The effect of ultra-violet irradiation on the hydroxide absorption band in potassium bromide crystals at room temperature
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THE EFFECT OF ULTRA-VIOLET IRRADIATION
ON THE HYDROXIDE ABSORPTION BAND
IN POTASSIUM BROMIDE CRYSTALS AT ROOM TEMPERATURE

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ABSTRACT

Potassium bromide crystals with varying amounts of hydroxide impurity

were irradiated with ultra-violet light of wavelength 225 mμ. No coloura-

tion was observed in pure crystals. The density of colouration produced

in impure crystals was approximately proportional to the hydroxide con-

centration. A bolometer was used to measure absolute light intensities.

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ABSORPTION BAND IN POTASSIUM BROMIDE CRYSTALS AT ROOM TEMPERATURE*

- H.A. Pearse and J. Rolfe -

INTRODUCTION

If alkali halide crystals are irradiated with short wavelength ultra-violet light, they become coloured through the formation of F-centres within the crystals. This phenomenon was first discovered by Goldstein [1] in 1896, but the first quantitative experiments were not made until 1930 by Smakula [2]. Smakula found that at the beginning of irradiation every quantum of ultra-violet light absorbed in the crystal produced one F-centre, but that the quantum yield decreased to a very small value on further irradiation.

It has been known for many years that the number of F-centres formed by ultra-violet irradiation is strongly dependent on the purity of the crystals, the purest crystals being least coloured. Indeed, Rexer [3] stated that some natural rock salt crystals could not be coloured at all by ultra-violet irradiation. Smakula intended his results to be typical of the purest crystals; however, it is now known [4] that all synthetic alkali-halide crystals contain hydroxide ions as impurities, unless extreme care is taken in drying the material used for crystal growing.

The present investigation of the effect of irradiation in the hydroxide band was undertaken as a first step in determining the properties of pure alkali halide crystals. Potassium bromide crystals were used in all the experiments because the hydroxide absorption band lies at a convenient wavelength (215 mμ), and because crystals with various concentrations of hydroxide were available.

Originally, the experiment was scheduled to take the following course: (i) to find qualitatively the effect of irradiation in the hydroxide band, without determining the energy of the ultra-violet light used, (ii) to measure the absolute intensity of the ultra-violet light in units of quanta sec^{-1} cm^{-2}, and (iii) to repeat the first part of the experiment using ultra-violet light of known intensity, so that quantum yields could be measured. Owing to lack of time, however, only the first two parts of the experiment were carried out.

ENERGY DISTRIBUTION OF ULTRA-VIOLET LIGHT SOURCES

In order to find the most intense source of light in the wavelength region 200 - 240 mμ, the energy distribution with wavelength of a number of ultra-violet light

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* This report describes experimental work carried out during the summer of 1958 by Miss H.A. Pearse under the direction of Dr. J. Rolfe.

sources was investigated. A Bausch and Lomb grating monochromator and an ultra-violet sensitive photocell, type 935, were used for these measurements.

i) Medium Pressure Mercury Arc Lamp — The outer glass envelope was removed from a General Electric A100H4 mercury lamp. The light from the lamp was focussed on the entrance slit of the monochromator by a quartz lens, and another quartz lens placed just outside the exit slit was used to form an image of the diffraction grating. The cathode of the photocell was placed at the grating image. Both slits were set at 1 mm. These experimental conditions were used for all the succeeding measurements. The variation of photocurrent with wavelength is shown in Fig. 1, Curve A.

ii) Hydrogen Discharge Tube — The photocurrent obtained with a Hanovia hydrogen tube, type 71A32, in the region 200-240 $m\mu$ was found to be about 10 times smaller than that obtained from the mercury arc.

iii) Condensed Spark Sources — The radiation from a spark gap working at about 10 kv, with gap lengths of 3 to 4 mm, and a parallel capacity of 0.02 μf, was investigated using various electrode materials. Aluminum, silver, and nichrome electrodes were used, but in all cases the intensity in the range 200-240 $m\mu$ was at least 10 times smaller than that obtained from the mercury arc. This was probably due not to low brightness of the source, as was the case with the hydrogen lamp, but to the small size of the source. The entrance slit of the monochromator could not be filled by the image of the spark gap.

