JOURNAL OF MATERIALS SCIENCE 7 (1972) 7–13

Quantitative Analysis of Boron in Solids by Autoradiography

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A non-destructive method of quantitative analysis for boron is described. The method, which depends on the use of a plastic film to record tracks from the $^{10}B(n, \alpha)^{7}Li$ reaction, is in general applicable to any solid material but is here described in detail for the analysis of ferrous alloys. Boron contents from 1 ppm to 10% may be determined, and the technique may be applied also to microanalysis of individual features such as precipitates and grain-boundaries in the metal structure.

1. Introduction

For some years there has been considerable interest in the effect of boron on the properties of metals and alloys. The quantities involved are commonly very small (overall concentrations rarely exceed 100 ppm by weight) and a simple method of analysing boron at these levels is desirable.

There are many methods reported in the literature for the quantitative analysis of boron in various materials; comprehensive reviews have been published by Lerner and Rynasiewicz [1] and by Nemodruk and Karalova [2]. Virtually all these methods employ classical methods of chemical analysis, the most important being titrimetric and colorimetric. Few have a sensitivity of better than 5 ppm (though with care 1 ppm can be achieved in some cases) and all have several disadvantages in common. They are tedious and time consuming, require blank runs for low-level determinations because of boron present as an impurity in the reagents used, and involve the destruction of the sample. A few nuclear methods have been reported, measuring either the attenuation of a neutron flux due to the $^{10}B(n, \alpha)$ reaction or the quantity of helium produced in this reaction [3]. Again these involve destruction of the sample.

In view of the difficulties involved in these techniques, it was felt that there was a need for a simple, rapid, non-destructive technique for the analysis of boron in various materials down to the part-per-million level. The autoradiographic method developed by Hughes and Rogers [4] for determining the spatial distribution of boron in solids has been extended, therefore, to permit the quantitative determination of boron down to 1 ppm. More limited experiments utilising the same principle have been reported recently by Loveridge and McInnes [5] and Chrenko [6]. This method has the advantage of being non-destructive and, as only about one atom in 10^{7} of the boron present in the sample undergoes fission during any one experiment, the analysis may be performed many times if required. The specimen need only be a few millimetres square, although when necessary, specimens up to 20 cm square have been examined.

The technique used is similar in many respects to that reported in [4], the fission products resulting from the nuclear reaction of the ^{10}B isotope with thermal neutrons being recorded by means of a plastic film. As in [4], the detector used is cellulose aceto-butyrate (CAB). The major difference between the two techniques is that while for high-resolution autoradiography the film must be in intimate contact with the sample, for quantitative work the film is spaced off from the sample thereby achieving a deliberate loss of resolution. The distance between the film and the sample may be varied to suit the particular problem. For example, close contact enables the boron concentration within metal grains or between boron-rich inclusions to be measured while a slightly greater spacing allows assessment of segregation to precipitates or grain-boundaries. A large spacing, by averaging the contribution from different areas, enables the overall boron content of the sample to be measured. Micrographs of typical results obtained at the two extremes of spacing are shown in fig. 1. The present work is concerned only with overall boron analyses and work on the quantitative aspects of boron segregation will be reported in a subsequent publication.

2. Procedure

2.1. Sample Preparation

The specimen, which typically will be about 6 mm square, is mounted in Bakelite and ground to a reasonably good surface finish, e.g. 0000 grade silicon carbide or 25 μm diamond. In practice, it is normally polished to metallographic standards because high-resolution autoradiographs will be taken from it subsequently, but this is not essential for purely quantitative analysis. A piece of polythene sheet up to 0.5 mm thick and punched with 2 mm diameter holes is then placed over the specimen and secured at the edges with a pressure sensitive adhesive tape, e.g. Sellotape. The polythene, which has been shown in trial autoradiographs to have a very low boron content (< 0.5 ppm), acts as both mask and spacer allowing α-particles to travel only through the holes. Over this mask, and again secured at the edges with Sellotape, is placed the film which has been prepared as described below.

Because both Bakelite and Sellotape contain appreciable quantities of boron, it is essential that the holes in the polythene mask should be located at least 1 mm inside the edges of the specimen and a similar distance from any Sellotape. The arrangement is illustrated in fig. 2.

