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A SIMPLE DIFFRACTOMETER HEATING STAGE

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ABSTRACT: The construction is described of a heating stage for examining oriented clay specimens in a Philips' diffractometer. The stage, which is simple and cheap to make, is interchangeable with standard specimen holders, operates over the range 20–265°C and does not require the diffractometer to be specially modified. The maximum temperature attained at the surface of the specimen collapses freely-expanding Mg-saturated vermiculite and prevents re-expansion of layer silicate minerals once they have been collapsed.

INTRODUCTION

Changes in X-ray diffraction patterns produced by chemical and thermal treatments are often used as diagnostic tests for identification of clay minerals. Rehydration after heating, which can occur rapidly, may lead to errors. Milne & Warshaw (1956) recommended the use of dry air in the specimen chamber of a diffractometer to prevent rehydration. We have used a heated specimen stage for the same purpose.

Many devices have been described that allow specimens to be examined by X-ray diffractometry at temperatures above ambient (for examples, see Goldschmidt, 1964) but none satisfied our requirements. We needed a device that: (i) would allow the examination of specimens at temperatures ranging from room temperature to about 250°C; (ii) could be used interchangeably with conventional specimen holders without realignment of the diffractometer; (iii) incorporated the excellent radiation protection shielding provided in the Philips' instrument; this set a maximum size of about $5 \times 5 \times 1$ cm for the whole stage. For routine identification of clay minerals in our laboratory, oriented films of clay are prepared on the surface of glass slips $3{\cdot}8 \times 1{\cdot}27 \times 0{\cdot}12$ cm (see Appendix) that are laid on the stepped surface of a duralumin specimen holder to align the clay surface with the reference surface of the diffractometer. The heating stage described below supplements the duralumin holder by holding similar clay-coated glass slips in the diffractometer for examination at elevated temperature. The dimensions of the completed heated stage are

4·0×3·2×0·6 cm. It uses a small electrical heater set in a duralumin block, which is in contact with the glass slip, but otherwise supported by asbestolite. Thus, for a given temperature at the clay specimen surface, heat reaching the stage and transferred to the goniometer is minimized and special modifications for cooling are unnecessary.

Although the heating stage described is specifically made for clay mineral studies using a Philips' PW 1050/25 diffractometer, little modification in design would be needed to make a stage for use with other diffractometers or with other kinds of specimens.

DESCRIPTION

Figure 1 shows the components of the heating stage*.

The insulating block, (1) is formed from Asbestolite†. Its reference face (S), which is held against the reference surface of the goniometer shaft, is ribbed to minimize heat transfer to the shaft.

The metal block, (2) is made of duralumin. When components 1 and 2 have been permanently fixed together, surface (S) is machined parallel to, and 0·050 in. (1·27 mm) above, surface (P). The specimen slips are prevented from sliding on surface (P) by the small phosphor–bronze bracket (9).

The heating coil, (14) is positioned in the cylindrical hole in block 2 inside a double insulating sleeve of woven glass fibre (12) and protected by a steel outer cover (11). This cover is held in position by two screws that also attach the mica-filled P.T.F.E. insulating block (4) to block (2).

The heating coil is formed from a soldering iron element, 15 W, 240 V, Type CN manufactured by A.N.T.E.X. Ltd‡.

As supplied, the ceramic tube former of the heater is too long to fit the sample holder. It is therefore removed from its stainless steel sheathing tube and woven glass fibre cover and shortened to give a total length of 4·3 cm. The leads connecting the heating coil to the supply have to be re-attached following this operation. The ends of the wire of the heating coil are twisted on to 0·25 mm-diameter nichrome wires and then welded using an electric arc from a pointed carbon electrode and a 40–50 V battery. The modified heating coil is then resleeved in its glass fibre and steel covers, secured in block (2), and the leads, cut to about 3 cm and insulated with silicone rubber sleeving, are soldered to the terminal pins (6), in block (4). A *control unit* conveniently supplies power from the 240 V mains supply through a small auto-transformer to give 0–270 V to the heating coil. Figure 2 shows a suitable circuit. Thin insulated flexible leads from XY (Fig. 1) connect the heating stage to the transformer unit. The heating stage leads are brought into the specimen chamber of the diffractometer through the removable cover. We have modified a *replacement*

* Working drawings for construction may be obtained from the authors.

† Asbestolite is a composite of asbestos and cement.

