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TRITIUM DETECTION BY β -RADIOLUMINESCENCE IN STANDARD MEDIA FOR THIN-LAYER CHROMATOGRAPHY

II. A FURTHER STUDY OF THE SENSITIVITY ENHANCEMENT AND OTHER PROPERTIES OBTAINED BY VARIOUS SCINTILLATOR AD-MIXTURES

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SUMMARY

Results are reported concerning detection of radionuclides by thin-layer chromatography using electron-induced luminescence in added scintillators. Photoelectric detection has been applied. This method is faster than other ones based on direct electron detection and is much more accurate than photographic detection. It is therefore better suited for quantitative measurements.

Relative luminescence efficiencies have been estimated for several commercial scintillators, and, for some, detailed information based on performances under ordinary conditions for measurement has been obtained. A basis for the comparison of different methods of measurement emerges from a brief discussion of such terms as "sensitivity of detection" and "minimum detectable activity".

INTRODUCTION

During the last ten years tritium (^3H) has been applied at an ever increasing rate as a tracer in radiochromatography. Apart from other radionuclides, however, ^3H introduces great difficulties in its determination due to the low electron energies ($E_{\text{max.}} = 18.5 \text{ keV}$, $E_{\text{av.}} = 5.7 \text{ keV}$). For radiocarbon (^{14}C), the electron energies are larger by a factor of approx. 10, and the problems in detection therefore are greatly reduced.

Various methods for measurement have been discussed earlier in Part I (ref. 1). In recent years radioluminescence (fluorography, scintillation fluorography, scintillation autoradiography) has been developed and applied as a sensitive method for detection by thin-layer radiochromatography (TLRC). Due to the weak β -radiation from ^3H , the use of β -radioluminescence in TLRC is especially applicable for the measurement of this radionuclide.

In the present work, a detailed investigation of certain scintillators used as powdered admixtures in the TLC media is made. Even if liquid scintillation counting is known as the most sensitive technique, the use of a powdered solid scintillator applied as admixture to the TLC media sometimes is very convenient, giving chemically inert preparations which are easy to handle; the measurements also introduce no damage to the sample. It is important then to find efficient β -scintillators and to establish suitable conditions to assure reproducibility and to facilitate fast quantitative measurements. Organic scintillators (anthracene, PPO, etc.) as well as inorganic ones (e.g. manganese-doped zinc silicate) may be useful. While direct recording on photographic emulsions permits spot localization and documentation, more precise methods should be applied for all quantitative measurements of spot activities. Using photomultiplier detection, one obtains a greatly increased sensitivity and gets rid of errors otherwise introduced by fading of the film exposure (during long-lasting exposures) by nonlinear response in the blackening of the emulsion and by uncertainties involved in the densitometric and calibrational work.

In Part I of this investigation¹, a single-photon counter was used. As is discussed later, photon counting might give another result than photomultiplier current measurement (with the same photomultiplier and geometry of measurement). Therefore, the main results of Part I have been rechecked and extended by the last method, which to a greater extent reflects the largeness of the individual photon bursts (scintillations) induced by the single-electron absorption in the various scintillators. The main conclusions given in Part I are confirmed. Furthermore, with special emphasis on practical detection techniques, the linearity of the system for measuring β -radioluminescence has been investigated for varied contents of scintillator as well as for various activities of ^3H or ^{14}C . Finally, various relationships influencing the accuracy of the method have been studied.

PHOTOELECTRIC DETECTION OF RADIONUCLIDES

As has been mentioned, the scintillation detection of radionuclides can be achieved either by photographic techniques or by using photosensitive electronic equipment. The photographic techniques will not be considered any further in this communication; the photoelectric technique permits true quantitative measurements of nuclide activities and such a method will steadily gain more attention.