As reported in [4], the ability of the CAB film to register tracks depends on the heat-treatment which it has received. In this work it is necessary to heat-treat the film on the glass-slide on which it was prepared. The best treatment has been found to be 16h at 145° C, after which the film may readily be cut into squares, lifted from the slide and placed over the specimen and mask. Provided the glass slide is carefully pre-cleaned [4], boron pick-up at this stage is negligible.

The complete assembly is now placed in a polythene capsule and irradiated to a known dose in a thermal neutron flux as described in section 2.3. After irradiation, the film is separated from the specimen and mask and etched for 25 min at 50% KOH at 50°C. The film is then washed in distilled water, dried and mounted on a microscope slide for optical examination. The use of a phase-contrast microscope renders the tracks more easily visible. In order to determine track densities, the eyepiece of the microscope

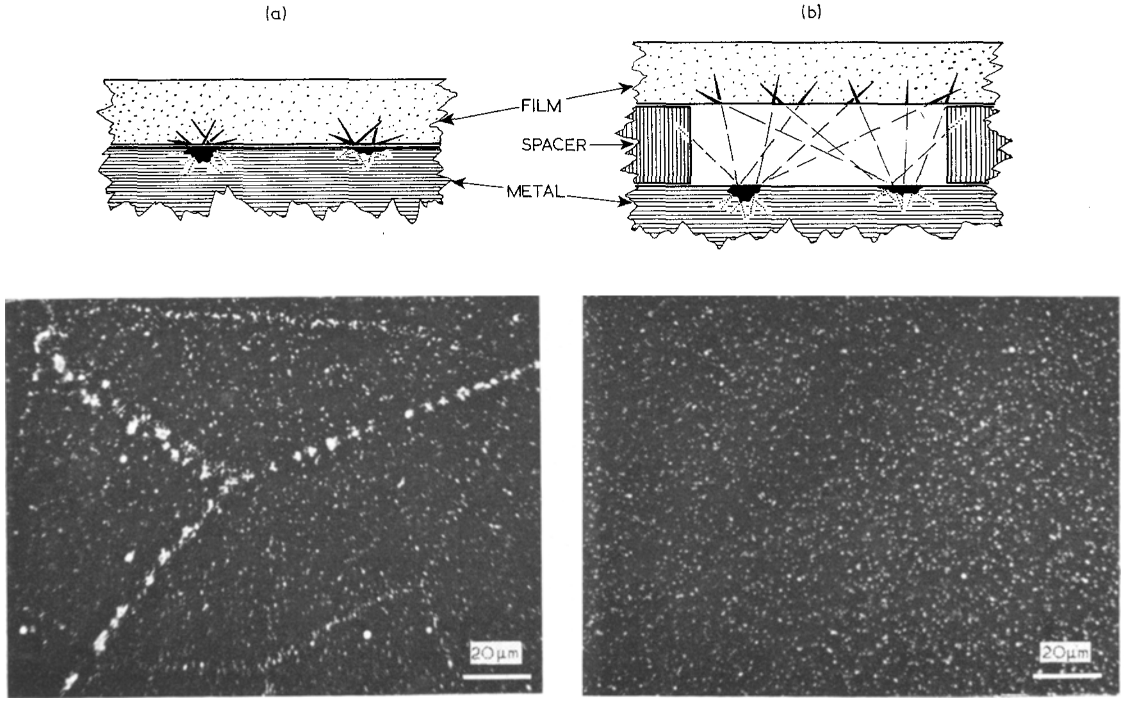

Figure 1 The location of tracks from boron-rich particles with different arrangements of sample and film (not to scale) together with typical autoradiographs; (a) contact, (b) spaced.

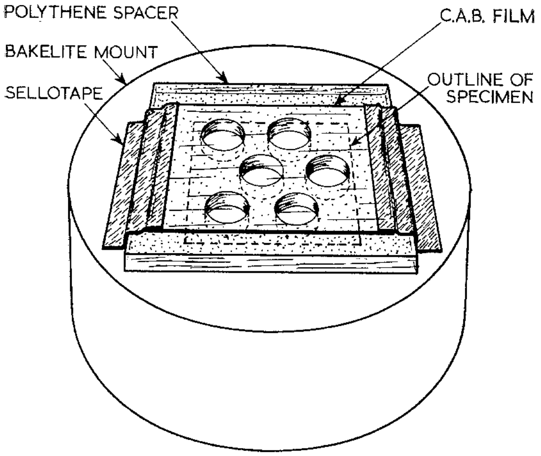

Figure 2 Arrangement of specimen assembly for overall boron analysis.

has been fitted with a graticule which gives an image of a 10 μm square grating coincident with the film surface when the magnification of the microscope is 600 ×. The track density is determined by optical counting, a mean being taken of at least six determinations from different areas of the specimen surface. Measurements are taken near the centre of each 2 mm diameter circle of tracks as the density near the edge of the circle decreases due to the masking effect of the polythene spacer. It has been found experimentally that within the limits of counting accuracy the track density does not vary over the central 0.7 mm diameter region.