As a result of these measurements, it was decided to use the mercury arc lamp as the source of ultra-violet light.

PRELIMINARY COLOURATION EXPERIMENT

A potassium bromide crystal was put at the position of the grating image of the monochromator, and shielded from extraneous sources of light. Both slits of the monochromator were opened to 10 mm, and the wavelength was set at 215 $m\mu$, the wavelength of maximum absorption of the hydroxide absorption band. It was found that visible colouration of the crystal occurred in about 2 minutes, and that after 15-20 minutes no further colouration occurred. The colouration extended throughout the crystal, but was not uniform across the area of the crystal irradiated. The last result was accounted for by the variation in wavelength across the grating image due to the dispersion of the monochromator (there was a 66 $m\mu$ bandspread across the crystal). The experiment was repeated with the wavelength set at 225 $m\mu$. In this case the colouration was more intense and uniform across the crystal. The fact that maximum colouration was not obtained at 215 $m\mu$ was due to the sharply rising output of the mercury lamp with increasing wavelength. Presumably the product of the energy emitted by the lamp and the absorption coefficient of the crystal reached a maximum at 225 $m\mu$.
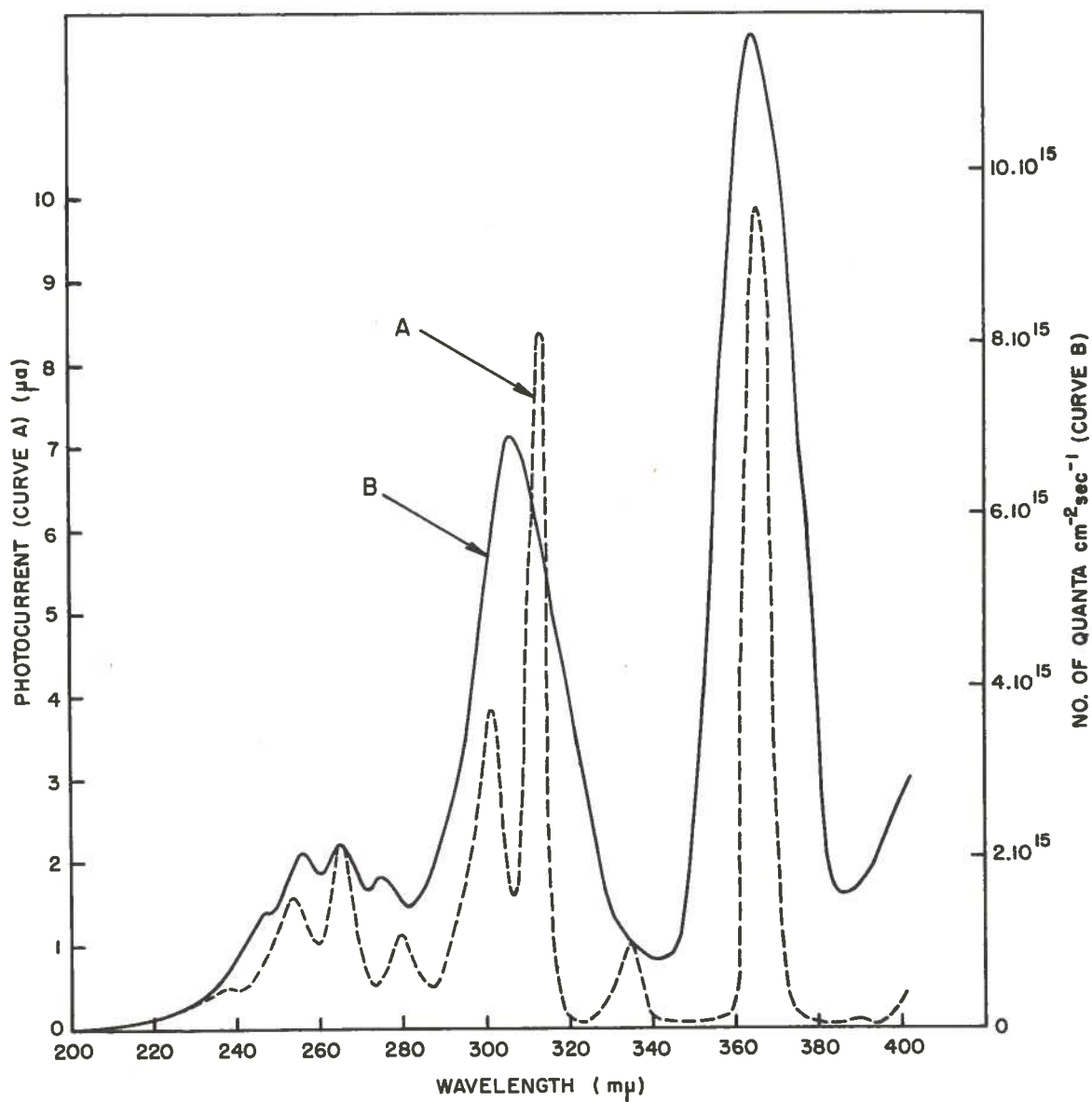
Fig. I Mercury Lamp Spectrum using Monochromator and
A. Photocell (with slits I mm wide)
B. Bolometer (with slits 5 mm wide)

