PHOTOMULTIPLIERS FOR THE SCINTILLATION COUNTING OF C^{14} AND TRITIUM

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1. The efficiency of a counting assembly for the scintillation assay of compounds tagged with a low energy beta emitter such as C^{14} or H^3, which can be dissolved (or suspended) in a liquid phosphor, is very greatly dependent on the quality of the Photomultiplier tube used. This is illustrated by the bias curves of Fig. 1, which shows the curve given by 10 mμcurie of H^3 in a standard phosphor *, d, the thermionic electron curve from a tube with a standard S-11 cathode, a, and the much more useful performance of tubes made specially for H^3 counting (b & c)

It is the purpose of this paper to consider the steps by which acceptable performance has been achieved, to report on results obtained in various designs of counting head and to outline those areas in which improvement may still be obtained.

2. In a standard * liquid phosphor, the average energy from a tritium disintegration to give a photoelectron from a semitransparent Cs Sb cathode with a phosphor vial designed to give effective light coupling to the cathode, is about 2500 eV, so a large proportion of the disintegrations will give only a single photoelectron and an appreciable proportion (which turns out to be between 30 and 50%, will fail to give a detectable signal. The rate of emission of thermionic electrons from a 2" diameter Photomultiplier tube with a typical S-11 cathode of photosensitivity 70 uA/L, which has a peak quantum efficiency of about 15% at 4200 AU and a red threshold around 6800 AU, is about 30,000 electrons per second at 20°C and about one tenth of this at -20°C.

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* Toluene + 5g/litre p-terphenyl & 16 mg/litre POPOP

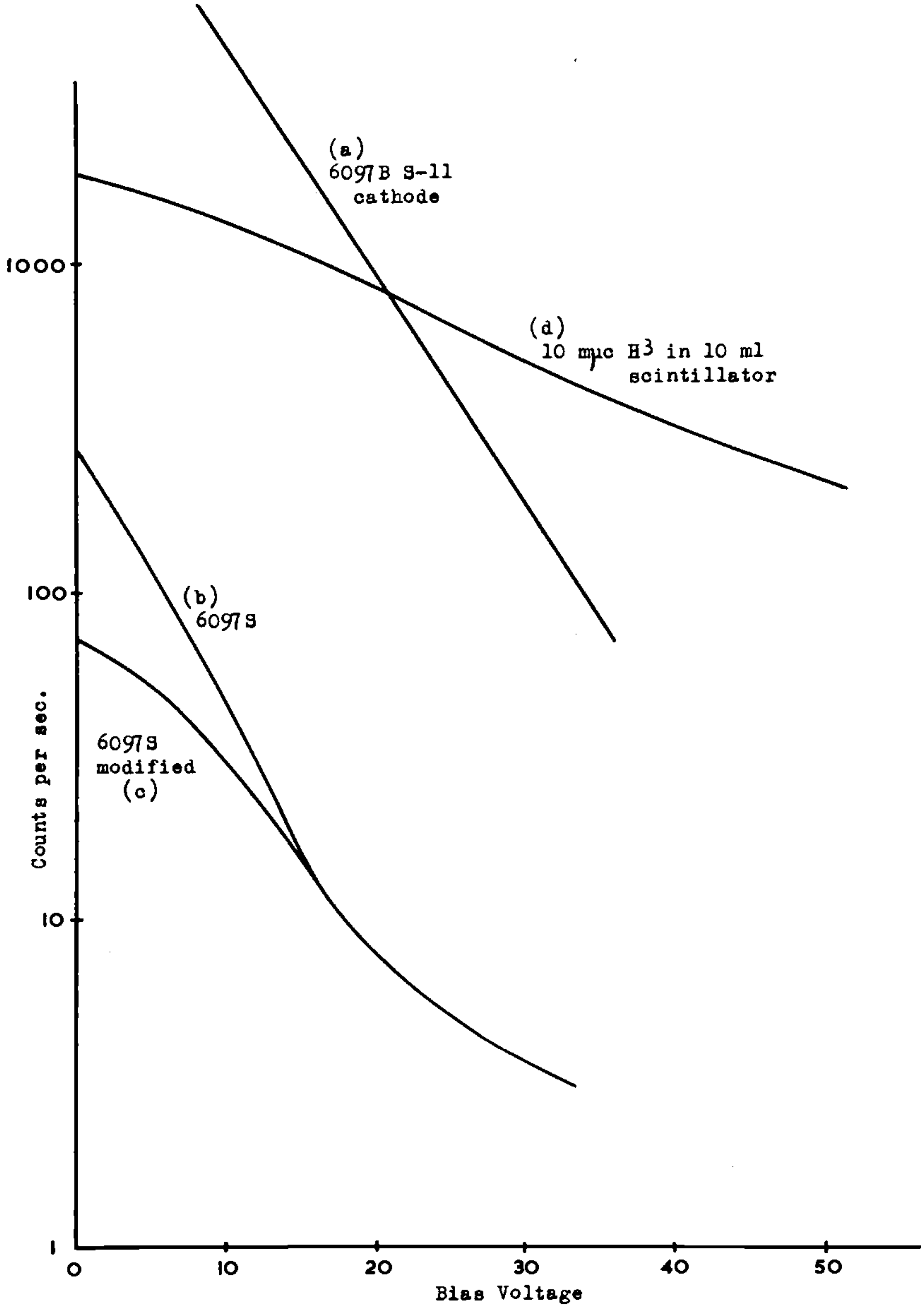


Fig. 1. Bias curves 6097B, 6097S, modified 6097S and 10 mμc H^3 scintillator at 23°C.

If a tube of this type is to be used for tritium counting in a single tube assembly (with which we are at the moment solely concerned) it is obvious that a bias point corresponding to a signal amplitude much greater than one electron must be chosen and the counting efficiency will be relatively low. In fact, for a tube background of 1 count per second at 20°C an efficiency of 0.7% is obtained for a 10 ml sample.

The first step, then, in making a Photomultiplier tube more suitable for tritium counting is to modify the cathode processing to reduce the thermionic emission as much as possible without unduly depressing the quantum efficiency of the cathode in the spectral region of interest, which for most phosphors is between 3500 and 4500 AU. Since the high value of thermionic emission from a standard S-11 cathode is associated with an appreciable sensitivity in the red region of the spectrum, our initial criterion for improvement was a decrease in the ratio of red to blue sensitivity and work along these lines was reported at the 1958 Scintillation Counter conference (1). It was soon found essential, however, to introduce an operational tritium counting test, since neither the red-blue ratio, nor the tube dark current, gave an adequate guide to a tube's performance. This test is carried out in a counting head at room temperature with a sealed 10 ml hemispherical vial containing tritiated toluene phosphor mounted over the tube face, with an interposed shutter assembly (the optical coupling is relatively poor). After an adequate period in the dark (between 1 and 4 hours usually), the tube is adjusted to a standard overall sensitivity and the bias is adjusted until the count rate with the shutter open is an arbitrary figure of 90 counts per second. The shutter is closed and the tube background rate is measured. The tube performance is then expressed as a ratio, e.g. 90/7 and the smaller the background the better the tube. The correlation between the performance rating and the tube dark current is shown in Fig. 2 and at the present time more than half of the 'S' tubes made are rated 90/10 or better, while 15 to 20% are rated 90/5 or better. These latter tubes give efficiencies of 15-17% for a tube background of 180 cpm with a 10 ml sample at 20°C.

