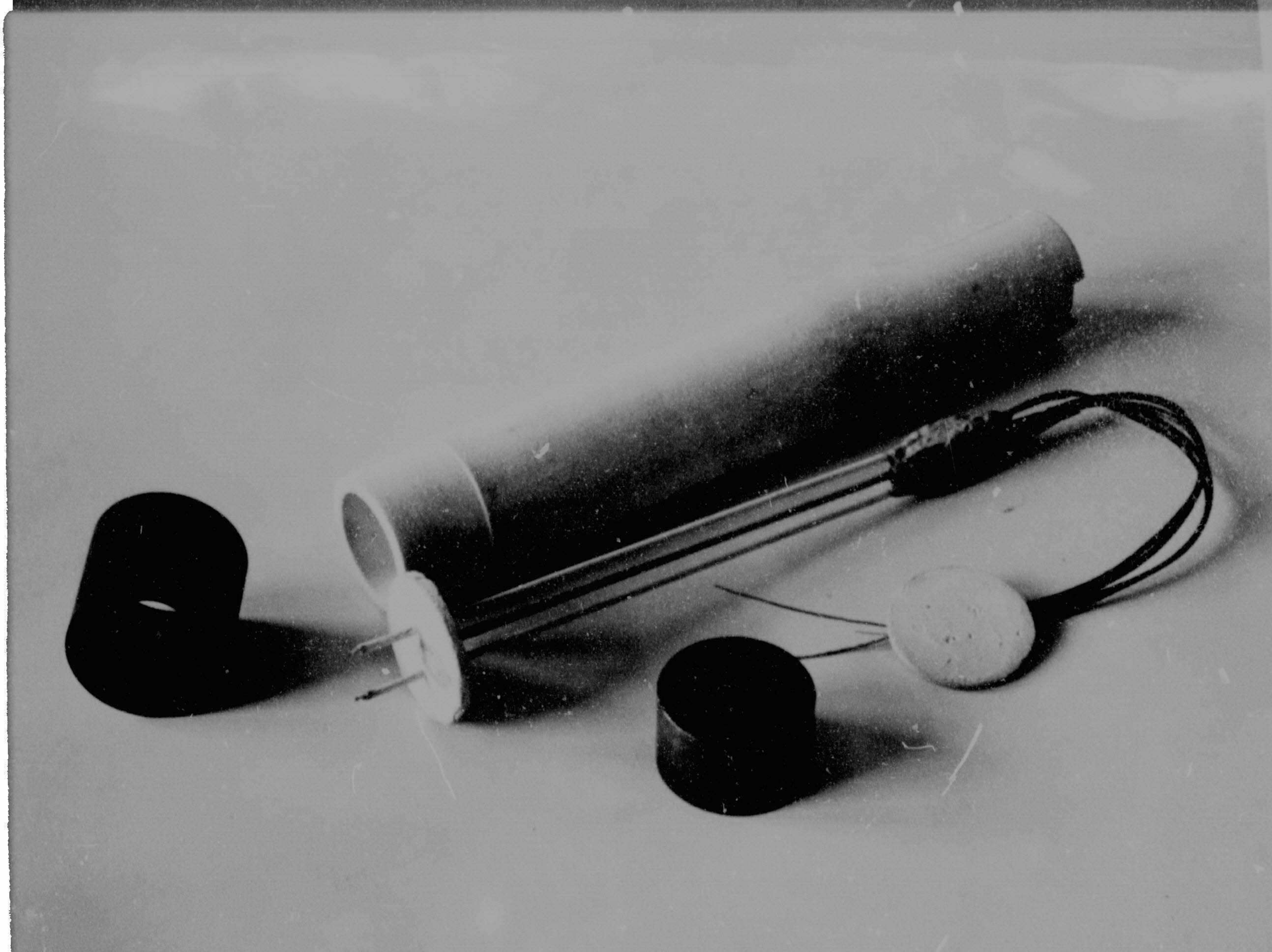


FIGURE II, 6. VERTICAL FURNACE SAMPLE HOLDER. COMPONENTS DISMANTLED.