In all subsequent colouration experiments the same experimental conditions were used; both monochromator slits were opened to 10 mm, and the wavelength was set at 225 mμ.

FURTHER COLOURATION EXPERIMENTS

The absorption spectra of the crystals before and after irradiation were determined with a recording spectrophotometer (Perkin-Elmer Spectracord, Model 4000).

i) <u>KBr No. 23</u> — (Starting material carefully dried in vacuum)

This crystal was the purest of the three used, and had a very small absorption at 215 mμ. The colouration produced was so feeble that it could not be measured accurately.

ii) <u>KBr No.31</u> — (Starting material not dried)

The effect of irradiation on this crystal was to bleach the hydroxide absorption band, and to produce an F-band, of maximum absorption at 625 mμ. The absorption in the F-band first increased, reached a maximum after about 15 minutes, and then decreased. The absorption of the hydroxide band first decreased, then stayed constant after about 15 minutes. The results are plotted in Fig. 2.

iii) <u>KBr No. 33</u> — (Potassium hydroxide added)

This crystal had initially a strong absorption band at 215 mμ. The behaviour of the hydroxide band and the F-band on irradiation followed the same course as in crystal No. 31, but the changes in absorption coefficient were larger. The results are also plotted in Fig. 2.

SHAPE OF HYDROXIDE ABSORPTION BAND

Since the hydroxide absorption band overlaps the long wavelength tail of the fundamental absorption band, absorption values for the fundamental absorption band were subtracted from the observed values. In order to find values of fundamental absorption, a KBr + CaBr$_2$ crystal was used, since the addition of calcium has the effect of completely suppressing the hydroxide absorption band. All measured values were first corrected for reflection losses. The results obtained are shown in Fig. 3. Because of the large corrections needed at shorter wavelengths, only the long wavelength part of the absorption curve was used to evaluate the half-width, which was found to be 0.67 ev.