The photomultiplier: photocurrent recording or pulse counting

Irrespective of the type of scintillator applied (liquid, gel or solid), the most suitable detector is the photomultiplier. In this unit single electrons released by a photoeffect give rise to electron cascades which are drawn through an electric field to be collected finally by an anode. Upon successive impingement on a series of interposed dynodes, held at increasingly higher potentials, an emission of secondary electrons results in a stepwise multiplication process. Using this principle, an amplification factor as high as 10^6 – 10^9 may be reached. Thus single photons may be counted by detecting amplification pulses in the photomultiplier. Alternatively these pulses might be integrated and the composite signal smoothed by introduction of a suitable time constant to give a steady current signal which may be recorded or read directly from a meter.

These two versions each have their specific advantages and drawbacks. We shall shortly reconsider some of them. The counting techniques accept all pulses larger than a certain discriminator level, and a resulting count number may be observed after a suitable period of detection. (The square root of this number gives the standard deviation in the estimate of the unknown activity.) A calibration curve is needed to establish the relation between activity and count rate. This curve reflects the detector sensitivity as well as the properties of the scintillating sample which is measured. On the other hand, the anode-current detection method would make available, during the same period of time, a current signal which could be recorded. The mean level could then be estimated from the graph.

There is, however, a main difference between the two methods described above which becomes of great importance when scintillations are recorded. The number of photons released depends upon the kinetic energy of the particle being absorbed in the scintillator. The lifetime of the excited state being responsible for the photon emission may vary for different scintillators from several minutes down to fractions of nanoseconds. From fast scintillators the photons of a particular scintillation will arrive simultaneously at the photocathode of the photomultiplier and produce one large composite detection pulse. From slower scintillators the individual photons may be detected as discrete pulses of smaller magnitudes.

Anode-current detection does not discriminate between these two situations. The current level is a direct measure of the total number of photons released per second. The measurement of photomultiplier anode currents thus permits a true comparison of the β -radioluminescent efficiencies of different scintillators. Furthermore the method truly reflects differences in light output from β -emitters with different electron energy distributions.

Also, one may expect to more accurately follow changes in light emission from a scintillating sample, due for example to changes in temperature, because thermal or other quenching of β -excited luminescence or its scattering or absorption principally reduces the number of photons emitted in each of the scintillations, while the scintillation (pulse) count rate will be found more constant (provided one has a good geometry of measurement, a large enough scintillation efficiency, and a high quantum efficiency photomultiplier). It should be added, however, that the pulse-counting method permits a simultaneous pulse-height analysis, which might constitute a means of discriminating between noise pulses, ^3H -induced pulses and ^{14}C -induced pulses, in solid as well as in liquid scintillator systems. Such a method of discrimination could be a very valuable tool in double-labeling TLRC experiments².

Several parameters determine the practical efficiency of a scintillator present as an admixture to a chromatographic adsorbent. Such parameters are, among others, the true scintillator efficiency, the percentage of scintillator added to the medium, the grain sizes and optical properties of the components, and the temperature and humidity of the sample.

Linearity of the measuring system

To enable good quantitative measurements, a high degree of reproducibility is required. A linear relationship is preferred provided a large enough measuring range is then experimentally attainable. In Fig. 1 are shown curves giving the relationship between spot activities (given in nCi of either ^{14}C or ^3H) and photomultiplier response