‡ A.N.T.E.X. Ltd., Mayflower House, Plymouth, Devon.

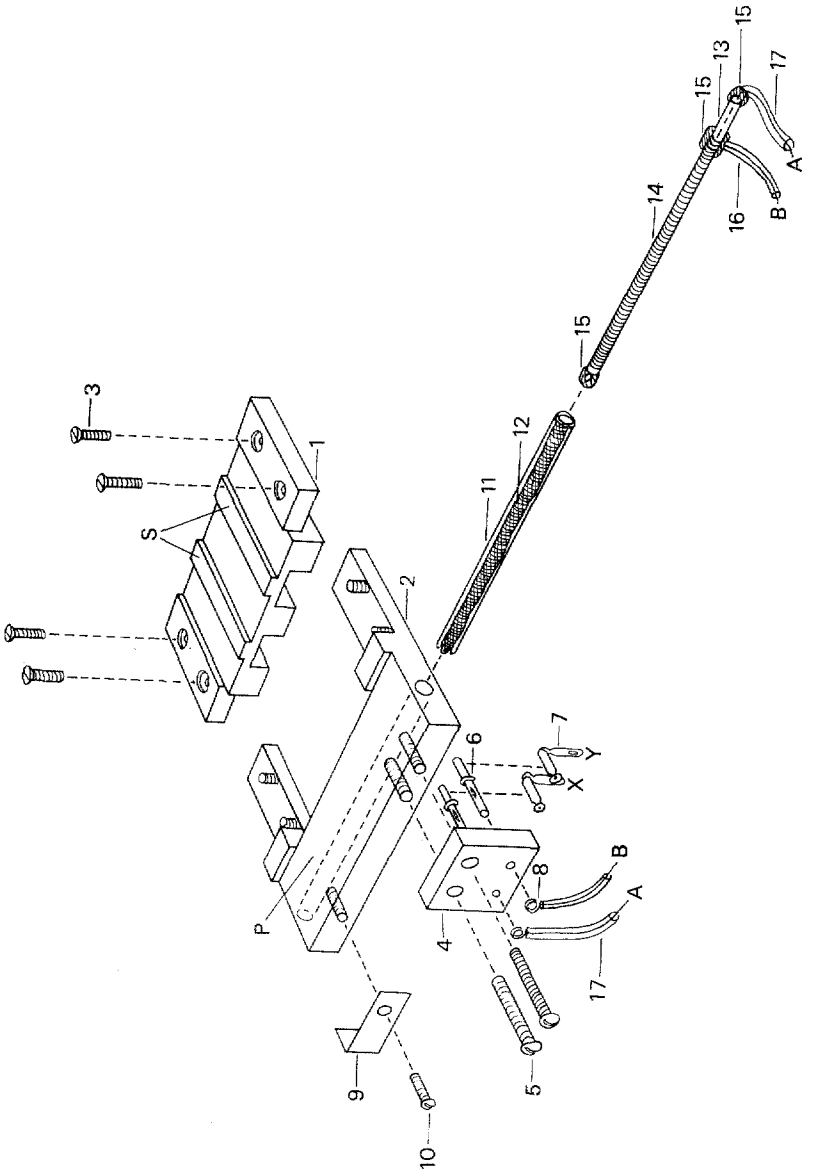


FIG. 1. Diagram showing components of the heating stage. 1. Insulating and support unit; 2. Heating unit; 3. Brass screws 10 B.A. C.S.H.; 4. Insulating block; 5. Brass screws 8 B.A. R.H.; 6. Terminal pins; 7. Pick-up tags; 8. Soldered connections from heater; 9. Slide retaining bracket; 10. Brass screw 10 B.A. R.H.; 11. Steel outer cover; 12. Woven glass-fibre insulation (2 layers); 13. Ceramic tubular heater support; 14. Heater winding (0·003 mm diam.); 15. Ceramic cement; 16. Nichrome connecting wires (0·254 mm diam.); 17. Silicone rubber sleeving.