APPROXIMATE CALCULATION OF NUMBER OF CENTRES
PRODUCED OR DESTROYED BY IRRADIATION

From the results obtained above, the approximate number of hydroxide absorbing centres destroyed by irradiation, and the number of F-centres formed by irradia-
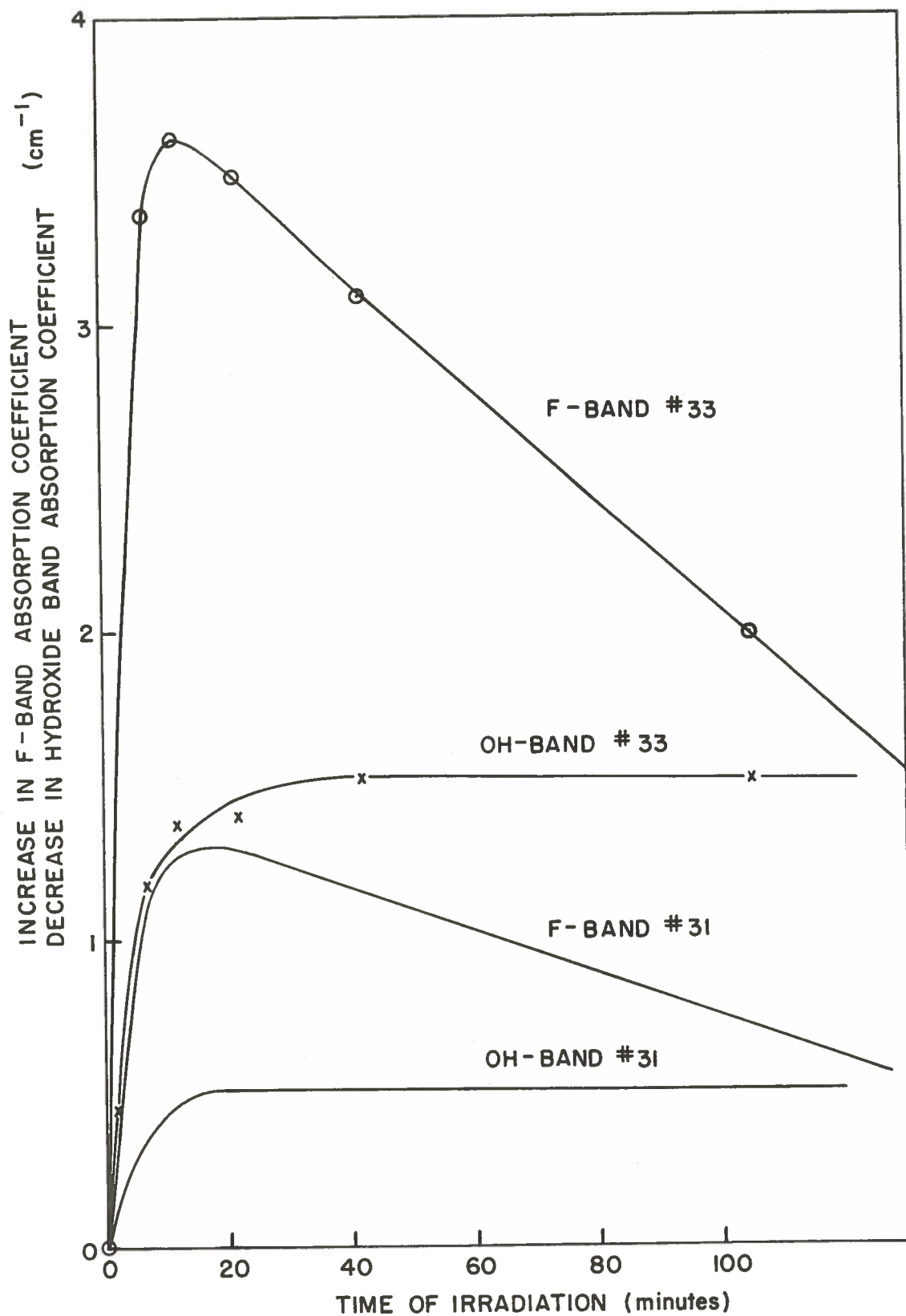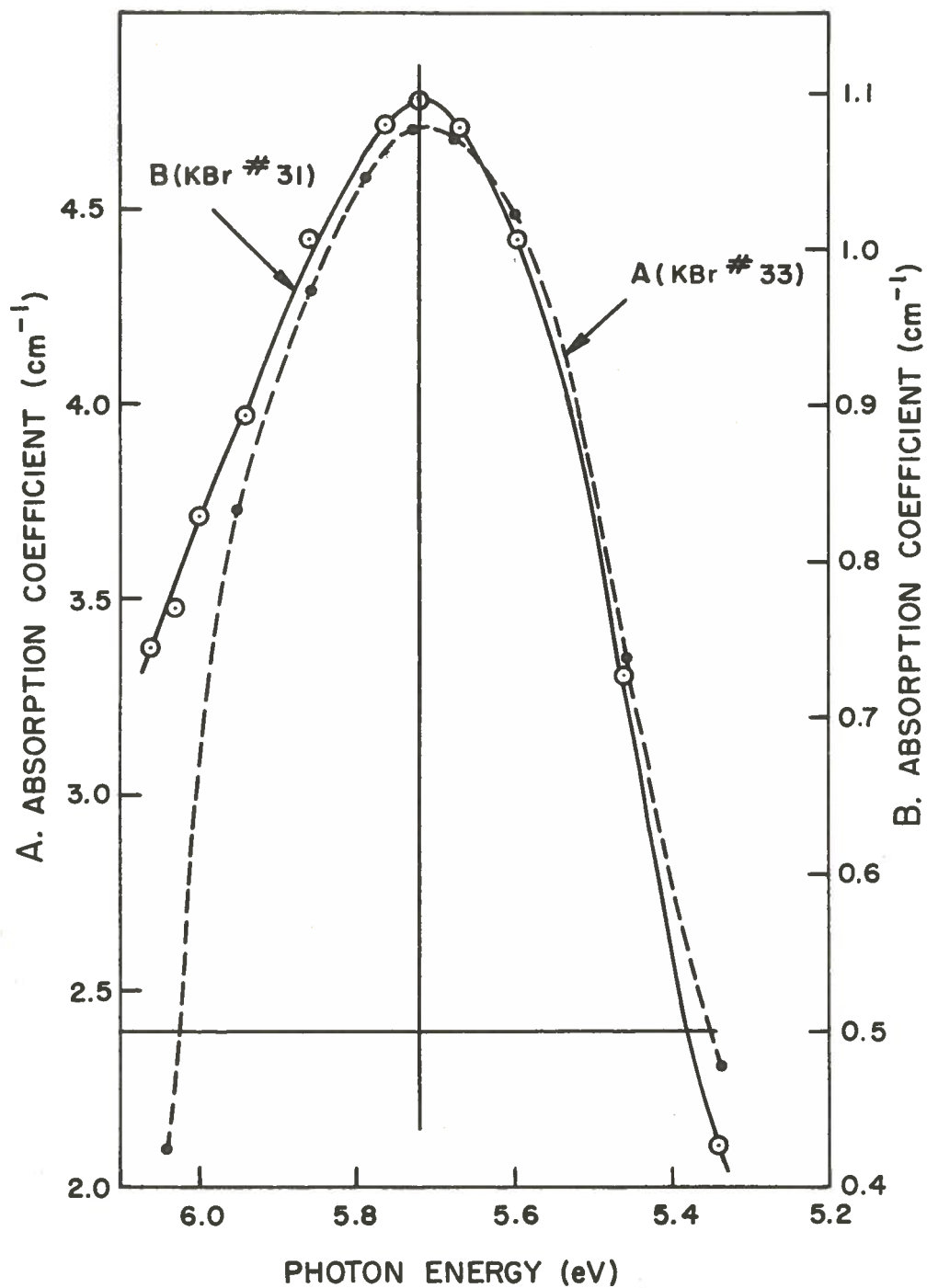
Fig.2 Effect of Irradiation on KBr Crystals #31 and #33