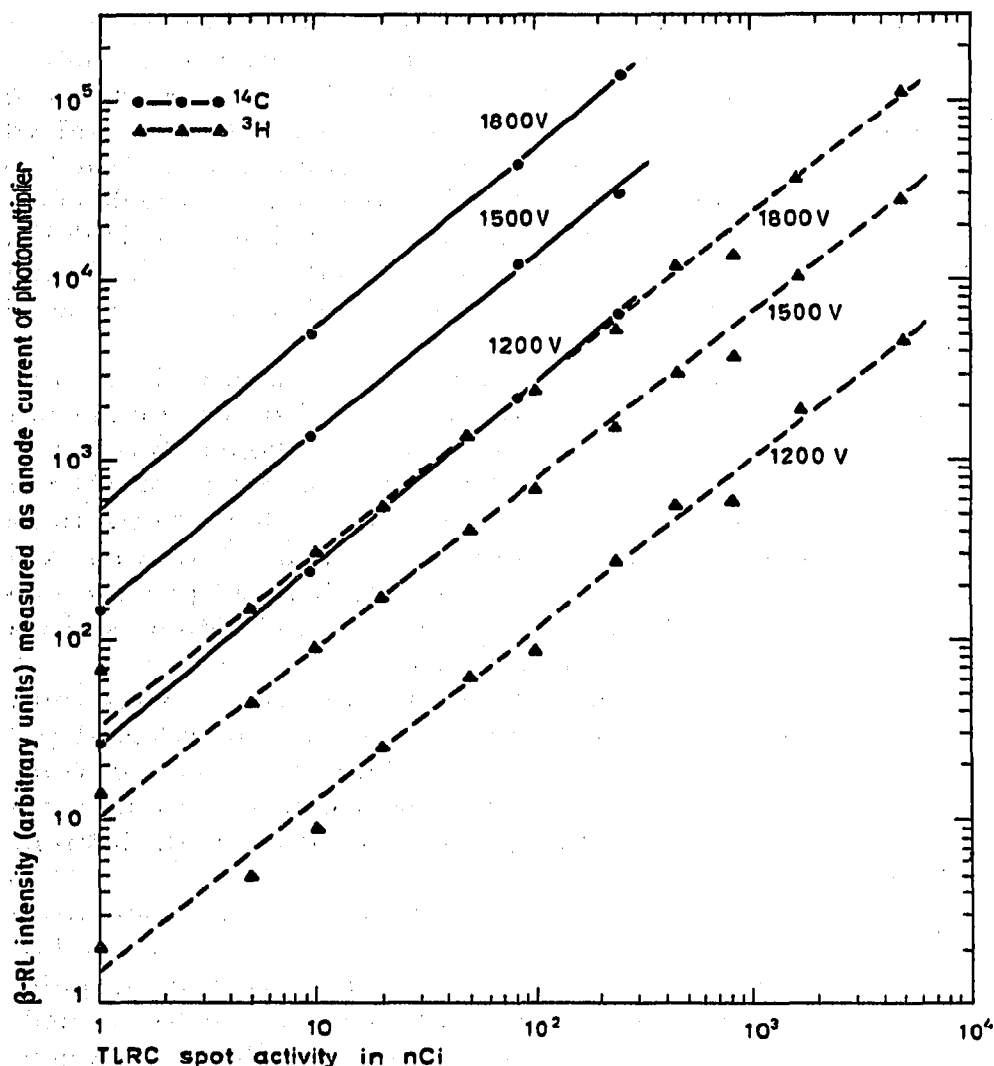


Fig. 1. The β -RL intensity for various values for the high voltage of the photomultiplier shown as a function of ^{14}C and ^3H activity of spots applied on Silica Gel 7736 H (Merck) with 75% w/w admixture of the scintillator $\text{Zn}_2\text{SiO}_4\text{-Mn}$, $[\text{Mn}]:[\text{Zn}] = 3 \cdot 10^{-2}$.

(anode current). The curves are seen to be linear to a good approximation. Generally the detection response to 1 nCi of ^{14}C is about 20 times larger than to 1 nCi of ^3H , since the scintillations produced by the former radionuclide are larger due to the larger ^{14}C β -energies. Another general trend which may be seen is the increase in the detector response resulting from an increasing high voltage (1200–1500–1800 V). The anode current is increased because a higher interdynode potential gives a larger amplification factor in each step of multiplication. From Fig. 1 it can be judged that 1 nCi of ^3H and less than 0.05 nCi of ^{14}C may be relatively easily detected.

Optimum conditions for photomultiplier detection

As discussed already either pulse counting or current measuring techniques can be used for detection of β -radioluminescence using a photomultiplier. One important difference between these two methods of measurement is that measurement

of anode current, as opposed to pulse counting, is rather insensitive to changes in the scintillator decay time, provided one has a constant light intensity.