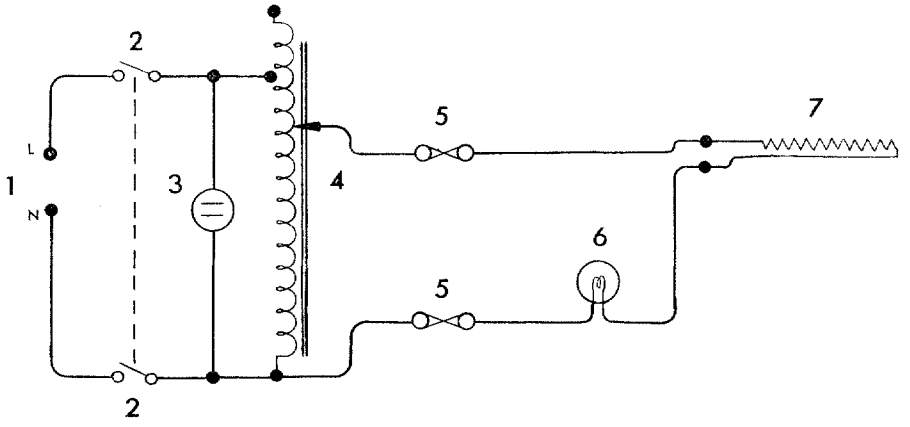


FIG. 2. Circuit diagram for the control unit of the heating stage. 1. Mains, 240 V; 2. ON/OFF switch; 3. Mains ON, neon; 4. Autotransformer, 2 A rating, input 240 V, output 0–270 V; 5. Fuse, 200 mA; 6. Heater ON, filament lamp, 6 V, 0·1 A; 7. Stage heating element.

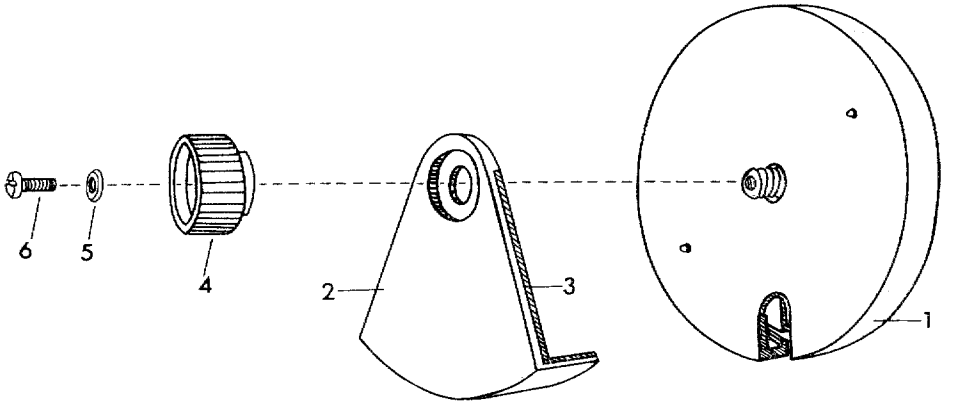


FIG. 3. Diagram showing components of the modified specimen chamber cover. 1. Modified cover plate; 2. Movable sector; 3. Lead lining; 4. Knurled securing knob; 5. Brass washer 6 B.A.; 6. Brass screw 6 B.A. C.H.

cover by cutting a 12 × 6 mm slot through the periphery of its inner and outer components (Fig. 3). To prevent scattered radiation escaping through this slot, a 55° sector of lead-lined duralumin is added, pivoted about the central locking screw. When the cover is in position the sector is rotated to cover the slot and is then clamped. The leads emerge from the radiation shielding via the 12 × 6 mm slot

and the 3 mm gap between the perimeter of the cover and the flange of the sector. With the sector in position scattered radiation could not be detected outside the radiation shielding.

TEMPERATURE CALIBRATION

The temperature of the specimen is controlled by varying the voltage applied to the heating coil. Equilibrium at each temperature is attained in about 10 min and a calibration curve of temperature versus applied voltage is given in Fig. 4. The temperature of the clay specimens was determined by observing the melting of powdered crystals of pure substances of known melting points in contact with the clay surface. The temperature range over the surface of the specimen does not exceed the error in measurement, estimated to be about $\pm 2°C$.

