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Standardization of Alpha-Emitters by Liquid-Scintillation Counting

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H. R. Ihle, A. P. Murrenhoff, M. Karayannis

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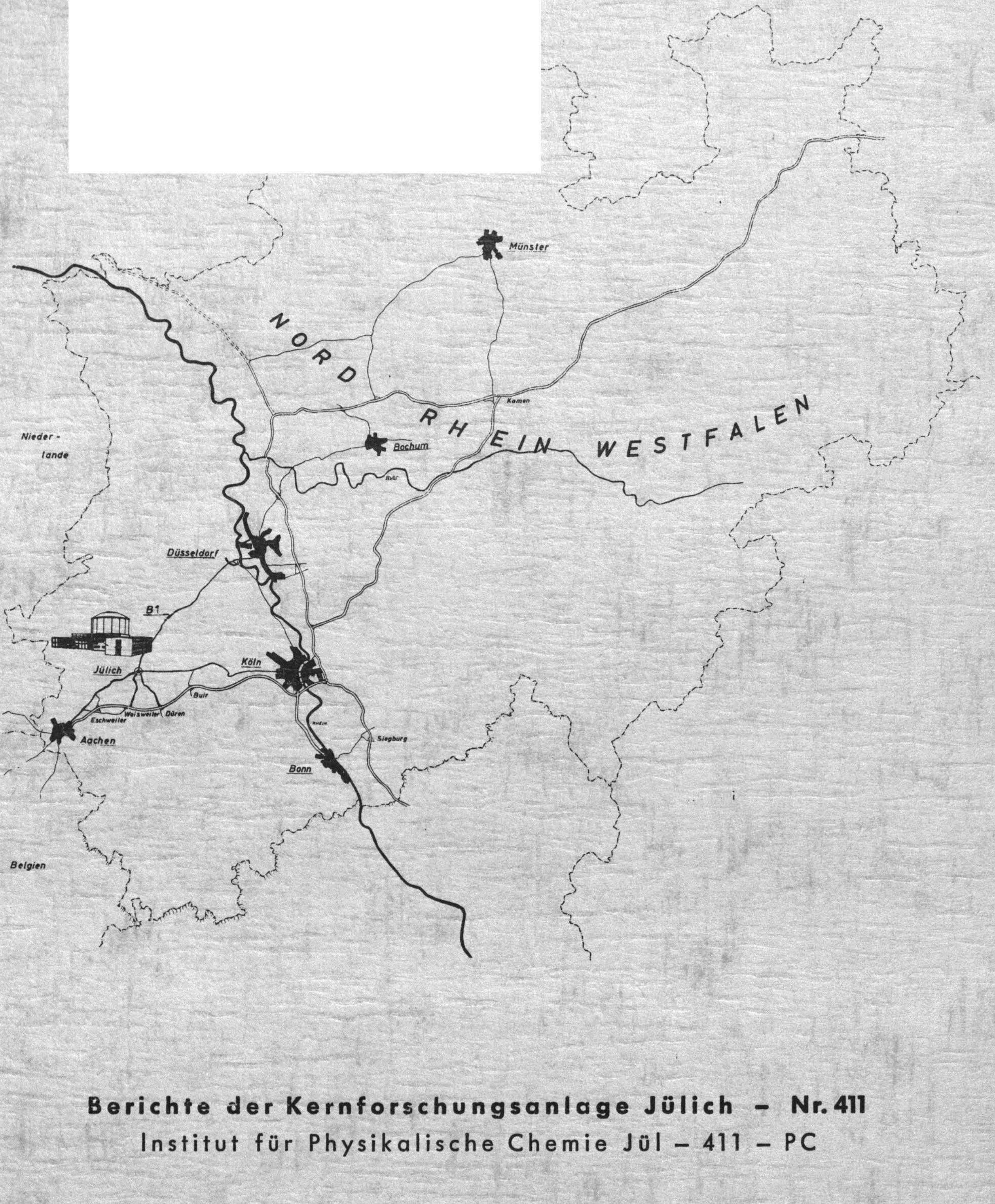

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Revised Abstract
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Standardization of α-Emitters by Liquid-Scintillation Counting

by H.R.Ihle, A.P.Murrenhoff, M.Karayannis

Arbeitsgruppe Physikalische Chemie
der Kernforschungsanlage Jülich,
Bonn, Federal Republic of Germany

Internal liquid scintillation counting allows a high precision in the standardization of solutions of α-emitting nuclides.