We have previously mentioned the linear relationship found between spot activity and photomultiplier response. For pulse counting detection this linear relationship can be expressed mathematically as

$$\dot{N} - \dot{B} = K \cdot C$$

where \dot{N} and \dot{B} are the count rates for the total number of pulses and the background pulses, respectively, K is a constant depending on the high voltage of the photomultiplier and C is the activity of the radioisotope. A similar equation can be set up between the corresponding quantities pertinent to current measurement. The constant K in the equation above may be called the "sensitivity of detection" because a large value of K would imply a high sensitivity of detection. Using a high voltage of 1500 V and measuring ^3H by means of the scintillator $\text{Zn}_2\text{SiO}_4\text{-Mn}$ (75% w/w scintillator), we find $K \simeq 20 \text{ (s} \cdot \text{nCi)}^{-1}$. The distance between the sample and the detector was about 4 cm.

Due to the statistical nature of nuclear disintegrations (*e.g.* β -emissions), the number of nuclear particles emitted per unit time is not constant even for a radioactive sample of constant strength but rather obeys the POISSON distribution. Consequently, the number of photons emitted per second from our samples and therefore the size of the recorded signal varies around some mean value. The variation is partly due to changes in the external background radiation and in part due to variation in the detector noise. This variation in the recorded signal as well as the accompanying uncertainty in the result of measurement is principally unavoidable. It is commonly assumed, as we shall do here, that the Poisson distribution is also valid for the number of pulses arriving per unit time at the photomultiplier anode. The uncertainty (usually the standard deviation) in the result obtained can be calculated on the basis of this assumption. For examples of such calculations for both pulse and current measurement, the reader is referred to the book by PRICE³ and to the references given there.

For the case of pulse counting, to which we shall limit our discussion, a very simple calculation shows that the relative standard deviation in the number of recorded pulses is equal to the inverse of the square root of this number. This is assumed to be true whether the counts are due only to the background of the photomultiplier or include the pulses produced by photons from the sample. Hence, the relative standard deviation can be made arbitrarily small provided the time of measurement is taken to be sufficiently large. A small relative standard deviation can be obtained within a short measuring time with a high-activity sample giving a total count rate much larger than the background rate. The situation is different when the total and the background count rates are comparable in magnitude. To investigate this case for our geometry of measurement, we have measured the background and total count rates for low-intensity samples with various amounts of tritium for different high voltages of the photomultiplier. The results of these measurements are reported in Table I. The background count rates given there include pulses produced in the photomultiplier tube (with no photons impinging on the photocathode) and in addition pulses due to photons emitted by a nontritiated sample excited by external background radiation.

Supposing that we measure total N pulses in time t_N and B background pulses

in time t_B , the corresponding count rates \dot{N} and \dot{B} are readily found and so is their difference $\dot{S} = \dot{N} - \dot{B}$ which is directly proportional to the sample activity. When \dot{N} is much larger than \dot{B} , the measuring times t_N and t_B are usually chosen to be different³. We shall be concerned, however, with the case where \dot{N} is almost equal to \dot{B} , and consequently put t_N and t_B equal. Then the square of the relative standard deviation in \dot{S} is given by the expression $(\dot{S} + 2\dot{B})/t\dot{S}^2$, when the relative uncertainty in the measurement of t is negligibly small. From this expression the time t necessary to obtain any predetermined relative standard deviation can be calculated. Values of t needed to obtain 10% relative standard deviation for samples with the scintillator Zn_2SiO_4 -Mn and different activities of tritium are given in Table I for four values of the high voltage of the photomultiplier. (A somewhat similar investigation has earlier been reported for anthracene⁴.) Clearly, we can measure tritium activities as small as 1 nCi with a relative standard deviation of 10% with less than 5 min total measuring time (background and sample), with our geometry of measurement and a suitable high voltage of the photomultiplier. (If one is using a manually operated stopwatch, the uncertainty in t becomes significant compared with the short times obtained for 98 nCi 3H using the above analysis. One should then take a somewhat larger measuring time.)