3. In order to put the results summarised above into proper perspective in the field of Photomultiplier tubes, it is desirable to consider the characteristics of various dynode structures and their influence on tube background. Three types of dynode structure

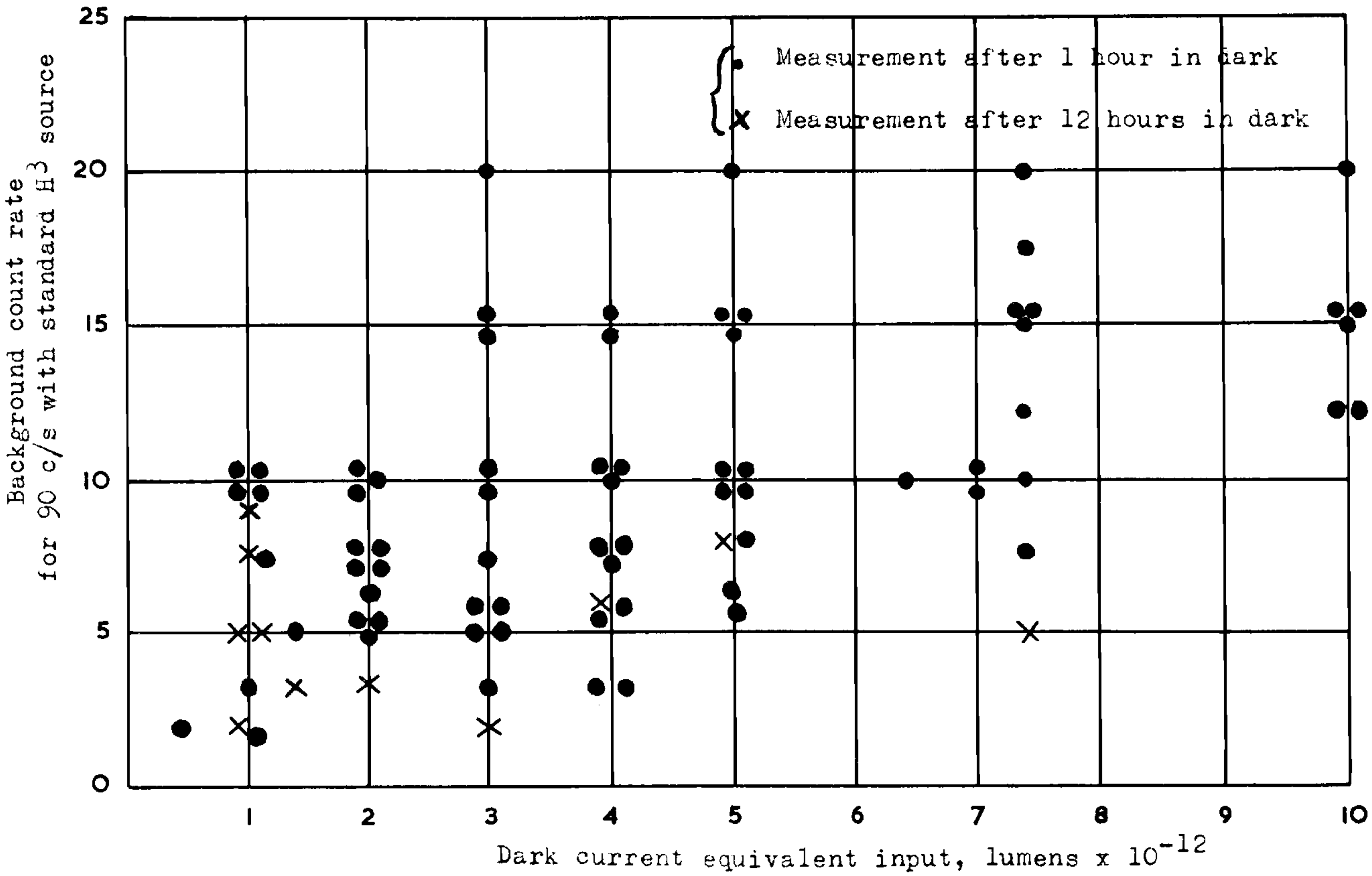


Fig. 2. Correlation between dark current and thermionic background for specified count rate from H^3 scintillation source in standard test jig.

are in common use; the linear focussed design (used in the RCA 6810A and EMI 9593B), the box and grid structure, (used in the DuMont 6292 and EMI 9524B) and the venetian blind dynode (used in the EMI 9536, 9514 and 6097). Two types of secondary emitting surface are in general use; Cs Sb, mainly used in EMI tubes, and Ag-MgO-Cs.

The variation of gain with voltage for representative tubes is shown in Fig. 3 and the increase in gain with a larger number of stages will be noted. This is important, since, in order to reduce the complexity of apparatus used to process the signal after the anode of the Photomultiplier tube, it is desirable to operate with as high tube gain as possible, provided this does not in turn produce feedback effects which increase the background signal.

A measure of the feedback stability of a given structure is provided by a plot of anode dark current divided by tube gain, which may be expressed in terms of cathode dark current, or in terms of the input light level to give an anode current equal to the dark current. However expressed, this parameter is found to be roughly independent of tube gain up to some critical value, as shown in Fig. 4. While the limiting value of gain varies from tube to tube, as does also the cathode dark current, nevertheless typical values may be given to particular tube designs and it is found that the box and grid type of structure has a relatively low limiting gain, around 5×10^7, independent of the number of dynodes (above 10), while the venetian blind structure has a limiting gain which increases with the number of dynodes, values of 10^9 with 13 stages being readily obtained. The focussed structure appears to lie midway between the other two designs in its behaviour. (The above comparisons refer to tubes with S-11 cathodes.)