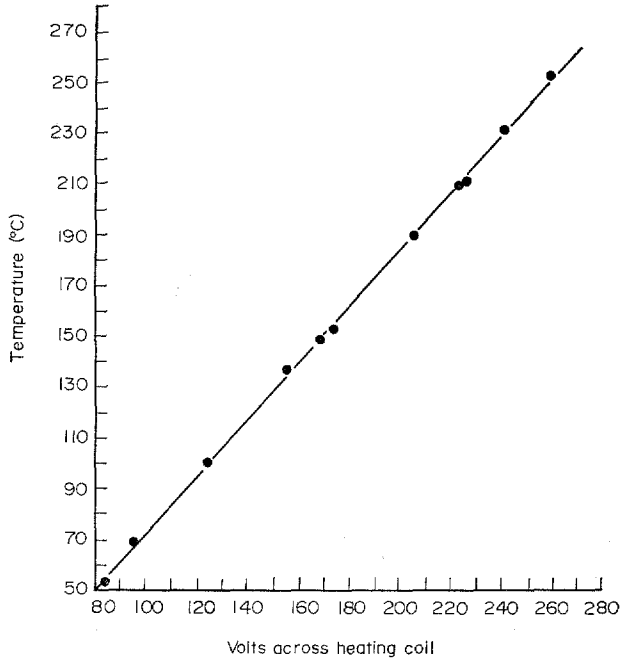


FIG. 4. Calibration curve of specimen; surface temperature against applied voltage.

	M.P.°C		M.P.°C
p-dichlorobenzene	53	citric acid (anhyd.)	153
stearic acid	68·5	salophene	190
citric acid	100	dicyandiamide	210
phenacetin	135	silver nitrate	212
cholesterol	149	tin	232
		phenolphthalein	254

MEASUREMENT OF 2θ

Because the heated stage is a composite of different materials, tests were made to discover whether heating caused the position of the specimen surface to change. Measurements of 2θ from a specimen of diamond powder, which has a very small coefficient of thermal expansion (Skinner, 1957), showed that over the temperature range 20–250°C changes in 2θ caused by thermal expansion of the instrument do not exceed 0·01° 2θ.

The only aberration introduced by replacing conventional specimens with those we use for examination of clay films occurs because the glass slips, which are cut from 7·62 × 3·81 cm microscope slides, may range in thickness between 1.17 mm and 1·35 mm. The surface of the clay film is therefore usually displaced from the reference plane of the goniometer causing shifts in the position of reflections, to larger angles if the specimen surface is inside the focussing circle and to smaller angles if the surface is outside, by

$$\Delta 2\theta = 2S \cos \theta / R \text{ radians},$$

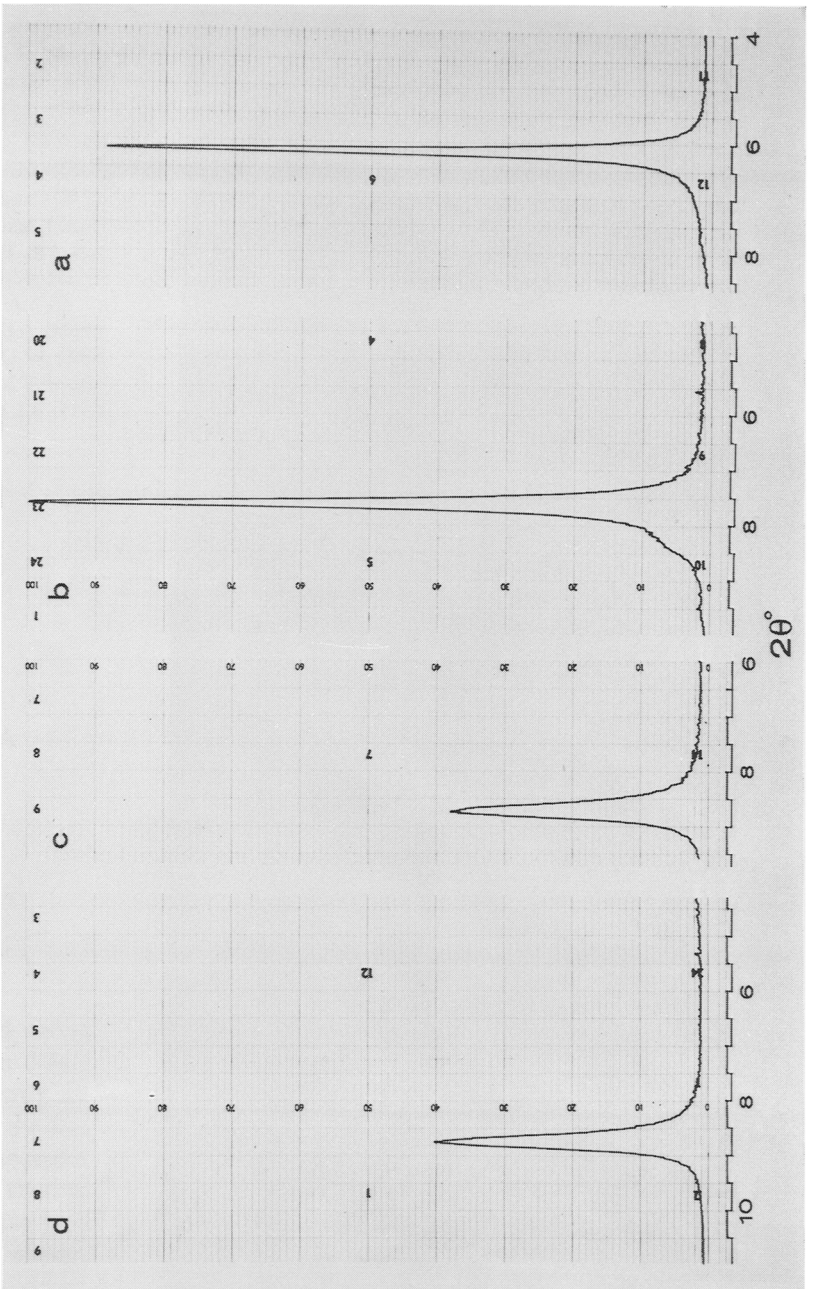
where S is the distance between the specimen surface plane and the reference plane, and R is the radius of the goniometer (Wilson, 1950). For unheated specimens an internal standard can be used for correction, but because of changes in spacings caused by thermal expansion, it is difficult to use internal standards to correct the observed 2θ values of heated specimens. For both unheated and heated specimens of the kind described here, a correction can be made conveniently for routine work by measuring the thickness of the slip + clay film with a micrometer and reading the corresponding $\Delta 2\theta$ from a graph or table.