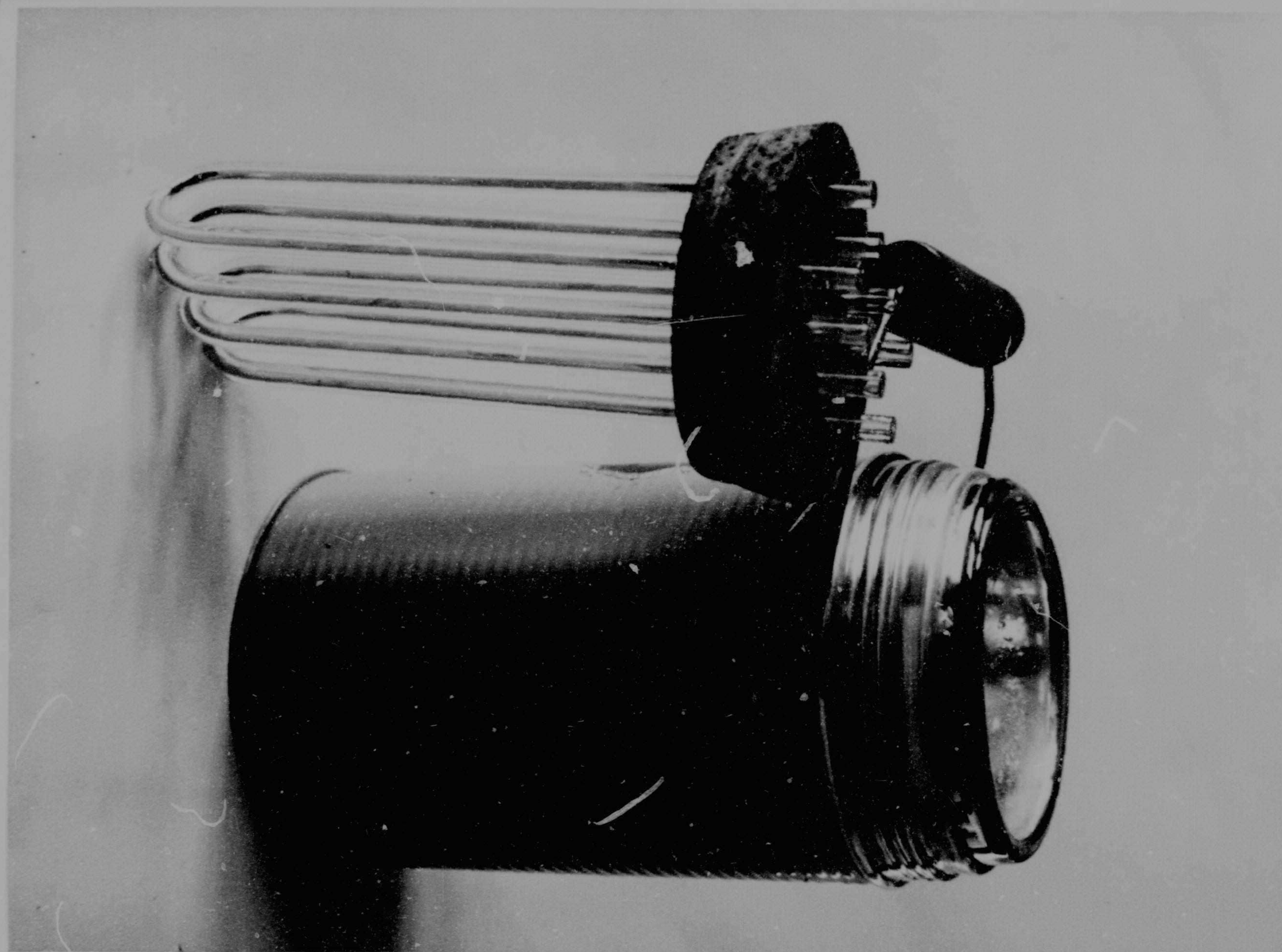


FIGURE II, 7. WIDE NECKED THERMOS FLASK, SHOWING MERCURY-FILLED U-TUBES IN CORK TOP.