Recently, a statistical study of the variation of dark current among tubes of a given type, has shown that there appears to be a median value characteristic of a given dynode structure, for tubes made with S-11 cathodes of very similar parameters. This is illustrated by the distribution curves of Fig. 5, from which it will be seen that the venetian blind structure gives the lowest value of dark current, while the linear focussed structure is worse by a factor of 20. The fact that the curves appear to be Gaussian when plotted against the log of the dark current suggests that the variation is due to a statistical spread in the work function of the cathode, but there is no obvious explanation for the difference in the median values, since the S-11 cathodes were all very similar. The results are not due in any obvious way to feedback processes, since the tubes were all operating well below the limiting value of gain and it may

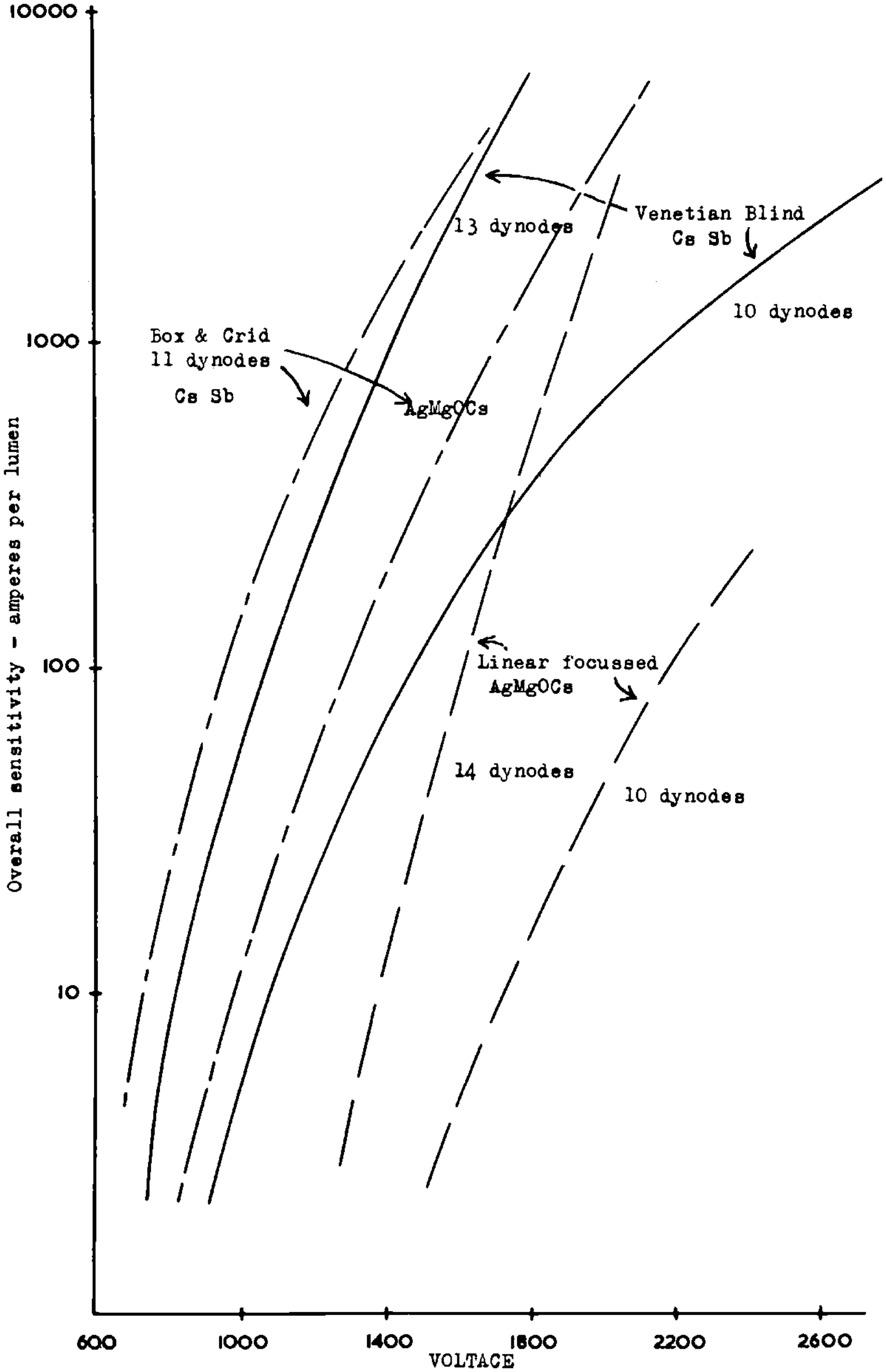


Fig. 3. Variation of gain with voltage for representative tubes.

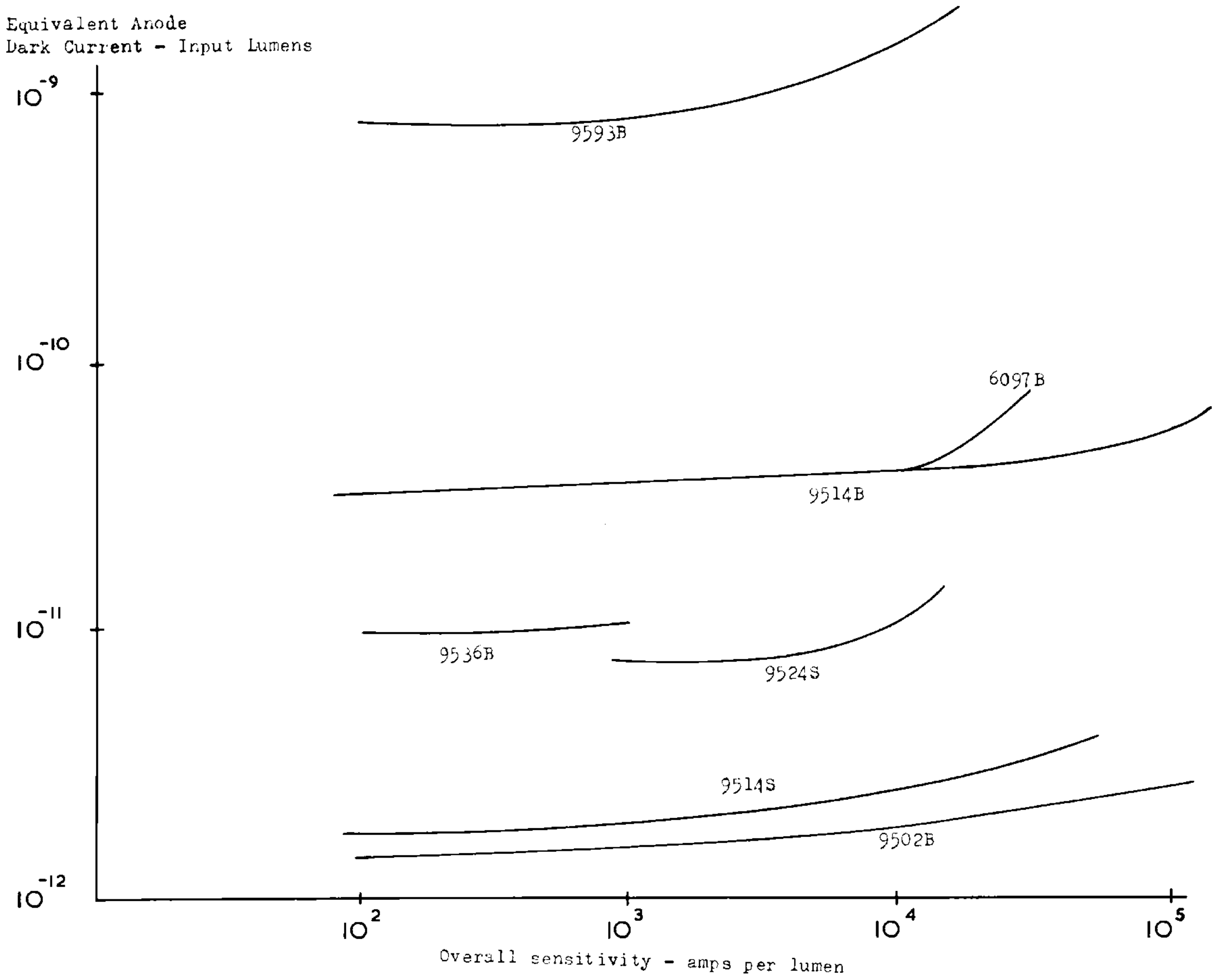


Fig. 4. Variation of dark current with over-all sensitivity for various tube types.