Fig. 3 Hydroxide Absorption Band
Corrected for Fundamental Absorption

tion, can be calculated. If an absorbing centre produces a single absorption band in a crystal, then the concentration of these centres can be calculated from measurements of the half-width and the maximum absorption coefficient of the band produced. The formula used was originally derived by Smakula [5], and is sufficiently accurate for this purpose, but will not be quoted in full here. When the appropriate constants are inserted, together with the measured half-widths, one obtains the following formulae:

$$n_{OH} f_{OH} = 5.24 \times 10^{15} \; \alpha_m \; cm^{-3} \qquad \text{and}$$

$$n_F f_F = 3.38 \times 10^{15} \; \alpha_m \; cm^{-3},$$

where n_{OH} and n_F are the concentrations of hydroxide and F centres, respectively. α_m is the value of the absorption coefficient obtained at the wavelength of the peak of the absorption band, and f_{OH}, f_F are the "oscillator strengths" of the hydroxide and F-centres. The oscillator strengths of absorption centres in alkali halide crystals can be determined only when the concentration of absorbing centres can be measured chemically, after a determination of α_m by an optical experiment. There are theoretical grounds for believing that the value of f should be nearly unity in the case of F-centres in alkali halides, but unfortunately there are at present no experimental values of f_F or f_{OH}. In the following calculations, therefore, the values of f_F and f_{OH} will both be taken as unity.

Table I shows the results of calculations made from the results obtained by irradiation of crystals No. 31 and No. 33.

TABLE I

EFFECT OF IRRADIATION ON CRYSTALS NO. 31 AND 33

	No. 33 (KBr + KOH)	No. 31 (not dried)
Initial hydroxide concentration* (cm^{-3})	26×10^{15}	5.5×10^{15}
Maximum number of hydroxide centres destroyed (cm^{-3})	7.9×10^{15}	2.6×10^{15}
Maximum number of F-centres formed by irradiation (cm^{-3})	12.2×10^{15}	4.2×10^{15}
Ratio: $\dfrac{\text{F-centres formed}}{\text{OH centres destroyed}}$	1.55	1.6

* The hydroxide concentration in dried crystal No. 23 was 0.8×10^{15} cm^{-3}

CHOICE OF DETECTOR FOR ULTRA-VIOLET
ENERGY MEASUREMENTS

No photometric standard sources exist for the ultra-violet region 200-240 mμ. Hence the detector used for measuring the energy of the ultra-violet beam must be calibrated at a different wavelength, and must thus have a known sensitivity characteristic as a function of wavelength. The best detectors in this respect are thermal detectors, which measure the energy falling on a sensitive element from the change in a temperature-dependent property. If the receiving element is perfectly black, the sensitivity is the same for all wavelengths. A thermistor bolometer unit kindly loaned to us by the Defence I Section of this Division fulfilled these requirements.

DESCRIPTION OF THERMISTOR BOLOMETER

The detector and associated electronic equipment were mounted in a portable unit which was originally intended to detect hot joints in overhead power transmission lines. The sensitive element of the bolometer was a semiconducting flake, made from a mixture of the oxides of manganese, cobalt, and nickel, 0.2×2.5 mm in area, and about 10 microns thick. The flake was blackened, and radiation incident on the front surface was converted into heat and detected by measurement of the change in resistance of the flake. An alternating current bridge operating at 1000 cycles per second was used for this purpose, the change in resistance of the flake being compensated by a change of setting of a 10-turn helical potentiometer in another arm of the bridge. Balance was indicated on a cathode-ray oscilloscope.

In the original equipment the bolometer was mounted at the focus of a paraboloidal mirror, so that the radiation from hot joints about 75 feet away would be focussed on the bolometer. It was decided to remove this mirror and allow the radiation to strike the bolometer directly, in order to avoid any corrections due to the change in reflectivity with wavelength of the surface of the mirror. A silver chloride window which covered the bolometer in the original equipment was removed since it was opaque to ultra-violet light.

CALIBRATION OF BOLOMETER

It was originally intended to calibrate the bolometer with a standard tungsten lamp of known colour temperature, but since the infra-red transmission of the lamp envelope was unknown this approach had to be abandoned. A black body radiator whose temperature could be accurately measured with a thermocouple was therefore constructed [6].