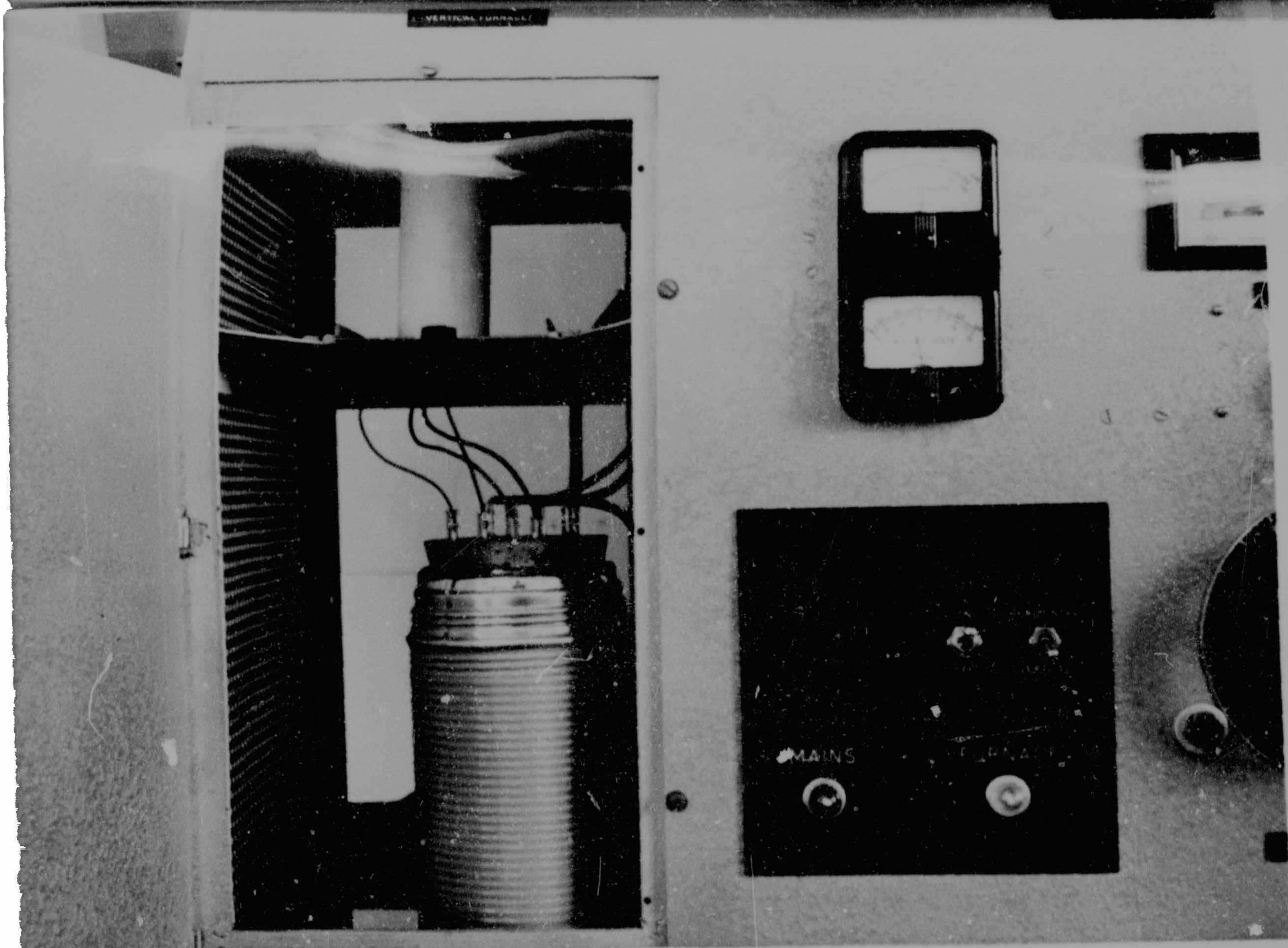


FIGURE II, 8. THERMOS FLASK, SHOWING LEADS FROM VERTICAL FURNACE IN POSITION.

amplifer. (Fig: II, 9). Its front panel embodies a meter, an "on-off" switch, a "non-linear-linear-recorder" selector switch and a "Range" switch. This has six positions, 50, 100, 200, 500, 1,000 and 2,000 which correspond to the full-scale microvolt deflection on the meter with the other switch in the "linear" position. Maximum amplification (on range 50) is 200, so a full-scale deflection on any range corresponds to an output of 10 millivolts.