Under the heading "Figure of merit" in Table I are given the values of the expression $(\dot{S} + 2\dot{B})/\dot{S}^2$, which is seen to be equal to the square of the relative standard deviation in \dot{S} multiplied by the time t . The value of the figure of merit thus defined is equal to one hundredth of the time necessary to reach 10% accuracy in \dot{S} , as is easily verified. The smaller this figure of merit, the shorter the time needed to measure the sample intensity with a predetermined accuracy. With this figure of merit experimental arrangements with one and the same photomultiplier as well as with different photomultipliers can be compared. It is seen from Table I that our figure of merit decreases with increasing high voltage of the photomultiplier. In the literature⁵ other figures of merit have been chosen, perhaps better suited to specific operational conditions (within the related field of liquid scintillation detection).

TABLE I

PERFORMANCE OF A PHOTOMULTIPLIER PHOTON COUNTER MEASURING 3H -INDUCED β -RL IN 75 % w/w Zn_2SiO_4 -Mn IN SiO_2 (MERCK, 7736 H)

Activity of 3H (nCi)	High voltage (V)	Total count rate (sec ⁻¹)	Background count rate (sec ⁻¹)	Efficiency (c.p.m./d.p.m. %)	Figure of merit	Time to reach 10% accuracy (sec)
98	900	80	10	2	$180 \cdot 10^{-4}$	$180 \cdot 10^{-2}$
	1200	1500	156	36	$9.2 \cdot 10^{-4}$	$9.2 \cdot 10^{-2}$
	1500	2100	220	52	$6.6 \cdot 10^{-4}$	$6.6 \cdot 10^{-2}$
	1800	2400	258	58	$5.8 \cdot 10^{-4}$	$5.8 \cdot 10^{-2}$
10	900	19	10	2	$36 \cdot 10^{-2}$	36
	1200	300	156	39	$2.2 \cdot 10^{-2}$	2.2
	1500	440	220	59	$1.4 \cdot 10^{-2}$	1.4
	1800	520	258	71	$1.1 \cdot 10^{-2}$	1.1
1	900	11	10	3	21	$21 \cdot 10^2$
	1200	170	156	37	1.7	$1.7 \cdot 10^2$
	1500	240	220	54	1.2	$1.2 \cdot 10^2$
	1800	280	258	59	1.1	$1.1 \cdot 10^2$

Let the standard deviation in the recorded count rates be s_N and s_B for the total and background count rates, respectively. When the high voltage of the photomultiplier is held fixed, the rate \dot{N} approaches \dot{B} as the sample intensity approaches zero. For a certain activity the following relation will be fulfilled,

$$\dot{N} - s_N = \dot{B} + s_B$$

implying that the rate of pulses recorded is just sufficient to allow a "certain" discrimination between sample and background intensities. We choose to call this activity the "minimum detectable activity". Clearly, the minimum detectable activity defined above depends on the time t of measurement, such that an increase in t results in a decrease in the minimum detectable activity. Conversely we can calculate, on the basis of our criterion, the value of t necessary to detect a certain activity, provided the values of \dot{N} and \dot{B} are approximately known. We are, for instance, able to detect an activity of 1 nCi ^3H in the scintillator $\text{Zn}_2\text{SiO}_4\text{-Mn}$ with t smaller than 3 sec, according to the \dot{N} and \dot{B} values in Table I. However, at this limit of detection the relative standard deviation in the observed sample intensity is larger than 70%.

Also in Table I is given the "detection efficiency", here defined as the ratio between the number of pulses recorded per unit time and the total number of nuclear disintegrations per unit time. As a consequence of this definition, the efficiency is directly proportional to $(\dot{N} - \dot{B})/C$, which we already have found to be independent of the sample activity when the high voltage of the photomultiplier is constant.

Lastly may be added that experiments with ^{14}C -labeled substances, instead of ^3H compounds, would yield exactly the same statistics, except that the values given in Table I would be reproduced for activities about 20 times smaller.

EXPERIMENTAL

Materials

Table II shows some data for the scintillators and the other substances used. In the upper part are listed commercial adsorbents for TLC and in the lower part the applied scintillators. (Data are also included for the chromatographic media applied earlier in Part I of this work (ref. 1)).