It is necessary to subtract a background count from the figure obtained, and this can often be estimated from an area of the film shielded from the sample by the polythene spacer. For accurate work, however, the background is obtained by mounting a piece of zone-refined silicon in the same mount as the specimen and covering both silicon and specimen with the same piece of film. The background normally contributes about 10% of the observed track density which, as described in section 2.3 is usually regulated to approx. 10 tracks per 100 μm^2. The chief cause of this background is chemical pitting of the film, though at high neutron doses a contribution arises from boron contamination and stray irradiation damage. This results in a decrease in accuracy near the limits of sensitivity of the method.

From the net track density obtained in this way, and knowing the neutron dose given to the sample, the overall boron concentration in the sample may be calculated.

2.2. Calibration

For accurate results, it is necessary that the track density in the film lies within certain limits. If it is too low, the errors arising from spurious chemical etching effects in the film become significant, while if it is too high tracks begin to merge and overlap. It has been found in practice that the track density should lie between 5 and 20 tracks per 100 μm^2 (although densities up to 50 are permissible for approximate work), with the optimum value at 10 tracks per 100 μm^2 (i.e. 10^7 tracks cm^{-2}).

Provided these limits are not exceeded it is found that the thermal neutron dose required is inversely proportional to the boron concentration. The linearity of this relationship has been tested over nearly five orders of magnitude using a large number of iron and steel samples with boron contents (from subsequent chemical analysis) ranging from 2 ppm to 4%. (Unless otherwise stated, all concentrations in this paper are expressed as weight fractions.) In order to calibrate the technique, the neutron dose for each sample (normalised where necessary to a track density of 10 tracks per 100 μm^2) was plotted against boron concentration. From the slope of this line it was established that

$$\phi . c_b = 7.6 \pm 0.4 \times 10^{14} \qquad (1)$$

for boron in iron and steel, where ϕ = thermal neutron dose (n.cm^{-2}) and c_b = concentration of boron in ppm by weight.

It must be emphasised that while a similar relationship will hold for the analysis of boron in any material, the proportionality constant is a function of the range of the α-particle in that material and will in general be different from that obtained above. In view of the errors inherent in calculating the ranges of α-particles of these energies (see below), it will in general be necessary to carry out calibration experiments for accurate analyses of materials other than iron-base alloys. This comment applies also to large (> 5 μm) non-metallic inclusions in ferrous alloys.

2.3. Irradiation

In order to carry out quantitative analysis it is necessary to know approximately (within a factor of 5) the boron content of the sample. In many cases this will already be known with sufficient accuracy for this purpose, but if not it may quickly be established by a short series of trial irradiations. Once an approximate value is established, the thermal neutron dose required to give 10 tracks per 100 μm may be calculated from equation (1).

At Harwell, irradiations are carried out in a specially designed rig in the DIDO reactor. Within this rig the specimen may be placed for a known time in a thermal neutron flux which can be varied over three orders of magnitude. The flux at any point in this rig has been calibrated and may be predicted to within 15% (this being due largely to power variations within the reactor). When higher accuracy is required, the dose is monitored using gold foils of a standard size. In this way, the uncertainty on the dose is reduced to below 2%.

2.4. Limits of the Method

The overall accuracy of the method is limited by the errors inherent in optical track density determinations. It has been found experimentally that provided at least 1000 tracks are counted the best accuracy obtainable is $\pm$ 10% for concentrations of boron greater than 30 ppm. The errors increase at lower levels of boron (due to the increasing background at higher neutron doses) through $\pm$ 20% at 10 ppm to $\pm$ 70% at 1 ppm which is close to the limit of sensitivity of the method.