(x) A "Sunvic" 10 millivolt potentiometer recorder (Fig: II, 10) for which the above instrument serves as a pre-amplifier in its "Recorder" position. The recorder has three switches marked "mains", "motors" and "test" respectively. There is a separate switch for the illuminating lights in the recorder. The chart speed can be set at 1, 2 and 3 inches per minute or per hour respectively by means of two gears.

(Details relative to the maintenance and operation of the above two instruments are given in their respective handbooks).

(xi) A special wooden stand for the horizontal furnace sample holder. (Fig: II, 3).

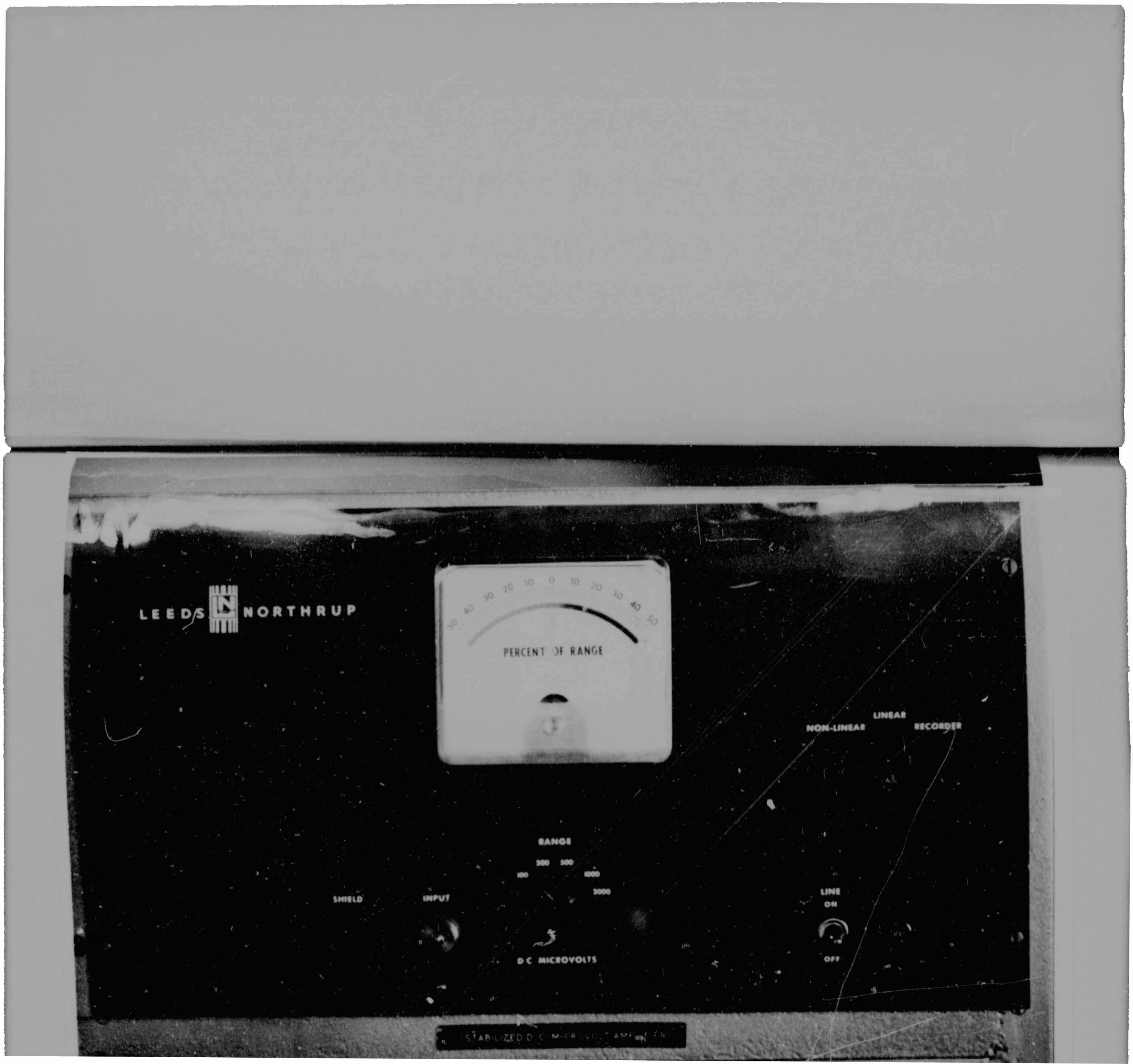
(xii) A knob for setting the recorder zero. (Fig: II, 2).