On the Eastman chromatogram sheets, a 100- μm layer of silica gel is bound with polyvinyl alcohol to a flexible solvent-inert base of polyethylene terephthalate. The fluorescence indicator added in the K 301R is calcium silicate: (Mn, Pb).

A manganese-doped gypsum was prepared by TENGSAREID⁶ at this institute according to a recipe of BJÄRNGÅRD⁷. The UV fluorescence indicator used in the F media (Merck) had been found to be a very efficient scintillator useful for β -RL detection⁸. For the present investigation this scintillator, $\text{Zn}_2\text{SiO}_4\text{-Mn}$, was made available by the producer in a range of dopant concentrations ($[\text{Mn}]:[\text{Zn}] = 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}$) in addition to a manganese-free zinc silicate and their standard F media. (These contain 1.5% zinc silicate.)

From mass spectrometric measurements, one may roughly estimate the Mn content to be 3% in the standard type $\text{Zn}_2\text{SiO}_4\text{-Mn}$ and the impurities given in Table II are found to be present.

TABLE II

DATA FOR INVESTIGATED SUBSTANCES

Chromatographic media	Binder CaSO ₄ (%)	Maximum impurity contents (%)			Fluorescence indicator (%)	pH of suspension	Grain dimen- sion (μ m)	Com- ments
		Fe	Cl	Cu				
<i>Alumina (Merck)</i>								
1090 G	10	0.02	0.05			7.5	5-30	
1092 GF ₂₅₄	10	0.02	0.05		1.5	7.5	5-30	^a
1085 H		0.02	0.05			9.5	5-30	
1094 HF ₂₅₄		0.02	0.05		1.5	9.5	5-30	^a
<i>Silica Gel (Merck)</i>								
7731 G	12-13.5	0.03	0.02	0.0002		7	10-40	
7730 GF ₂₅₄	12-13.5	0.03	0.02		1.5	7	10-40	^a
7736 H		0.03	0.02			7	10-40	
7739 HF ₂₅₄		0.03	0.02		1.5	7	10-40	^a
K301R (Eastman)	polyvinyl- alcohol				(see text)			Prefabricated
K301R2 (Eastman)								layers ^b
SilicAR TLC-7F (Mallinckrodt)					white			
MN-Silica Gel N-HR (Macherey, Nagel & Co.)					254 nm			^c
Silica Gel DF-O					254 nm			^c
(Camag)					254 nm			^c
<i>Scintillating substances</i>								
	<i>Impurities</i>				<i>Dopant concentration</i>	<i>Comments</i>		
Woelm fluorescent indicator						Green		
Anthracene	Purity as for scintil- lation purposes					254 nm		^c
2,5-diphenyloxazol (PPO)	Purity as for scintil- lation purposes					Merck product 1454		
Glass (powder) NE 901						Merck product 2946		
						Nuclear enterprises grain dimension 10-40 μ m		
Gypsum CaSO ₄ -Mn	Main: Al, As, Ca, Cr, Fe, K, Na Faint: Cd, Ca, Ga, Ni, Se, V				[Mn] : [Zn] = 3×10^{-2}			Preparation: see ref. 6,7
Gypsum CaSO ₄ · $\frac{1}{2}$ H ₂ O								Merck "binder"
Zn ₂ SiO ₄ -Mn								^a
Zn ₂ SiO ₄ -Mn (varied concentration of dopant)					[Mn] : [Zn] = 10 ⁻³ , 10 ⁻⁴ , 10 ⁻⁵ , 10 ⁻⁶			
Zn ₂ SiO ₄ (undoped)					[Mn] = 0 (?)			

^a Standard type of fluorescence indicator in the Merck F media

^b CaSiO₃-(Mn, Pb)

^c Type of indicator unknown. The Merck preparations were obtained from E. Merck AG, Darmstadt, G.F.R.; the Eastman Chromagram Sheets from Distillation Products Industries of Eastman Kodak Co., Rochester, N.Y., U.S.A., the SilicAR from Mallinckrodt Chemical Works, St. Louis, U.S.A.; the MN-Silica Gel from Macherey, Nagel & Co, 516 Düren, G.F.R.; and the DF-O Silica Gel from Camag (Chemie-Erzeugnisse und Adsorptionstechnik AG) 4132 Muttenz, Switzerland.