The method has a number of advantages: under appropriate experimental conditions, a 4π geometry is obtained; the difficulties with sample self-absorption and backscattering often encountered in methods necessitating mounting of the samples on plates are eliminated.

One condition of particular importance for standardization is the stability of the liquid scintillation sources over long periods of time. Measurements with actinide-nuclides from thorium to curium showed that the ions of the actinides can be stabilized by means of tri-n-octyl-phosphineoxide (TOPO), which simultanously acts as complexing agent and counteracts the quenching effects of acids.

A technique for the comparison of liquid scintillation counting with other absolute counting methods, which avoids the possible sources of errors from weighing or pipetting of aliquots, has been developed and verified.

The method was applied to new determinations of the specific activity of ^{239}Pu and ^{233}U with an accuracy of ± 0.3% and ± 0.2% respectively. In the liquid scintillation counting a precision of ± 0.05% was obtained.

Because of the high time resolution of liquid scintillation, further improvement in precision can be expected when fast electronic systems are used.

A.) Introduction

A considerable amount of work has been done in recent times to develop and to verify the possibilities of liquid scintillation as a method of absolute counting, and to find suitable conditions for high precision measurements. One can readily imagine that it should be feasible to use a liquid scintillator for 4π α-counting by dissolving the sample in the scintillation mixture and viewing the scintillator - if necessary from all directions - with a sensitive low noise photon detector arrangement. In addition, the internal liquid scintillation method offers especially for α-counting some advantages which can also be easily recognized in advance: there is no necessity to correct for influences like self-absorption of the sample, or backscattering and absorption in a sample mount, if the sample is dissolved in the detector. The weight of the liquid sample aliquots of the radioactive solutions can be precisely determined in a relatively simple and straightforward manner by weighing in scintillation vials specially made for precision weighing of small amounts of liquids.

B.) The liquid scintillation counting arrangement used for this investigation

If not indicated otherwise, the data given in the following chapters for the performance of the liquid scintillation method have been obtained by use of the following means [1;2] : the scintillator is a solution containing 0.7 g 2,5-diphenyloxazole (PPO), 0.03 g 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP), 10 g naphthalene, and 4 g tri-n-octylphosphine oxide (TOPO) per 100 ml dioxane. The solution is used air saturated; it mixes with aqueous as well as with organic samples.

The scintillation vials are cylinders of 28 mm diameter with a flat, but not ground, bottom. If the same vial is used for weighing the sample aliquot of the radioactive solution and for subsequent counting, a light weight type with 30 mm height is employed. For reduction of the radiation background, the vials may be made from low activity glass.

Into the vial an amount of e.g. 30 to 50 mg of aqueous radioactive sample is pipetted; this sample weight can be determined with an accuracy of better than 0.1%. About 5 ml scintillator solution are added, dissolution is speeded up by swirling the vial.

The counting arrangement (Fig.1) is an ambient temperature single multiplier phototube detector (multiplier: EMI 6097 S or equivalent) connected to a printing scaler equipped for the registration of a series of measurements with programmed automatic variation of the discriminator setting. The arrangement may be monitored by a multi-channel analyzer.

The optical coupling between the phototube and the bottom of the scintillation vial is made by silicon grease or a viscous silicon oil.

The reflector is a cylindrical glass cap with a hemispherical end; the inside is painted with a TiO_2 reflecting paint. The dimensions of the cap for use with a 2 inch phototube are: inner diameter: 45 mm; total height: 55 mm.