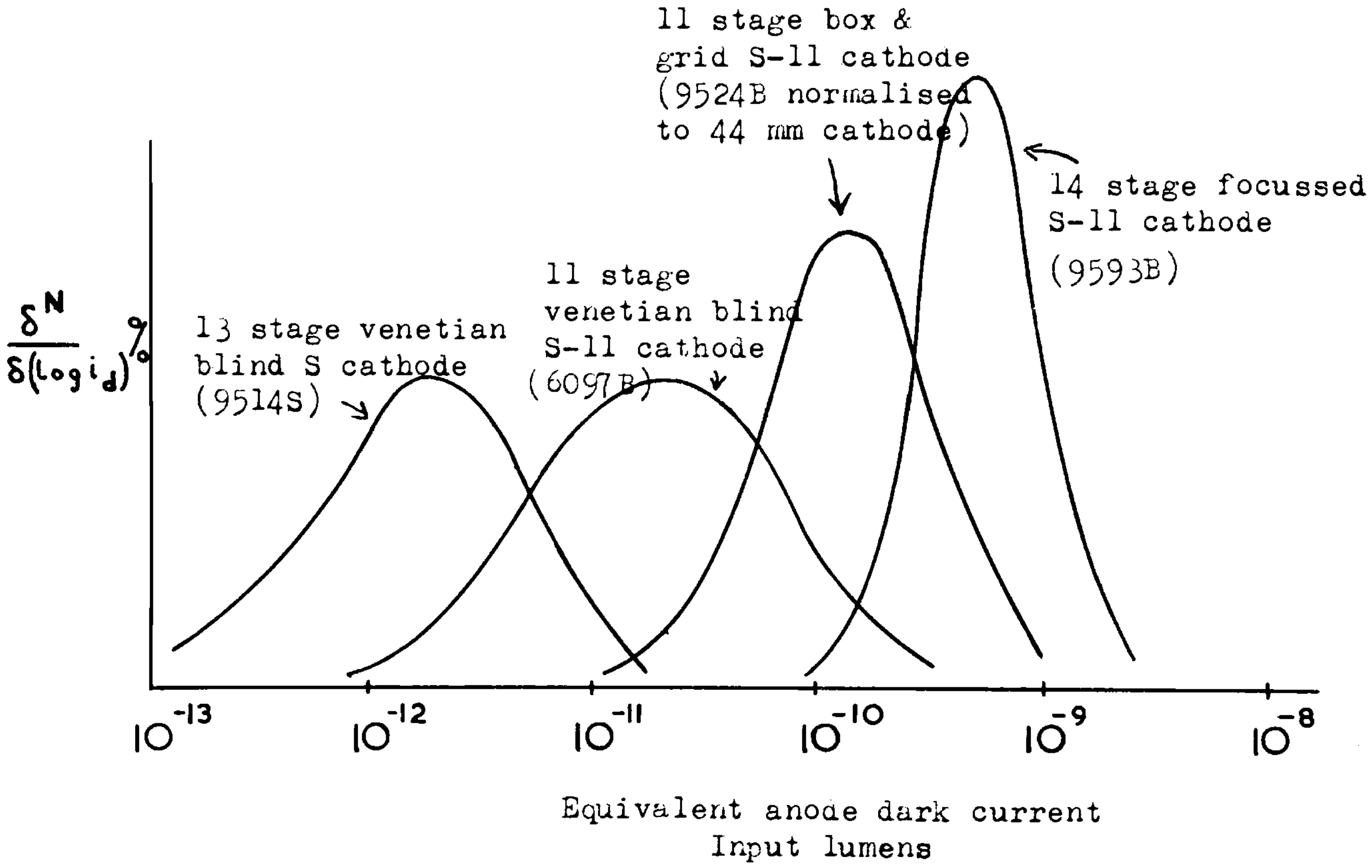


Fig. 5. Distribution curves of dark current for various tube types.

be that the phenomenon is associated with particular processing techniques which are individual to a dynode design, but the fortunate fact remains that the venetian blind structure, with which EMI has most experience, appears to be very suitable for low dark current tubes.

When tubes are made with 'S' cathodes, the dark current is reduced by a factor of 10 or more and it is found that the $1\frac{1}{8}$" diameter 9524S box and grid tube (with Cs Sb dynodes) becomes very competitive with the 9514S, only partly due to its smaller cathode area. This reinforces the suggestion that the difference shown in Fig. 5 may in part be due to processing.

A further observation relating to dark current is illustrated in Fig 6. (2). A tube was fitted with a fine grid parallel and close to the cathode so that a small negative PD sufficed to bias off electrons from the end window deposit. Under these conditions it was found that whilst 92% of the anode current produced by illumination of the cathode was cut off, only 14% of the dark current was affected, showing that the major part of the tube background was generated by regions of the cathode-D1 space which were of little utility for the production of photoelectrons. This result was not entirely unexpected, since the production of a uniform deposit of antimony on the window requires that the source of this material be situated in a position ideally suited for coating the walls of the cathode screen with antimony, which will absorb caesium to become an efficient generator of thermionic electrons.

Various artifices have been considered for the reduction or elimination of this undesirable wall coating and in recent months an ingenious arrangement has been developed by V.A. Stanley, at Ruislip. This consists of lining the cylindrical wall with a fine mesh, of small shadow area, spaced away by a millimetre or so. A small amount of Sb is deposited on the inner facing of this mesh but the greater part passes through onto the wall of the tube. After sensitisation, the small area of CsSb on the mesh can emit electrons into the C-D1 space for collection into the first dynode, but the electrons from the wall coating are biased back by the contact potential between the suitably chosen mesh material and the cylinder of the cathode screen.