Sample preparation

The Eastman Chromagram prefabricated sheets were cut into circular discs (5 cm in diameter) so as to fit into the measuring apparatus. Using the other standard adsorbents, samples were made by applying thoroughly mixed aqueous suspensions to glass discs in amounts giving 0.2-mm-thick layers, and the discs were dried in air at room temperature. Variations in thickness are believed to be unimportant, regarding the accuracy and reproducibility in our measurements.

Two-component mixtures of various adsorbents with different amounts of scintillators were prepared by grinding in an agate mortar for 10 min or more. Prior to this any large-grain component had to be ground separately. For anthracene, homogeneous mixtures were not easily obtained. Thin-layer preparations from these mixtures could be best obtained from slurries made with benzene or 96% alcohol⁹. For some of the measurements, anthracene was added to the media by pipetting a saturated benzene solution onto Eastman prefabricated layers.

Even if our samples are different from those found in practical TLC, they fully serve our purpose of investigating the β -induced luminescence and its dependence on various parameters.

Either ^3H or ^{14}C activities in the range from 1 to 5000 nCi were applied by pipetting small volumes (5 or 10 μl) of glucose stock solutions made by dilution from commercial standard solutions* onto the dry samples.

Separation in layers with scintillator admixtures

A study of the changes occurring in the separation properties upon addition of scintillator to the TLC media was undertaken as a separate project¹⁰ at the Central Institute for Industrial Research. TLC plates with layers containing either anthracene or $\text{Zn}_2\text{SiO}_4\text{-Mn}$ in amounts from 25 to 100% were prepared after various pretreatments of the scintillator. As base material either Kieselguhr G, Silica Gel G or cellulose was used.

Mixtures of the materials used for the separation studies were chosen from the following chemical groups: amino acids, carbohydrates and phospholipids. The separation quality in the scintillator-containing media as determined from coloring techniques could be compared with that in the pure media for development under identical conditions.

The investigated systems are given in Table III. As a general conclusion it can be said that anthracene introduces very small changes in the separation patterns. Addition of zinc silicate gives some modifications. A poorer separation is obtained for the amino acids, especially in cellulose media upon addition of the silicate scintillator.

Methods of measurement

The first practical application of β -RL with photomultiplier detection seems to be that of SELIGER AND AGRANOFF⁴ in 1959.

For our measurements of luminescence intensity, an EMI 9558 AQ photomultiplier specially selected to have high photocathode sensitivity and low noise was used. The photomultiplier was mounted with the front window (5 cm in diameter) at a

* Obtained from The Radiochemical Centre, Amersham, Buckinghamshire, Great Britain.

TABLE III

SELECTED CHROMATOGRAPHIC TEST SYSTEMS WITH DEVELOPERS AND COLOR REACTIONS

	<i>Test system</i>		
	<i>Carbohydrates</i>	<i>Phospholipids</i>	<i>Amino acids</i>
<i>Components</i>	Rhamnose, xylose, arabinose, mannose, glucose, and galactose (Eastman Organic Chemicals)	Lecithin, unpurified (A/S Norsk Soyamel-fabrik)	Cystine, glycine, leucine, lysine (Shandon standard solutions)
<i>Adsorbents</i>	Kieselguhr G (gypsum)	Kieselgel G	Cellulose and Kieselgel G
<i>Developing solvents</i>	Butanol-acetone-water (40:50:10)	Chloroform-methanol-water (65:25:4)	Chloroform-methanol-17% ammonia (40:40:20)
<i>Color reagents</i>	Phthalic acid-aniline in acetone	Molybdenum reagent	Ninhydrin reagent
<i>Color reactions</i>	Brownish spots on all types of adsorbents. Zinc silicate weakens the color strength. Luminous spots visible in UV light (350 nm)	Bluish spots in daylight; on anthracene layers there was a blue-grey background	Blue-grey to violet spots on silica gel and cellulose layers without scintillator. Orange spots with zinc silicate present in the former case, and red-grey to violet spots with anthracene present in the latter case

distance of 4 cm from the sample to be measured. The light-collecting power was not greater than about 8%. Scattering and self-absorption gave a further signal reduction. By cooling with dry ice, one could maintain the temperature of the photomultiplier at about -78° . This cooling resulted in a 20-fold reduction in the dark current. The corresponding mean pulse count rate obtained was about 130 per second with a high voltage of 1500 V.