A diagram of the black body is shown in Fig. 4. The output of thermocouple (b) was amplified and converted to a 400 cycles per second signal by a transistor
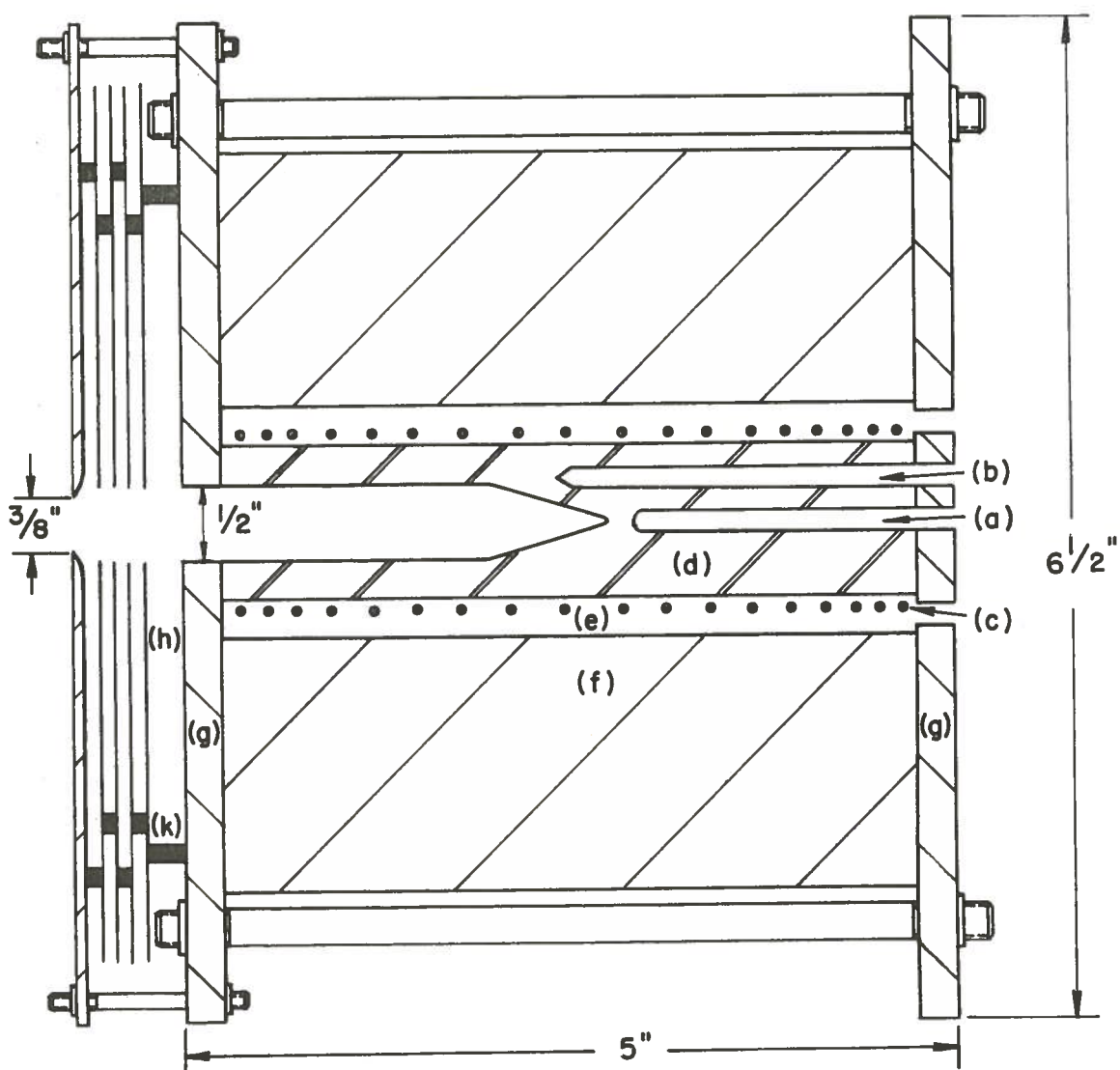
Fig. 4 Black-Body Radiator for Calibrating Bolometer