The electron bias curves of tubes of this type have an unexpected shape. In place of the nearly linear relationship between amplitude and log-count-rate, exemplified by curve b of Fig. 1, which is found with a conventional 'S' cathode tube (and which was the subject of some controversy at the last Scintillation Counter Conference in Washington), a pronounced fall-off in the number of counts as low amplitude is observed, (curve c, Fig. 1), although at higher amplitudes the two

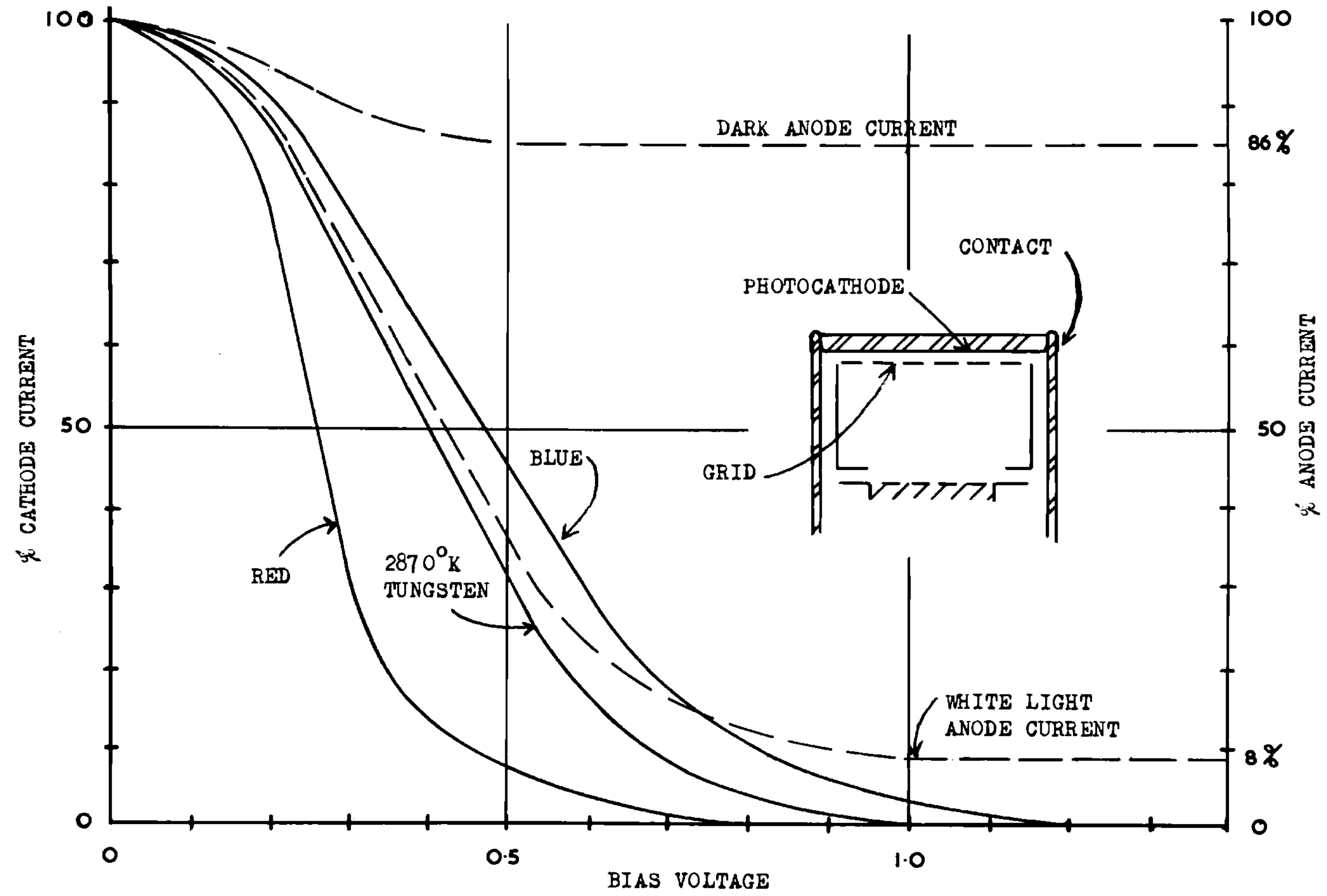


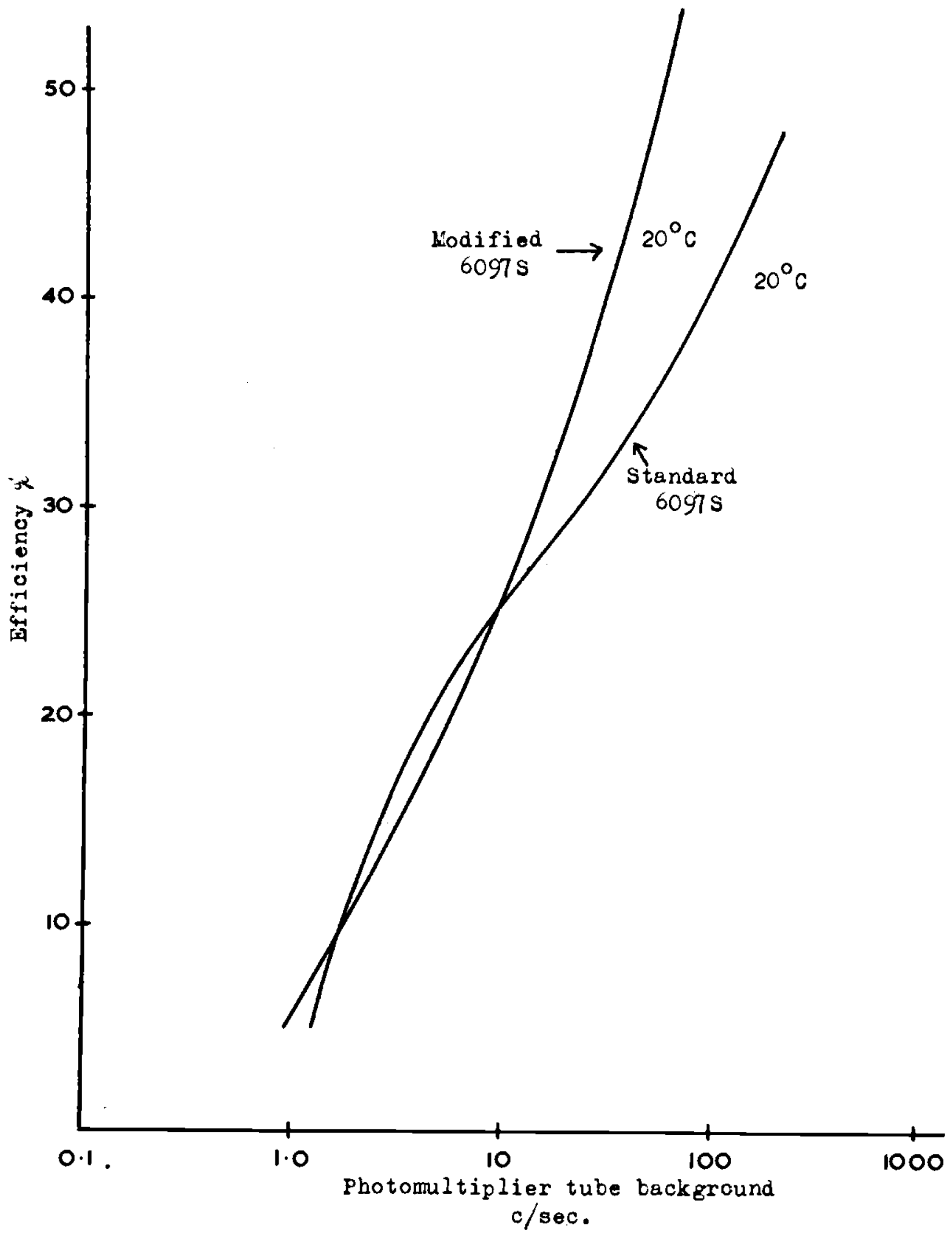
Fig. 6. Characteristics of 6097 with grid control of cathode emission.