Apart from fissionable elements giving a high fission-track density, lithium is the only element which can interfere with the analysis. This occurs via the ${}_3{}^6\mathrm{Li}(\mathrm{n}, \alpha){}_1{}^3\mathrm{H}$ reaction. The cross-sections of natural boron and natural lithium for (n, α) reaction are 750 and 70 barns respectively. The sensitivity of the reaction for lithium is therefore at least a factor of ten (depending on film sensitivity and particle range) down on that for boron. In any case, it is rare for ferrous alloys to contain significant quantities of lithium, though the point should be borne in mind when extending the technique to analysis of other materials, e.g. ceramics and geological specimens.

3. Theory

It has been shown that both particles emitted in the ${}^{10}\mathrm{B}(\mathrm{n}, \alpha){}^7\mathrm{Li}$ reaction are capable of producing tracks in CAB film and, once formed, these tracks are indistinguishable by the present technique [7]. When the compound nucleus undergoes fission, however, the two fragments travel on reciprocal courses and therefore only one particle will travel towards the detector for each event. Furthermore, tracks can only be recorded from events which occur at a depth below the surface not exceeding the range of the particle in the metal. Hence the technique examines a layer of material of depth equal to the range of the particle. The ranges of the particles are discussed below.

In order to predict the total number of tracks which will be observed in the film it is necessary to calculate the fraction of particles which will penetrate the film sufficiently deeply to give rise to a track of appreciable projected length when viewed normal to the surface. This is derived for the general case in the appendix (section 5), and the results expressed graphically in fig. 4.

Though the final results are indistinguishable, it is convenient to consider separately those events which give rise to an α-particle penetrating the film and those giving rise to a Li-particle. The observed track density in the film will be given by

$$\rho_t = K \phi \sigma N C_a r$$

where ρ_t = track density (cm^{-2}), K is the geometrical factor (see appendix), ϕ = total thermal neutron dose (n.cm^{-2}), σ = capture cross-section for natural boron (cm^2), N = no. of atoms per unit volume of specimen (cm^{-3}), C_a = atom fraction of boron atoms, and r = range of the emitted particle in the metal. Considering the α- and Li-particles separately, this becomes

$$\rho_t = \phi \sigma N C_a (K_\alpha r_\alpha + K_{\mathrm{Li}} r_{\mathrm{Li}}) \qquad (2)$$

In order to evaluate this equation, it is necessary to obtain values for the ranges of the particles in the metal and in the film. Unfortunately it is difficult to calculate these ranges accurately because of the relatively low energies involved in the reaction [8]:

$$ {}_5{}^{10}\mathrm{B} + {}_0{}^1\mathrm{n} \left[\begin{array}{l} 93.7\% \rightarrow {}_3{}^7\mathrm{Li}^* (0.83\ \mathrm{MeV}) \\ \qquad\qquad + {}_2{}^4\mathrm{He}(1.48\ \mathrm{MeV}) \\ 6.3\% \rightarrow {}_3{}^7\mathrm{Li}(1.01\ \mathrm{MeV}) \\ \qquad\qquad + {}_2{}^4\mathrm{He}(1.79\ \mathrm{MeV}) \end{array} \right. $$

The semi-empirical equations developed for calculating ranges of heavy particles begin to fail at energies below about 2 MeV. For example, Friedlander and Kennedy [9, 10] give two such equations which allow a comparison of ranges for a particle of mass M and energy E in air and in a medium of atomic no. Z, atomic weight A, and density ρ:

$$\text{(i)}\quad R_{\text{z}} = R_{\text{air}}\left\{1.52 \times 10^{-4} \cdot \frac{A}{\rho} \cdot \frac{\sqrt{Z+10}}{Z}\right\}$$

(units of length)

$$\text{(ii)}\quad R_{\text{z}} = R_{\text{air}}\left\{0.90 + 0.0275\,Z + (0.06 - 0.0086\,Z)\log\frac{E}{M}\right\}$$

(units of mass per unit area)

(iii) Ranges of α-particles in different materials may be derived also from tabulated values of relative stopping powers of different elements together with the Bragg "$A^{-\frac{1}{2}}$" Law [11].

The ranges in different materials of the 1.48 and 1.79 MeV α-particles from the boron reaction have been calculated using these methods in conjunction with the known range of these particles in air (0.73 and 0.88 cm respectively) [11]. The results are listed in table 1, where they are compared with the ranges inferred from the size of damage regions observed in the electron microscope around boron-rich particles in irradiated specimens of these materials. From these figures, it appears that method (iii) is the most reliable. For the purposes of this work, therefore, a mean value of 2.4 μm has been assumed for the range of these α-particles in iron and steel. Similar calculations suggest that the range of the Li-particles is approx. half that of the α-particles in any material. Again this is supported by direct observation [14, 15], and therefore a value of 1.2 μm has been assumed for the range of the Li-particles in iron and steel.