(a) Thermocouple (chromel-alumel) for temperature measurement
(b) Thermocouple (chromel-alumel) for temperature control
(c) Heating coils, asbestos-covered Chromel A, no. 24 gauge.
(d) Graphite block——cylinder, 1" dia.
(e) Asbestos cement
(f) Firebrick
(g) Transite
(h) Radiation shields, aluminum sheet
(k) Ceramic spacers

circuit. This signal controlled the current input to the furnace by means of a thy-ratron circuit [7]. When the bolometer was 19 cm away from the $\frac{3}{8}$-inch-diameter aperture, a calculation showed that all lines drawn from the bolometer through the aperture passed inside the $\frac{1}{2}$-inch-diameter hole in the graphite cylinder. The $\frac{3}{8}$-inch-diameter aperture can therefore be regarded as a source of black-body radiation at the temperature of the graphite cylinder, and the energy falling on the detector per second is thus:

$$E = \frac{\sigma (T^4 - T_0^4) A_1 A_2}{\pi d^2} ,$$

where E = energy in ergs, σ = Stefan's constant, 5.70×10^{-5} ergs cm^{-2} sec^{-1} deg^{-4}

T = temperature of the black body (°K)

T_0 = temperature of the surroundings (°K)

A_1 = area of source (area of front aperture) in cm^2

A_2 = area of detector, in cm^2

and   d = distance between aperture and detector, in cm.

The bolometer was calibrated by finding the change in resistance necessary to rebalance the bridge when the bolometer element was irradiated by black-body radiation of a known temperature. Four steady temperatures between 350 and 500°C were used, and an average value calculated for the sensitivity. This was 0.48 ohms μwatt^{-1} cm^2.

ULTRA-VIOLET ENERGY MEASUREMENTS WITH THE BOLOMETER

In all colouration experiments the crystals were placed 2 inches from the exit slit of the monochromator, at the grating image formed by the exit slit lens. However, it was not possible to measure the energy directly at this position, because the bolometer could not be removed from the tube and mount which originally held it at the focus of the paraboloidal mirror. In this mounting, the bolometer element could not be placed nearer than 7 inches from the exit slit. The exit slit lens was, therefore, moved away from the monochromator until an image of the slit was formed on the bolometer, and a mount was made to hold the lens in this position. The energy spectrum of the mercury lamp was measured using this arrangement, and is plotted as curve B in Fig. 1.

The photocell was used in conjunction with the bolometer to estimate the energy incident on the crystals in the colouration experiments. The following measurements were taken with the wavelength set at 225 mμ:

i) With slits opened 5 mm, the energy at the slit image was measured with the bolometer.

ii) Under the same conditions, the photocell current was measured.

iii) With the slits opened 10 mm, the photocell current at the grating image was measured.

With the wavelength set at 546 mμ, the areas of the grating image and the slit image were measured. The bolometer element area was smaller than both the image areas, and the photocathode of the photocell was larger than either area. The number of quanta at the grating image was calculated from these measurements, and was found to be 10^{15} cm^{-2} sec^{-1}. The quantum efficiency for the formation of F-centres in crystal No. 33 by irradiation in the hydroxide band was found to be 0.01. This very low figure has two possible explanations: (i) that the oscillator strength of the hydroxide band is small, or (ii) that after 2 minutes, the shortest irradiation time, the quantum efficiency had already decreased considerably from its initial value.

EXPERIMENTS PLANNED FOR THE FUTURE

In the present experiments we have established satisfactory experimental procedures for ultra-violet colouration of potassium bromide crystals, and for measurement of the number of quanta in the ultra-violet light used for irradiation. We have also shown that the amount of colouration is proportional to the hydroxide ion concentration in the crystal. Some information, however, is still lacking; in particular, values of the quantum efficiency at all stages of the irradiation process. A new bolometer apparatus is being designed which will enable the intensity of the irradiating light to be measured while the crystal is being irradiated. This will enable the quantum efficiency to be determined at all stages.

The bleaching of F-centres which occurs in the later stages of irradiation may be an effect dependent on the intensity of irradiating light, or a thermal bleaching process, which should take place at constant velocity regardless of the irradiation intensity. This question will be resolved by irradiation experiments in which the intensity of the ultra-violet light is varied. The effect of irradiation in the fundamental absorption band will also be studied. Finally, the whole experiment may be repeated at different temperatures, using alkali halide crystals other than potassium bromide.

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