curves are similar. This suggests that the majority of the thermionic electrons from the tube wall are incident on D1 in a position which gives a lower value of stage gain than those coming from the cathode, while a porportion may skip D1 and produce still smaller pulses from D2, so that the linear curve b is, in fact, made up of superposed distributions similar to curve c, but having a much wider statistical variation due to the inclusion of many signals of amplitude down to a fraction of one secondary electron, in place of the median value of 5 given by electrons from the cathode. In fact, analysis of the two curves shows that the average D1 gain for curve b is only half of that for curve c and in the latter case one electron amplitude is equivalent to 10 V bias.

4. We are now in a position to consider the results obtained on single tube assemblies by various workers. Fig. 7 shows a plot of tritium counting efficiency versus tube background at 20°C obtained at the Thornton Research Centre of the Shell Petroleum company. Using a standard 6097S (rating 90/7), a limiting efficiency of about 48% is obtained with a tube background of 200 counts per second and 14% for 3 counts per second. Using a modified tube with a mesh mounted around the cathode screen as described above, the background rate for efficiencies below 25% is about the same as for a standard 6097S, but above this level the effect of reduction in the small pulse background becomes very noticeable and a limiting value of 52% for 70 counts per second is obtained.

Fig. 8 shows the results obtained by Ekco Nucleonics, using a 9514S in an arrangement similar to that of the Shell counting head but cooled to -20°C and having better optical coupling. The limiting efficiency, using a tritiated toluene sample, has now increased to 64% for a tube background of 10 cps, while at 3 cps the efficiency is about 50%. It will be interesting to see the shape of curve given by a mesh lined tube when cooled, but this test has not been carried out at the time of writing.

It may perhaps be deduced from Fig. 9, which shows similar curves obtained by Nuclear Enterprises of Edinburgh, using a 9524 tube of $1\frac{1}{8}$" diameter, that cooling performs much the same function as the interposition of a mesh, since the small amplitude pulses seem to be reduced more than the larger background signals. Fig. 10 shows a bias curve of the arrangement, which differs from those mentioned previously, in having a cylindrical vial of height rather greater than its diameter and uses a newly developed phosphor type NE 213. The limiting efficiency is 64% at about 1 cps and is 20% at 0.15 cps from the tube. A comparison of the bias curves of Fig. 1 and of