USE FOR CLAY STUDIES

Plate 1 gives examples of diffractometer patterns made using the heating stage. The sample was a Mg-vermiculite, AP3, c.e.c. = 190 meq/100 g, prepared by Newman (1967) by removing potassium from phlogopite. The sample was heated to various temperatures on the heating stage and chart recordings made of the first order basal reflection at each temperature. At room temperature (Plate 1a), the reflection has $2\theta = 6{\cdot}17°$, $d = 14{\cdot}3$ Å corresponding to the two-layer water 14·36 Å phase of Walker (1961). Heating at 100°C for 20 min produces the one-layer water phase $d = 11{\cdot}59$ Å (Plate 1b) and heating to 265°C, the maximum attainable temperature, for 30 min gives a spacing of 10·1 Å (Plate 1c). Further heating at 265°C for 2·5 hr causes little change in the position of the reflection (Plate 1d). Heating the same sample at 700°C for 4 hr in an electric furnace followed by cooling to almost 250°C and transfer to the heating stage at 265°C, produced a further small collapse giving a spacing of 9·9 Å.

In routine analysis of clays, samples are heated on the glass slips in an electric furnace at 300°C and 500°C to collapse expanding minerals and destroy kaolinite. The heating stage is then used to prevent rehydration during X-ray examination.

PLATE 1



Diffractometer traces of basal reflections of Mg-saturated vermiculite AP3 held at various temperatures on the heated stage. (a) specimen at 20°C; (b) specimen at 100°C for 20 min; (c) specimen at 265°C for 30 min; (d) specimen at 265°C for 2·5 hr.

General conditions. Specimen: a slurry of vermiculite in water was dried to give a very thin oriented film, which with the glass slip measured 40 × 10 × 1·27 mm. Tube: CuK radiation, 40 kV, 20 mA. Goniometer: scan speed 1°/min, divergence slit 1/4°, receiving slit 0·1 mm, anti-scatter slit 1°, 0·178 mm Ni filter. Proportional counter: full scale deflection (a) 1 × 10^4 c.p.s., (b), (c), (d) 4 × 10^3 c.p.s. Chart speed: 1200 mm/hr.

(*Facing p.* 412)

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APPENDIX

A JIG FOR CUTTING GLASS SLIPS USED IN X-RAY DIFFRACTOMETRY OF CLAYS

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As noted above, the specimens for X-ray diffractometry were formed by drying a slurry on 3·81 × 1·27 × 0·12 cm (1·5 × 0·5 × 0·5 in.) glass slips. These slips are conveniently made by cutting standard 7·62 × 3·81 cm (3 × 1·5 in.) microscope slides in the jig in Fig. A5. Slides 0·127 cm (0·05 in.) thick are selected, placed in the jig, and scored with a standard laboratory tungsten carbide glass knife which has had its point sharpened to subtend an angle of not more than 30°. A laboratory diamond glass knife is unsatisfactory for this purpose as slivers of glass catch under the diamond mount and give a jagged cut that breaks unevenly.