Using the additivity rule for stopping powers of elements [10] the range of α-particles in CAB may be estimated at 4.5 μm. Hence (see appendix).

$$p = \frac{R_{\text{f}}}{R_{\text{m}}} = \frac{4.5}{2.4} = 1.88$$

For the resulting track to be recognisable using an optical phase-contrast microscope, it is found that the projected track length must be $\geqslant 1$ μm.

$$\therefore\ \beta = \frac{1}{p} = 0.53\ \mu\text{m}$$

whence, for α-particles,

$$\frac{\beta}{R_{\text{m}}} = \frac{0.53}{2.4} = 0.22$$

and, for Li-particles,

$$\frac{\beta}{R_{\text{m}}} = \frac{0.53}{1.2} = 0.44$$

Referring to fig. 4, therefore,

$$K_{\alpha} \simeq 0.15\,, \quad K_{\text{Li}} \simeq 0.08$$

In iron and steel, the concentration of boron by weight is 0.2 times the atomic concentration, and hence the concentration in ppm is given by

$$c_{\text{b}} = 0.2 \times 10^{6} \,.\, C_{\text{a}}$$

Assuming that the density of steel $\simeq$ 7.8 gm.cm^{-3} and assigning a mean atomic weight of 55.8,

$$N = \frac{6.02 \times 10^{23} \times 7.8}{55.8} = 8.4 \times 10^{22}\ \text{atom.cm}^{-3}$$

In practice, by controlling the neutron dose, the track density in the film is arranged to be approx. 10 tracks per 100 μm^2, i.e. $\rho_{\text{t}} = 10^{7}$ cm^{-2}. The capture cross-section for natural boron is 750 ± 10 barns, i.e. $\sigma = 7.5 \times 10^{-22}$ cm^2.

Substituting these figures into equation 2 and re-arranging

$$10^{7} = \phi \,.\, c_{\text{b}} \,.\left\{\frac{8.4 \times 10^{22} \times 7.5 \times 10^{-22}}{0.2 \times 10^{-6}}\right\}(0.15 \times 2.4 + 0.08 \times 1.2)\,10^{-4}$$

whence $\phi \,.\, c_{\text{b}} = 7.0 \times 10^{14}$.

The etching efficiency of the plastic film is close to 100% [6, 16] and so, provided the film will

TABLE I

Metal	Particle energy (MeV)	α-particle ranges (μm)				References to experimental work
		Calculated by method			Observed	
		(i)	(ii)	(iii)		
Fe	1.48	1.81	1.90	2.37	2.0 - 2.5	[12, 13]
	1.79	2.18	2.29	2.86		
Ni	1.48	1.61	1.86	2.15	2.2	[14]
	1.79	1.94	2.10	2.60		
Cu	1.48	1.66	1.75	2.23	2.6 ± 0.3	[15]
	1.79	2.00	2.18	2.67		

register all particles which impinge on it, we may expect that the product of the total neutrons dose ϕ, and the boron concentration in ppm, c_b, in ferrous alloys required to give a track density of 10^7 tracks cm^{-2} will be

$$\phi \,.\, c_b = 7.0 \times 10^{14}$$

Experimentally, we find that for iron and steel samples (equation 1)

$$\phi \,.\, c_b = 7.6 \times 10^{14}$$

Too much significance should not be placed on the rather close agreement between these figures in view of the difficulty in obtaining accurate values of the particle ranges, but it does appear that the registration efficiency of the CAB must be fairly high.

4. Conclusion

The registration of particle tracks from neutron-irradiated boron in solid samples (usually ferrous materials) by a plastic detector enables the local or overall boron concentration to be measured over the range 1 ppm to 10% boron. The accuracy is ± 10% down to 30 ppm, ± 20% at 20 ppm, and ± 70% at 1 ppm.

Calculation of theoretical track density gives results close to the measured value, and well within the limits of accuracy of the calculated particle ranges.

The method can be applied either to extended areas for overall boron analysis or to local areas such as individual grains. With a lower degree of accuracy, the amount of boron segregated to precipitates or grain boundaries may also be determined.