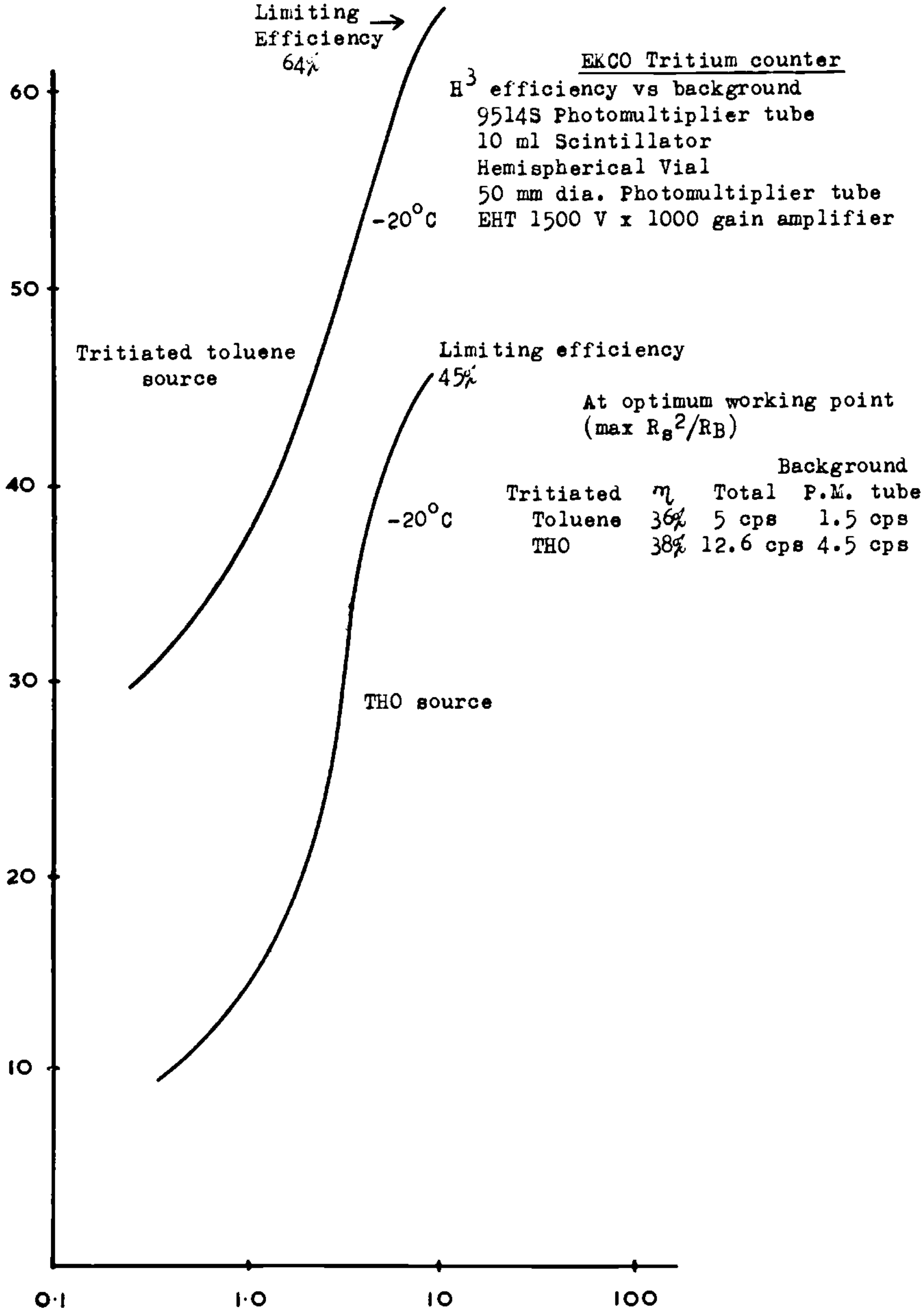
Shell Counting Head

H^3 Counting Efficiency vs Tube background

20°C. 10 ml Scintillator. Hemispherical vial

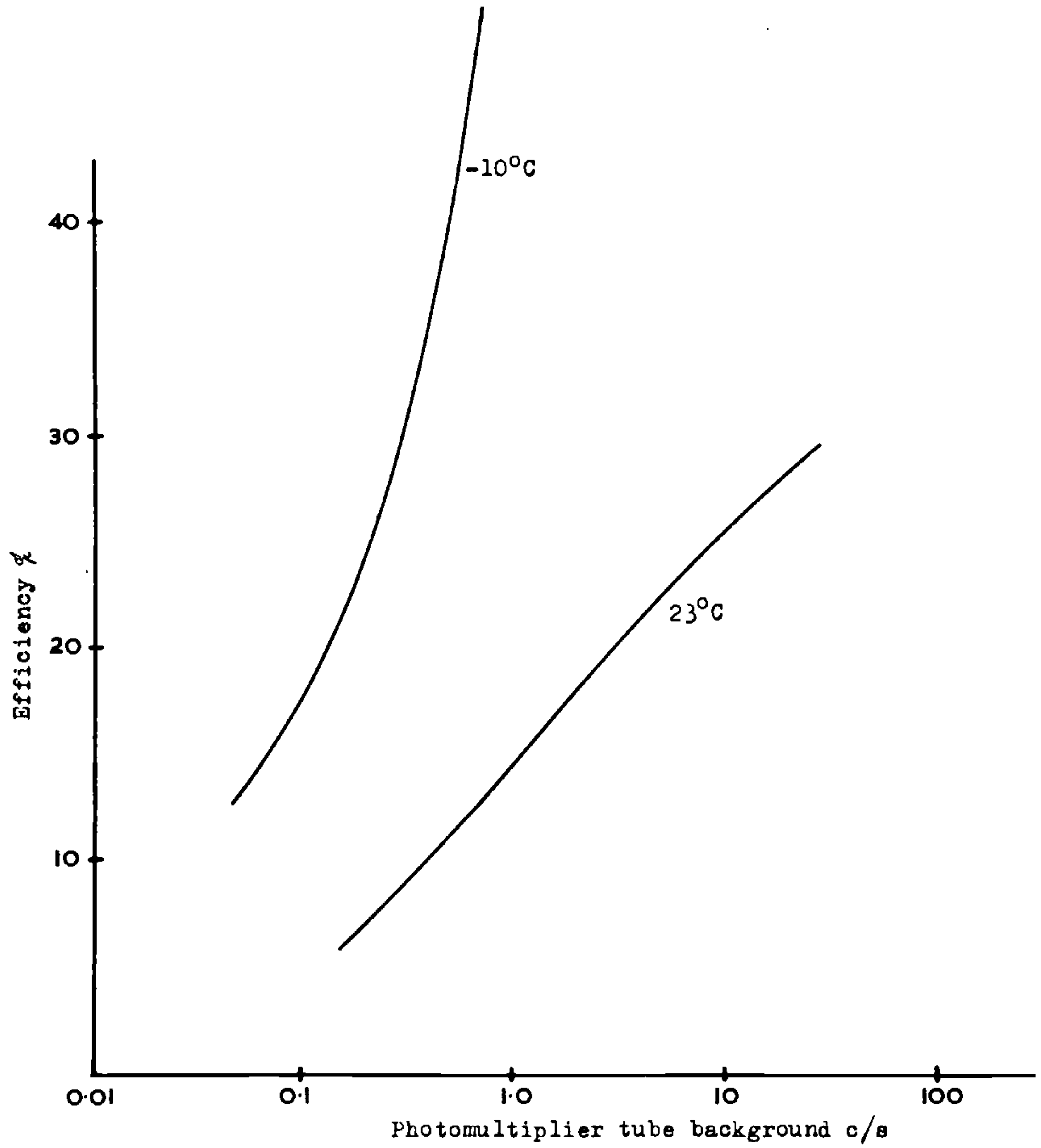
Amersham Hexadecane -1:2T in Toluene + 5 g/litre p-terphenyl + 16 mg/litre POPOP

Fig. 7. Variation of tritium counting efficiency with tube background: Shell Petroleum Company.



		Background	
Tritiated	η	Total	P.M. tube
Toluene	36%	5 cps	1.5 cps
THO	38%	12.6 cps	4.5 cps

Fig. 8. Variation of tritium counting efficiency with tube background: Ekco Nucleonics.



Nuclear Enterprises Tritium Counter

H^3 Counting Efficiency Vs Tube background

NE 5503 and 9524A
15 ml Scintillator Cylindrical Vial
28 mm dia. Photomultiplier tube.

Fig. 9. Variation of tritium counting efficiency with tube background: Nuclear Enterprises.