The slide is placed in the slot (Fig. A5) in the body (A) and under the bridge (B), and pushed against the stop of the head (C) which has first been adjusted to give the correct breadth of slip. The glass is scored using B as a straight edge and the slip broken along the score by depressing C.

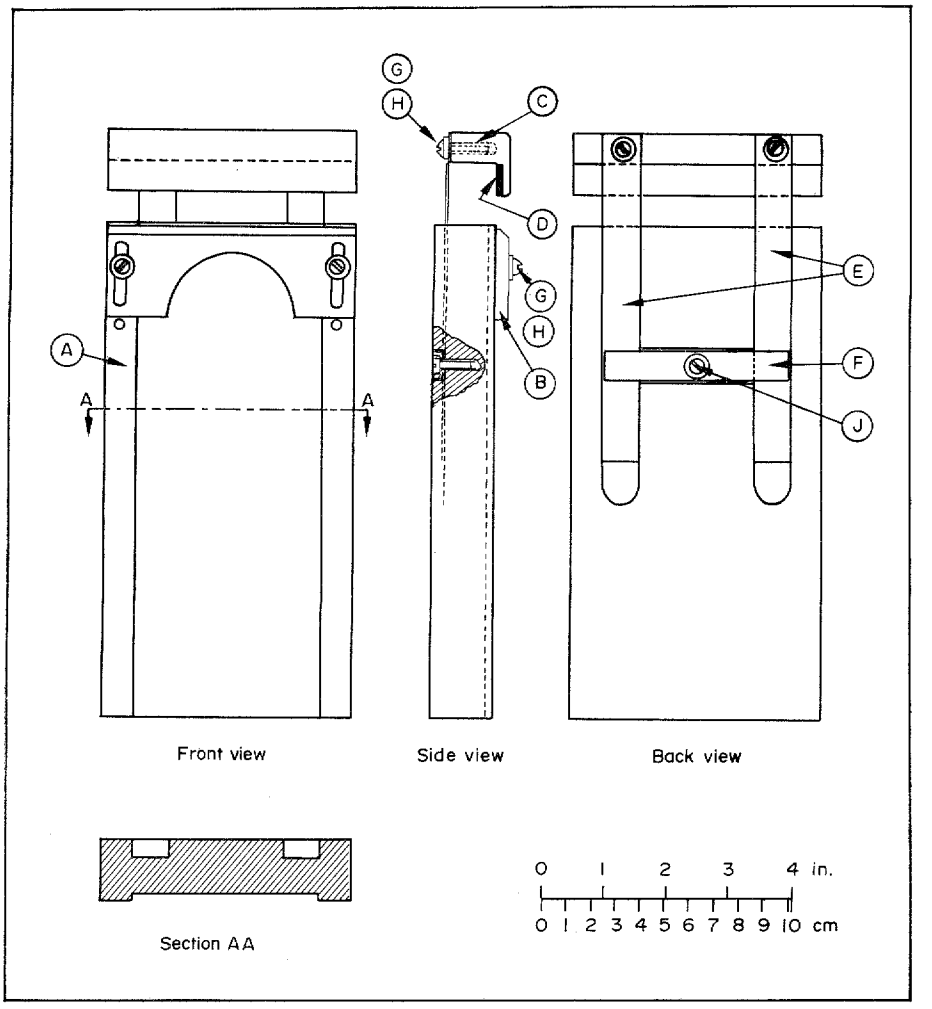

FIG. A5. Details of construction. A. Body, aluminium; B. Bridge, mild steel, cadmium plated; C. Head, aluminium; D. Pad, rubber; E. Springs, 0·290″ × 0·012″ tempered spring steel; F. Clamp, $\frac{1}{4}$″ × $\frac{1}{8}$″ mild steel, cadmium plated; G. Screws, 6 BA × $\frac{3}{8}$″ RD. HD., brass; H. Washers, 6 BA brass; J. Screw, 6 BA × $\frac{3}{8}$″ CH. HD., brass.