C.) Potential sources of errors and their suppression

For absolute measurements all sources of errors must be considered, and must either be eliminated by experimental precautions, or the errors must be corrected for. Therefore in the following list a compilation of the potential sources of errors connected with the use of a liquid scintillation detector in absolute α-counting is given.

C.1.) Potential sources of counting losses:

C.1.1.) Effects influencing the overall efficiency of the transformation of radiation energy to photoelectron production: light yield of the scintillator, low efficiency or inhomogenity of the photocathode-layer, unfavourable match between the wavelength range of the scintillator light and the spectral sensitivity of the photocathode, photon losses by absorption or total reflection in the window of the multiplier phototube, or in the optical coupling between the window and the liquid scintillator, reduction of the light yield of the scintillator by materials contained in the sample ("quenching").

C.1.2.) Incomplete absorption of the radiation energy in the scintillator for α-decay events taking place within a layer of one α-range thickness [3] from the outer surfaces of the scintillator a.) "α-range effect" b.) wall absorption of the radionuclides.

C.1.3.) Coincidence losses

C.2.) Potential sources of counting events not originating from the radioactive decay process to be measured: background due to penetrating radiation, noise of the multiplier phototube, radioactive contaminants in the sample, chemiluminescence caused by materials contained in the sample, phosphorescence of the scintillator after exposure to light.

C.1.1.) The emission of every single light flash is the summation effect of a great number of elementary photon emission events - order of magnitude 10^4 - [4]. It is therefore to be expected that the total light yield of every α-particle dissipating its total energy within the scintillator will fall into one common range given by a statistical distribution about one mean number and a mean spectral distribution of the photons emitted per α-particle. A multiplier phototube with a quantum efficiency of 5% for the scintillator spectrum will produce for the 10^4 photons per α-particle photoelectrons in a Poisson-distribution with a mean number of 500 electrons. Theoretically, losses of counting information due to the characteristics of the Poisson-distribution are negligable down to a mean number of about 10 photoelectrons per α-particle. Consequently, it should be possible to reduce the efficiency of the transformation of the radiation energy to photoelectron production considerably below the optimum values attainable without affecting the integral counting result; and this has been verified experimentally. (see D.5.)

In standardization work, it is usually possible to avoid the presence of most substances quenching the scintillation process exept water and mineral acids. It has been shown by FURST et al. [5] that the quenching effect of water can be counteracted by addition of naphthalene to the scintillator mixture. The addition of organic phosphine oxides to the scintillator reduces the quenching effect of mineral acids, probably due to the formation of compounds like $TOPO \cdot HNO_3$, as shown by figure 2. Here, the relative pulse-height of unity refers to a ^{233}U sample without TOPO and HNO_3.

C.1.2.a.) A certain percentage of the α-particles being emitted inside the scintillator from places within a distance of less than one α-range from its outer surface are not stopped inside the scintillator; and therefore a part of their energy is lost for light production. It can be shown by calculating the pulse-height spectrum to be theoretically expected for the α-particles influenced by this "α-range effect" that those α-decay events for which the pulse-height is reduced by the "α-range effect" down to the pulse-height range of the noise can be included in the counting result by linear extrapolation of the discriminator curve to zero pulse-height [1].

C.1.2.b.) It is relatively easy to distribute micro amounts of inorganic radionuclides highly dispersed in a liquid scintillator, especially if the scintillator mixes with a large proportion of water. However, one must expect for many inorganic substances that such a dispersion in an organic medium will not result in the formation of a stable solution unless some stabilizing agent has been added. The consequence of instability of the dispersion of the radionuclide are wall absorption, or the formation of precipitates, and these are causes for counting losses, since the α-particles emitted into a non-scintillating wall of the sample container will not be registered.