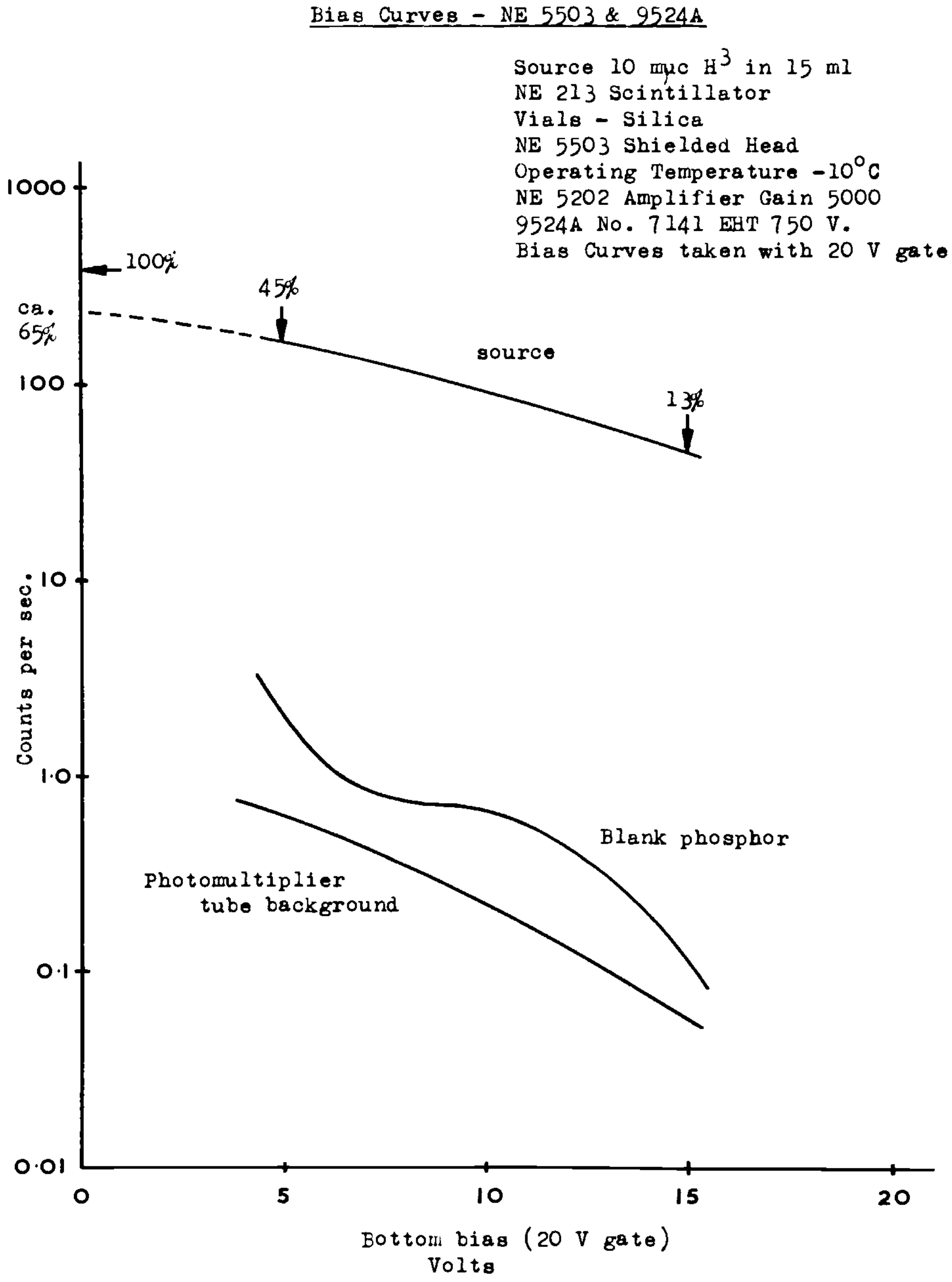


Fig. 10. Bias curves: Nuclear Enterprises.

Fig. 10, normalised to an equal electron amplitude scale, suggests that the amplitude of primary signals from the Nuclear Enterprise assembly at -10°C is about 20 to 30% higher than from the Shell assembly at 20°C. Part of this increase is undoubtedly due to the fact that the NE head is designed to give rather tighter optical coupling than is the Shell head which was designed for rather less onerous requirements. The tube background given by the particular 9524A appears to be 8 times lower than that of the 9514S used in the Ekco equipment and while part of this is undoubtedly due to the 4:1 reduction in area of the 9524 compared with the 9514 (23 mm diameter of 44 mm diameter), some part must also be due to the spread in tube parameters.

From the above it will be seen that for a single tube assembly, operating with an efficient phosphor and vial assembly, the limiting efficiency for H^3 counting lies between 48 and 64%. In all of the above measurements great care was taken to ensure that measurements were not falsified by phosphorescence of vial or phosphor. This was done by handling in light shields or dark rooms and by the use of identically handled blanks.

5. The disturbing effects of phosphorescence may be sufficient to demand the use of a coincidence arrangement for their elimination, particularly with some types of sample. From the data given above, we can see that a vial tightly coupled to two Photomultiplier tubes, so that the light from a scintillator is shared equally between the two cathodes will give a maximum efficiency for H^3 of between 25 and 40% (single tube efficiency squared.) Any reduction in the optical coupling will markedly reduce this efficiency.

The fact that two tubes are 'looking' at each other now immediately brings in the complication of tube interaction. In a preliminary set-up using two 9514S tubes, the random coincidence rate at room temperature (about 23°C) with the tubes optically isolated has been measured at 0.3 c/s. With the tubes coupled through an empty cylindrical vial with plane parallel end windows, a coincidence rate of 2 counts per second was obtained due to tube interaction and with a blank phosphor in the vial an extra background of 1.5 cps was obtained. These figures refer to an H^3 counting efficiency of about 15% (the arrangement was not optimised for light coupling) and the interaction count rate varied linearly with H^3 counting efficiency, which suggests that signals from the cathode are of only 1 or two electrons. The resolving time of the coincidence unit was about 0.5 usec.

Work has just begun on a study of this interaction and of means for reducing it but we have, as yet, little to report. Up to the moment, it has seemed reasonable to assume that the interaction is due to the passage of light from the anode region of one tube where excitation of Cs vapour will occur, to the cathode of the second tube. If this is the case, the use of a coincidence unit of resolving time shorter than the electron transit time (about 60 musec) should greatly reduce the effect. The observations that interaction is proportional to cathode area (checked by blacking out parts of the cathode) and also to H^3 detection efficiency, would not be inconsistent with such an explanation, but these would be equally consistent with a mechanism not involving anode light feedback. A very recent private communication from J.F. Cameron and I.S. Boyce at A.E.R.E., Harwell, suggests that they have made observations which, although tentatively, support a theory not involving anode light as a primary cause, since the coincidence rate is not affected by cooling, which materially reduces the anode current. If these observations are confirmed, many of the possible lines of work, involving modifications to tube structure, which we have in hand at the moment, will be fruitless and it is regretted that time has not permitted clarification of this point before the presentation of this paper.

One other aspect of tubes which must be examined in connection with coincidence arrangements is a possible advantage of tubes with tri-alkali cathodes (S-20) such as EMI 9558B. These have high photosensitivities with up to 20% quantum efficiency in the blue and rather lower thermionic emission than an S-11 cathode (between one quarter and one sixth, at 20°C).

Tested in our single tube head, such tubes are rated at 90/25, which compares unfavourably with the modern specially made 'S' cathode tubes, but they have not yet been checked by us in a coincidence head. The possibility also exists that re-examination of phosphors operating with quartz window versions of the 9558 and also with quartz window 'S' cathode tubes may lead to some improvement in counting efficiency.

6. CONCLUSION

At the present moment, Photomultiplier tubes are available capable of giving counting efficiencies for 10 ml samples of tritiated toluene phosphors of between 10 and 15% with a tube background of 3 counts per second at 20°C and of 50 to 60% for this background at -10 to -20°C. At this reduced temperature 30% is obtainable with tube backgrounds of only a few counts per minute.

Much work remains to be done to improve the performance of tubes in coincidence arrangements but significant improvements are hoped for in the next few months.

ACKNOWLEDGMENTS

I am indebted to my colleagues Dr. E.E. Thomson and Mr. V.A. Stanley for the close collaboration which they have afforded me in many aspects of this work and also to my very good friends at Shell, Ekco and Nuclear Enterprises for the information contained in Fig's. 7, 8, 9 and 10. Messrs. Boyce and Cameron at A.E.R.E. have very kindly allowed me to quote results from their work, which is still proceeding and thanks are also due to the Directors of E.M.I. Electronics Ltd., for permission to present this paper.

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