(b) <u>Description of Sample Holders:</u>

(i) <u>Horizontal Furnace :</u> (See Figs: II, 3 and 4)

/The ..

FIGURE II, 9. STABILIZED D.C. MICROVOLT AMPLIFIER.


LEEDS NORTHRUP
PERCENT OF RANGE
NON-LINEAR
LINEAR
RECORDER
RANGE
100
200
500
1000
2000
SHIELD
INPUT
D C MICROVOLTS
LINE
ON
OFF

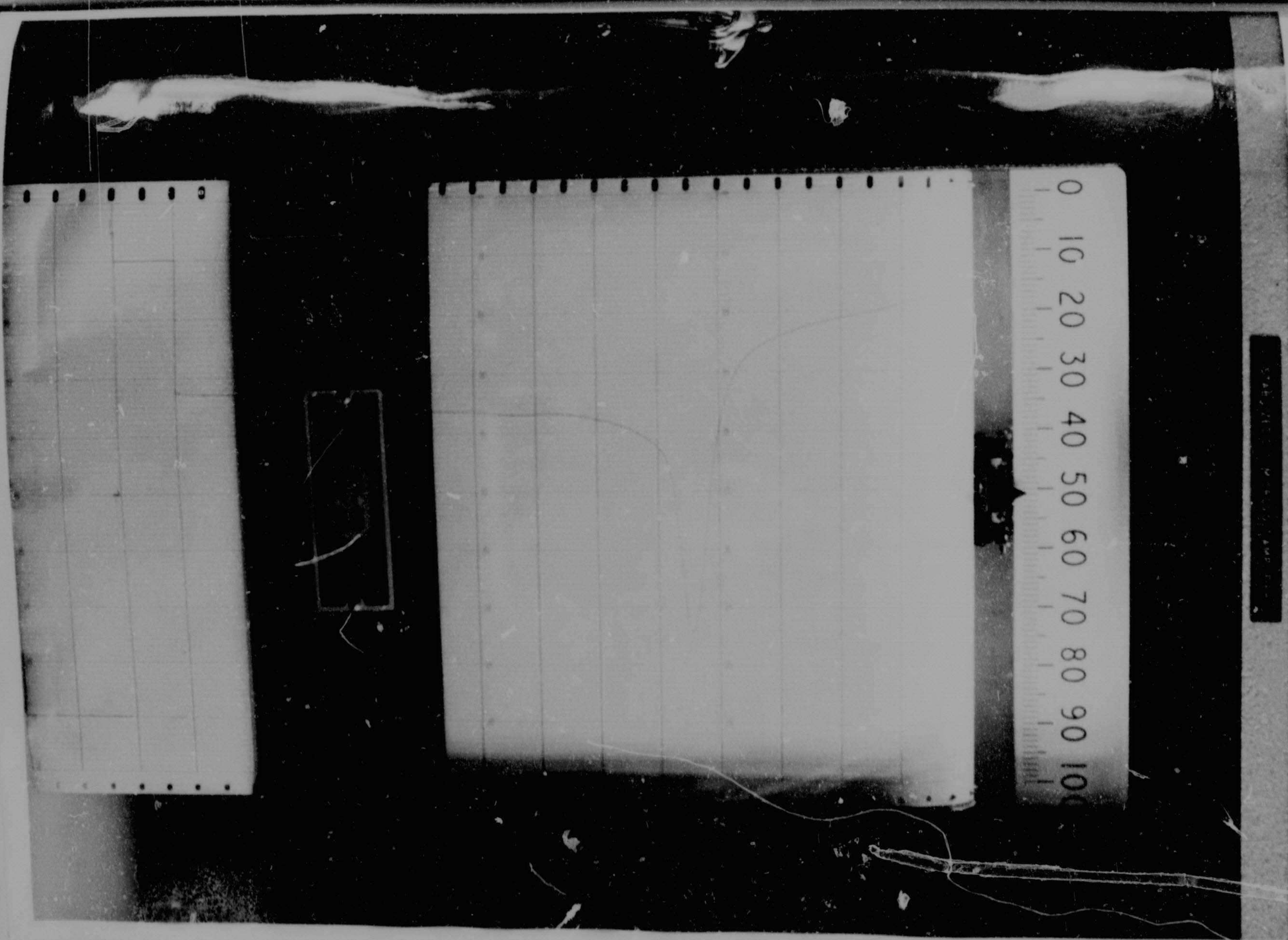


FIGURE II, 10. POTENTIOMETRIC PEN RECORDER.

The sample holder for this furnace consists of two cylindrical crucibles of 9 mm. height and 6 mm. diameter. These are located on a platinum baseplate which has two wells 1 mm. deep sunk into it to accept the crucibles. The differential thermocouple junctions enter through $\frac{1}{8}$ inch diameter holes in the baseplate which are aligned with corresponding holes in the crucibles. The thermocouple leads are insulated from the baseplate, crucibles and each other by twin-duct thermocouple insulating tubing of $\frac{1}{8}$ inch external diameter. These extend about 2 mm. up into the crucibles.

The baseplate is centrally mounted on a half-inch diameter ceramic tube. This extends the full length of the furnace and is held rigidly in position by an asbestos cement end-mounting. This is in turn held in position in the furnace by two knurled nuts.

The furnace-temperature thermocouple junction is located on the floor of the ceramic tube immediately below the centre of the platinum baseplate. All four leads from the differential and temperature-thermocouple emerge from the furnace at the front of the apparatus.
This end of the holder is protected by a cylindrical metal cap (Fig: II, 11) which has to be removed in order to remove the sample holder. The four leads emerge through a slit in the side of this cap, and are admitted to the thermos flask, which is in the space below the vertical furnace, through a slot in the door.

/ (ii) ...