Stabilizers especially favourable for liquid scintillation absolute counting are "non-quenching" complexing agents with a relatively inspecific complexing action such as organic phosphine oxides. It has already earlier been reported that tri-n-octylphosphine oxide (TOPO) is an efficient stabilizer for U, Pu, Am, and Cm [1;2] (also for Pm [6], Ce, Ru, Zr, and Nb [7]), and we have in the meantime verified that this is also true for Pa, Np, and Th.

C.1.3.) The resolving time of a counting arrangement can be determined by a series of measurements with stepwise increasing known activities. With a liquid scintillation counter such a series can be made with aliquots of an α-active spiked scintillator solution [1]. The scintillator vial is filled up to constant volume with non-radioactive scintillator. This procedure allows a high precision because the portions of the spiked scintillator can be chosen large enough to make precise pipetting or weighing possible.

C.2.) The liquid scintillator is more sensitive than other α-detectors against the background due to penetrating radiation, and against ß-γ-emitters contaminating the sample; in addition it is usually not possible to discriminate against contaminating α-active nuclides with the method described here [1;2]. In standardization work these drawbacks can normally be overcome by proper purification of the sample, and proper selection of the sample activity.

Consequently, for an absolute determination of the counting rate with this method one simply measures and extrapolates an integral discriminator curve, and corrects for the background and coincidence losses.

D.) Results verifying the possibilities of the liquid scintillation method in absolute α-counting

D.1.) Table I [8] shows the results of 16 measurements of the specific activity of a ^{233}U solution and mean values calculated in three different ways: (a) The activity has been plotted versus sample weight, and the best fitting straight line through the points of this plot has been determined by a least square treatment; the slope of this straight line yields a mean value of the specific activity; (b) the sum of the activities has been divided by the sum of the sample weights; (c) the arithmetic mean of the specific activity values calculated for the single measurements has been determined. Method (a) gives a higher statistical weight to the samples with large weight and activity; the methods (b) and (c) weigh all results equally. Systematic errors with a dependancy on the sample size can show up by differences between mean value (a) and the mean values (b) and (c). No significant differences are observed for the results in table I.

D.2.) A set of 10 pairs of comparative determinations by the liquid scintillation method against 4π proportional α-counting resulted in an average of the deviations of the activity values measured by both counting methods of 0.2% [1]. Each sample is first counted in the 4π proportional counter, then the sample carrier foil is brought into a scintillation counting vial with precautions against losses of sample material; after dissolving the sample and the metallization of the foil in a small amount of acid, scintillation mixture is added. This technique eliminates for comparative experiments with liquid scintillation the determination of the sample weight and its errors; the technique is also applicable for a comparison with α-γ-coincidence counting or low geometry counting. Similar close agreement between liquid scintillation and other absolute α-counting methods has been reported, [9 to 14].

D.3.) Using the liquid scintillation method described the specific activities of ^{239}Pu and ^{233}U have been redetermined to be 136400 ± 360 dpm/μg for ^{239}Pu [15] and 21014 ± 40 dpm/μg for ^{233}U [8], in good agreement with the latest values reported in the literature [16 to 21]. The contribution of the counting measurements to the error is relatively small. The accuracy quoted above is mainly limited by errors in the mass analysis or specific activity data of isotopic contaminants present in the samples used for the measurements.

D.4.) If it is intended to use a sealed liquid scintillation sample of an α-emitter, e.g. ^{241}Am, as a standard for a long period of time, sufficient stability against the internal α-irradiation is one basic requirement. Usually, a counting rate of $\sim 10^3$ cps may be employed to obtain results with a precision better than 0.1% within a reasonable time, while the dead time correction is still of the order of a few tenths of one percent.

Irradiation with 3 MeV electrons has been used to obtain experimental information on the radiation stability of the liquid scintillator. 4 sealed ampoules filled with the scintillation mixture described in (B) and containing $\sim 10^3$ dps ^{241}Am in 5 ml solution have been irradiated with doses from 260 to 2,6 x 10^4 rad. The counting rates $\dot{N}$ and the most probable pulse-heights H of the samples have been determined prior and after the irradiation. As shown in Table II, the integral counting rates are not affected within the statistical error of ± 0.1%. The relative pulse-height is only decreased in case of sample 4. If one assumes a factor of 1 to 10 for the relative effects of the α and ß radiation, a "usable sample life" of 100 yr or 10 yr respectively can be expected.