5. Appendix. The Geometry of Track Registration

The film is viewed at right angles to the metal surface, hence it is the projected track length which is significant – see fig. 3.

(i) In the simple case, the range of the particle in the film (R_f) equals the range of the particle in the metal (R_m) and the projected track length is given by

$$y = AB \,.\, \sin\theta$$

(ii) In general, however, $R_f = p \,.\, R_m$ hence

$$y' = AB' \,.\, \sin\theta = p \,.\, AB \,.\, \sin\theta$$

Since

$$OA + AB = R_m\,,$$

then

$$OA + \frac{AB'}{p} = R_m\,,$$

or

$$R_m = \frac{x}{\cos\theta} + \frac{y'}{p \,.\, \sin\theta}$$

whence

$$\frac{y'}{p} = \sin\theta \,.\, \left(R_m - \frac{x}{\cos\theta}\right).$$

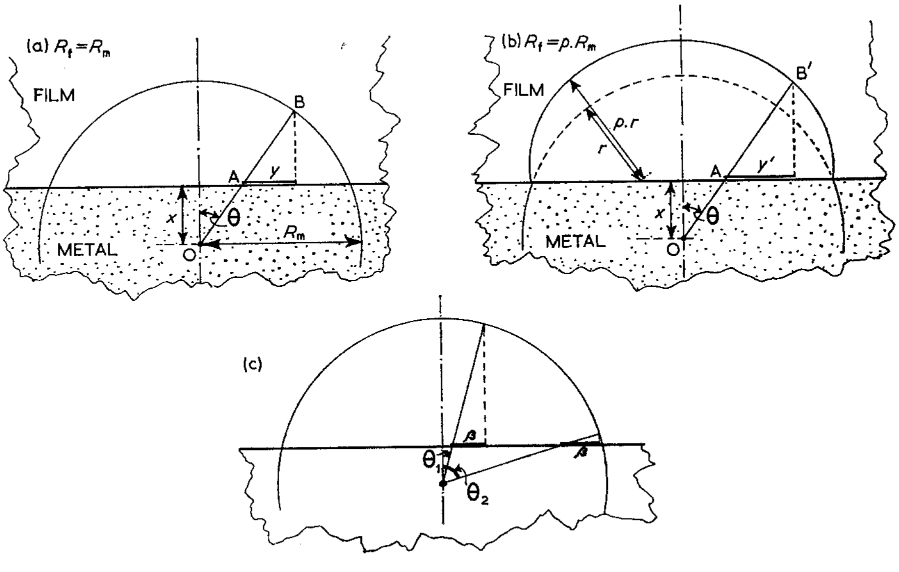

Figure 3.

Values of (y'/p) – in units of R_m – may be plotted as a function of θ for various values of (x/R_m), i.e. the depth of origin as a fraction of particle range, and from this may be interpolated the angular spread of tracks with a projected length (y'/p) greater than any desired critical value β/R_m. For any value of β/R_m there will be two limiting values of θ (see fig. 3c). It can be shown that the fraction of particles emitted with 4π geometry from the point 0 (x/R_m below the surface) and fulfilling this condition is given by

$$F = \tfrac{1}{2}(\cos\theta_1 - \cos\theta_2) .$$

Hence, the total fraction of particles emitted from the layer of depth R_m and giving rise to tracks of projected length $\geqslant \beta/R_m$ is given by

$$K = \int_0^{R_m} F \, . \, \mathrm{d}x$$

This integral may be evaluated graphically from plots of F v. x/R_m as a function of β/R_m, and the resulting curve is given in fig. 4.

K may be interpreted physically as the geometrical factor of track registration.

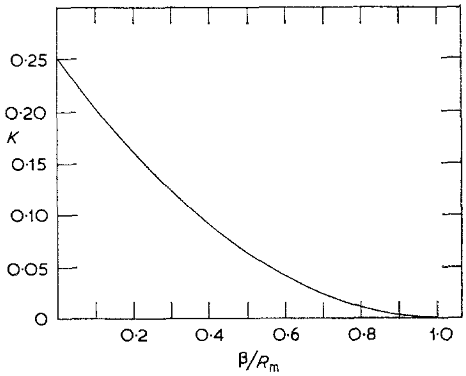

Figure 4 The fraction (K) of all particles emitted from a layer of material of depth R_m which give rise to tracks of projected length $\geqslant \beta$ in a film placed on one face of the sample.

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Received 3 May and accepted 12 July 1971.