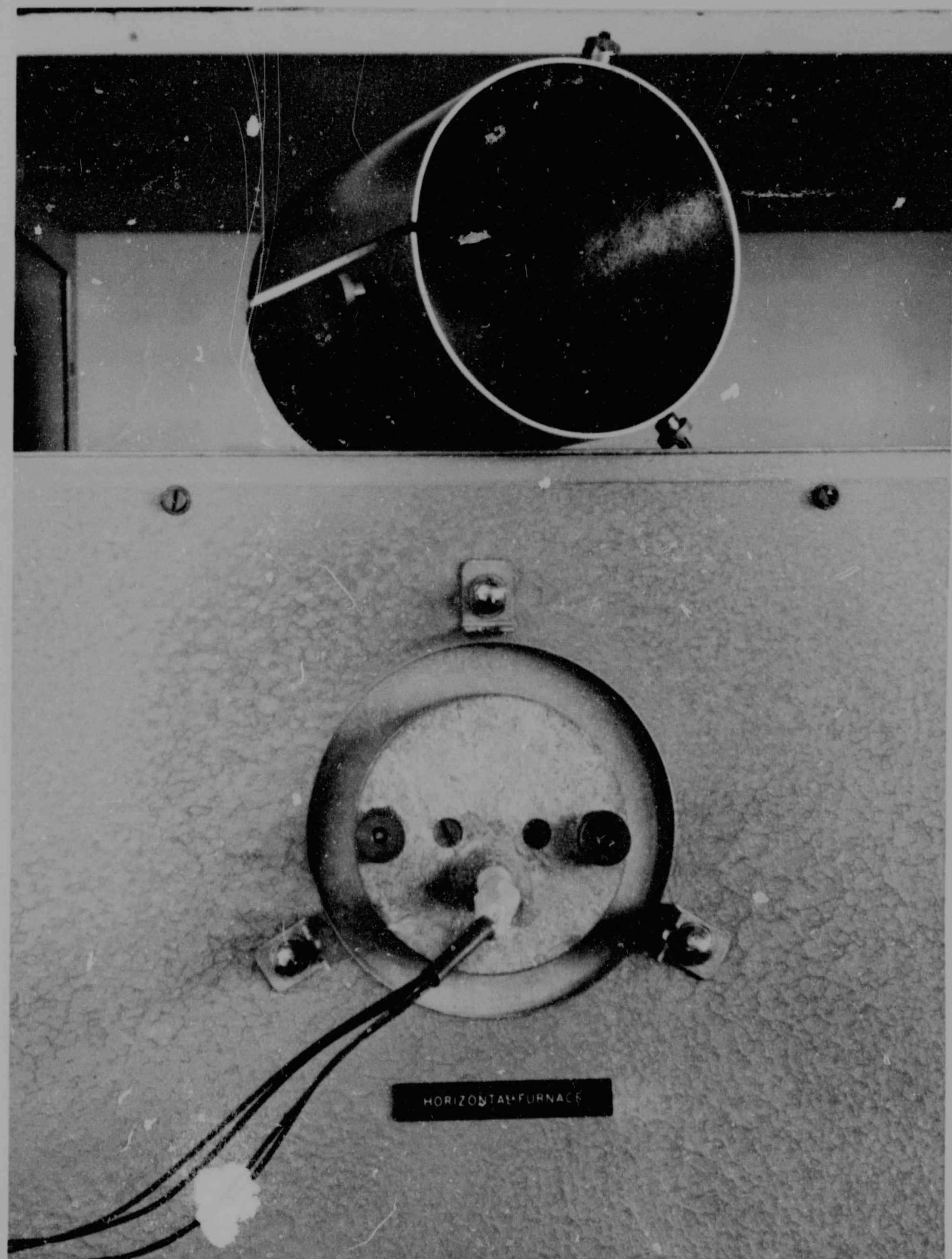


FIGURE II, 11. HORIZONTAL FURNACE WITH SAMPLE HOLDER IN POSITION, BUT CYLINDRICAL METAL CAP REMOVED.

(ii) Vertical Furnace : (See Figs: II, 5 and 6)

This sample holder consists of a cylindrical nickel block, 30 mm. high and 50 mm. in diameter, into which are sunk two identical wells, 9 mm. deep and 6 mm. in diameter. Two $\frac{1}{8}$ inch diameter holes lead up from the base of the block to the centre of the bases of the two wells; these admit the $\frac{1}{8}$ inch diameter twin-duct thermocouple insulating tubes which carry the differential thermocouple wires. The tubes are cast into position by means of a disc of alundum cement so that their ends are flush with the bottom of the wells.

The alundum cement disc also holds a third twin-duct tube which carries the temperature-measuring thermocouple. This does not extend above the disc, the junction actually lying on the disc. All this is supported by a two-inch diameter ceramic tube and a hollow nickel cylinder with an internal flange. The tube is twelve inches long, and is inserted into the furnace from below. It is located by a plate which slides into position below the furnace. (Fig: II, 8).

The four leads issue from the bottom of the tube, and pass through a slot in the sliding plate. Thence they pass directly to the thermos flask.