D.5.) The efficiency of the transformation of the α-radiation energy to photoelectron production has been varied by changing the conditions of light collection. The results summarized in Table III refer to the following conditions.

1.) Reflector, sample vial etc. as described in (B) - optimum conditions -.
2.) Small reflector cap (inner diameter 37 mm, height 50 mm), other conditions as (1.).
3.) Reflector replaced by a black cap.
4.) Bottom of scintillation vial covered with TiO_2 paint, other conditions as (1.).

The same vial was used for all experiments. For each condition 16 discriminator curves containing a total of $7 \cdot 10^6$ counts have been used to determine a mean counting rate $\bar{\dot{N}}$, and a standard deviation σ. In addition, the relative pulse-height - which is proportional to the relative number of photoelectrons - and the line width of the α-peak has been measured. Despite the considerable decrease in pulse-height caused by the variation of the light collection conditions, there is no significant change in the mean counting rate, or in the standard deviation of the results.

E.) Conclusion

Down to 0.1%, no essential obstacles against further improvements of precision and accuracy of liquid scintillation absolute α-counting inherent in the detector have shown up yet. When appropriate fast electronic equipment is available, the very short resolving time of the liquid scintillator will allow measurements with samples of unusually high counting rates, resulting in smaller statistical errors for a given counting time. The liquid scintillation method is therefore a valuable complement to the other high precision methods in the effort to achieve further improvements of the accuracy of absolute α-counting.

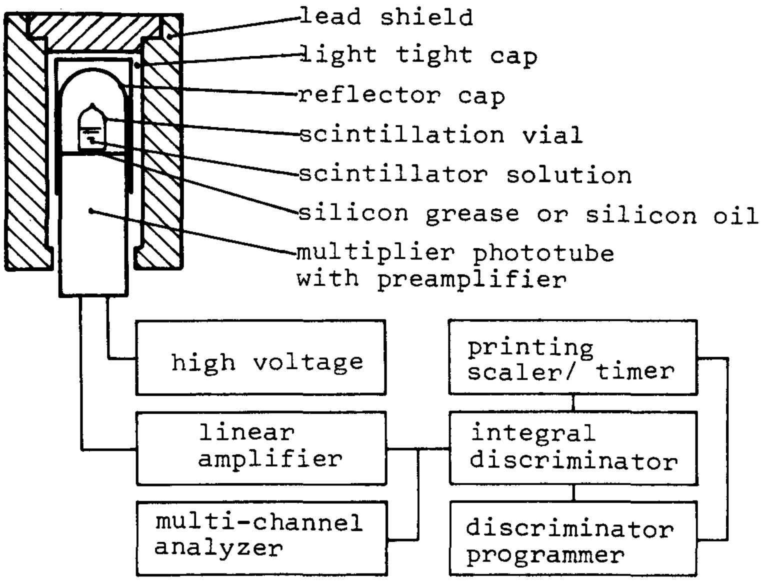

Fig. 1

Schematic diagram of experimental arrangement

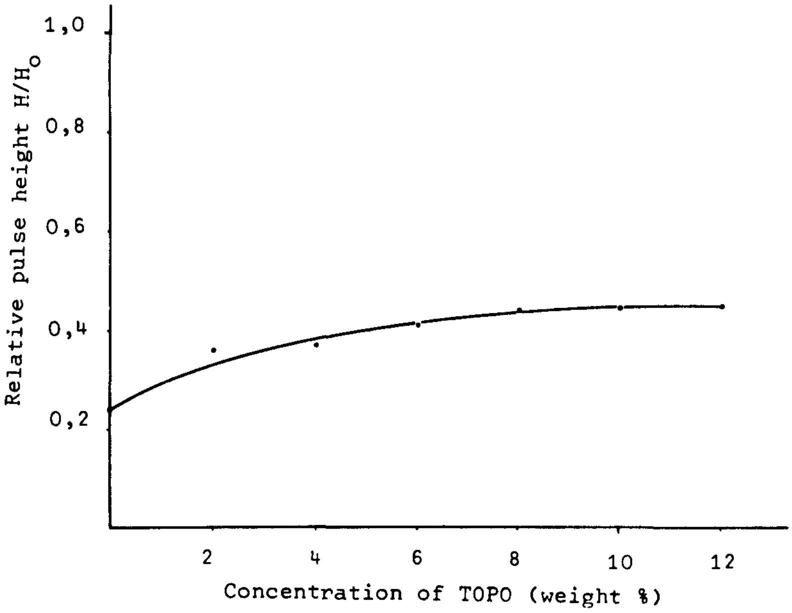

Fig. 2

Reduction of the quenching effect of HNO_3 by addition of TOPO to the scintillator solution

T A B L E I

16 DETERMINATIONS OF THE SPECIFIC ACTIVITY OF A ^{233}U-SOLUTION

corrected counting rate y [cpm]	sample weight x [mg]	specific activity [dpm/mg]	corrected counting rate y [cpm]	sample weight x [mg]	specific activity [dpm/mg]
121417	61,817	1964,14	114657	57,917	1979,68
136451	69,260	1970,13	80983	41,110	1969,91
62724	31,972	1961,84	89951	45,812	1963,48
85980	43,730	1966,16	131660	66,892	1968,26
123838	63,220	1958,84	42052	21,310	1973,35
120912	61,727	1958,82	120538	61,472	1960,86
113314	57,615	1966,74	87779	44,533	1971,10
131822	66,702	1976,28	73376	37,321	1966,08

$$\left.\begin{aligned}
&\text{a).}\quad \frac{n\sum_1^{16} x_i y_i - \sum_1^{16} x_i \sum_1^{16} y_i}{n\sum_1^{16} x_i^2 - \left(\sum_1^{16} x_i\right)^2} = \underline{1,9672} \cdot 10^3 \left[\frac{\mathrm{dpm}}{\mathrm{mg}}\right] \pm 0,5\,\%\mathrm{o} \\
&\text{b).}\quad \frac{\sum_1^{16} y_i}{\sum_1^{16} x_i} = \underline{1,9671} \cdot 10^3 \left[\frac{\mathrm{dpm}}{\mathrm{mg}}\right] \pm 0,5\,\%\mathrm{o} \\
&\text{c).}\quad \frac{1}{16} \sum_1^{16} \frac{y_i}{x_i} = \underline{1,9672} \cdot 10^3 \left[\frac{\mathrm{dpm}}{\mathrm{mg}}\right] \pm 0,5\,\%\mathrm{o}
\end{aligned}\right\}\ \begin{array}{l}\text{standard}\\ \text{error}\\ \text{of the}\\ \text{average}\end{array}$$

T A B L E II

EFFECT OF 3 MeV-ELECTRON-IRRADIATION ON THE LIQUID SCINTILLATOR

Sample No.	Dose D [rad]	Counting rates $\dot{N}_D/\dot{N}_{D=0}$	Relative Pulse-height $H_D/H_{D=0}$
1	0	1,000	1,000
2	260	0,999	0,960
3	2600	1,000	1,009
4	26000	0,998	0,809

T A B L E III

INFLUENCE OF LIGHT COLLECTION CONDITIONS ON COUNTING RESULTS

Condition i	Counting rate $\dot{N}$ [cpm]	Standard deviation σ [o/oo]	Relative Pulse-height H_i/H_1	Linewidth [%]
1	144888	0,16	1	26,7
2	144843	0,16	0,96	26,9
3	144972	0,24	0,63	37,8
4	144823	0,12	0,59	37,0

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