4. DISCUSSION

(a) Furnaces:

As already mentioned, an investigation of the literature did not reveal that either of the systems

/commonly ...

commonly employed, horizontally or vertically mounted furnace tubes, had distinct advantages over the other. The former system seemed to lend itself more readily to convenient mounting of platinum crucibles, and the latter to a metal block sample holder. The desire to try both these types of sample holders will be discussed later, but it was this that led to the decision to build both a horizontal and a vertical furnace. This did not add greatly to the cost of the apparatus, and there was the chance that it would greatly increase its value as a research tool.

It should be mentioned that many alterations were made to the equipment before it was considered to be satisfactory. Details of these will only be given where comparative thermograms of some interest are also available.

The horizontal furnace is comprised of a core 350 mm. long with an internal diameter of about 54 mm. The wall of the core is about 4 mm. thick, and it is wound with 17 s.w.g. nichrome wire to give a 2,000 watt element. The tube is centered inside a 250 mm. diameter metal container by asbestos cement end-pieces, and the intervening space is filled with vermiculite. This whole arrangement is horizontally mounted on the rack which was constructed for the D.T.A. Apparatus which is shown in Fig: II, 1. The back of the furnace tube is closed by means of an end-cover of asbestos cement similar to the one used for the sample holder mounting shown in Figs: II, 3 and 4. This is four inches in diameter and three-quarters of an inch thick, and has a $\frac{3}{8}$ inch internal flange which fits snugly into the furnace tube. It

/is ...

is held in position by two nuts and bolts.

The vertical furnace core is 450 mm. long, has an internal diameter of 58 mm. and has grooves of pitch 1/9 inch on the outside to carry the heating element. This consists of approximately 100 turns of 18 s.w.g. Kanthal A1 wire to give a 2,000 watt element. The tube is positioned by asbestos cement end-pieces which fit directly into the rack and which have recessed holes in them to admit the tube. An aluminium can 250 mm. in diameter surrounds this core, the intervening space again being filled with vermiculite.

A terminal block is attached to the rack between the two furnaces and the ends of the heating elements are connected directly to these terminals. A complete circuit diagram for the apparatus will be given in a later section. It should be noted that these furnaces have been built to give long life. The power input into either furnace seldom exceeds 1,000 watts so they are being operated well below their rated power. Kanthal A1 wire has considerably better temperature properties than nichrome, so should the horizontal furnace heating element give trouble, it will be replaced with one of this material.

(b) Sample and Thermocouple Holders:

A review of the literature showed that the greatest sensitivity could be obtained with twin platinum crucibles, but that the greatest reproducibility was likely to be achieved with the use of a nickel block holder. The heat of reaction of the $\alpha \rightleftharpoons \beta$ quartz inversion is small compared with that of most thermal reactions so it was decided to attempt

/to ...

to make the system as sensitive as possible. It was thought that very careful design would render possible improved accuracy of results (with platinum crucible sample holders) as compared with those reported by other workers. Following discussions with Dr. Webb of the National Building Research Institute, C.S.I.R., Pretoria, it was decided to try a nickel block sample holder as well. Hence, as mentioned above, two separate furnace and sample holder systems were designed and built.

These have been briefly described in Section 3(b), and are illustrated in Figs: II, 3 and 4 and Figs: II, 5 and 6 respectively. The internal dimensions of the crucibles and the wells in the nickel block are the same, namely a diameter of 6 mm. and a depth of 9 mm. It should be mentioned that the crucibles are mounted so that the gap between them is only 2 mm., whereas the wells are 10 mm. apart. As the nickel has a high thermal conductivity, it tends to minimise any temperature gradient that may exist between the test and inert samples due to any lack of symmetry in the furnace heating. This does not apply in the case of the crucibles, so they were mounted as close to one another as practicable.

The wall thickness of the platinum crucibles is 0.010 inches, their total mass together with that of the platinum base plate on to which they fit being 6.75 gm., so the heat capacity of the system is very small. The base plate has overall dimensions of 36 mm. length by 12.5 mm. width by 2 mm. thickness. The main feature of this system as compared with

/similar ...

Author Craig D K
Name of thesis Determination of the Percentage of Quartz (S1O2) in samples of Mine Dust by the Method of Differential Thermal Analysis 1959

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