MEASUREMENTS AND RESULTS

A general consideration leads to the requirement of efficient, powdered scintillators. Their decay times are of no interest as long as detection of film or photomultiplier current is applied. Their addition to the TLC medium should not disturb the fractionation procedure too much, and the scintillator should preferably be inert. Their scintillation properties should be very stable under normal conditions and the adopted method of producing thin-layer plates from the scintillator-adsorbent slurry should not result in an unacceptable variability in the practical luminescence efficiency. Several new scintillating substances have been investigated and a great range of ^3H activities have been used in the β -luminescence tests. Some ^{14}C measurements have been included for comparison. For two of the scintillators, anthracene and $\text{Zn}_2\text{SiO}_4\text{-Mn}$, extensive performance tests have been made.

In the following we shall present the results obtained and compare the various scintillators. (Most are in two-component mixtures containing silica gel.) For several of the media investigated (standard thin-layer adsorbents, Merck), it was found that gypsum, present as a binder, was a moderately good scintillator¹. This fact might explain the finding of WILSON AND SPEDDING¹¹ that Silica Gel 7731 G showed β -luminescence even with no extra scintillator added. Anthracene is known already to

have found some application in TLRC as a scintillator⁹. Among the scintillators investigated by us, it seemed that Zn_2SiO_4 -Mn (artificial willemite) had the highest β -sensitivity.

The reservation must be made that the established efficiencies for some of the scintillators are slightly erroneous. This is so because we have made no attempt to measure or compensate for the differences in the various emission spectra. All the samples have been measured in the same system and the full spectral sensitivity of the 9558 AQ photomultiplier has been used. Its response curve is relatively flat from 180 to 450 nm (the quantum efficiency is within the range 18–27%, and an appreciable sensitivity is retained even at 550 nm (11%)). Thus we believe that no very great errors are introduced in the efficiency comparison. In any case our comparison is directly valid for the applied photomultiplier, the quantum efficiency of which ranks among the highest obtainable at present.

Relative scintillation efficiencies

For several standard thin-layer adsorbents and scintillator materials, the properties of which are given in Table II, the scintillation efficiencies are given in Table IV. The adsorbents (Eastman; Camag; Macherey, Nagel & Co.; and Mallinckrodt) which already contain a scintillator, have been measured in 100% adsorbent samples. Their intensities are to be compared with those obtained from the commercial (Merck) adsorbents of the F-type.

TABLE IV

RELATIVE SCINTILLATION INTENSITIES, OBTAINED FROM MEASUREMENT OF PHOTOMULTIPLIER CURRENT AT A HIGH VOLTAGE OF 1500 V

All data are corrected for photomultiplier dark current.

Scintillator loaded medium		Activity, nCi	Relative intensities (arbitrary units)	Count rate to current ratio (arbitrary units)
Scintillator (%)	Adsorbent (%)			
Zn_2SiO_4 -Mn, standard (75)	SiO_2 7736 H, Merck (25)	3H , 238	100	2.4
Zn_2SiO_4 -Mn, standard (75)	SiO_2 7736 H, Merck (25)	^{14}C , 9.6	97	2.4
Anthracene (?)	Eastman K301R2, prefabricated layer (?)	3H , 238	15	1.2
Anthracene (?)	Eastman K301R2, prefabricated layer (?)	^{14}C , 9.6	11	1.0
Anthracene (75)	SiO_2 7736 H, Merck (25)	3H , 5000	95	1.4
Anthracene, old sample (50)	SiO_2 7736 H, Merck (50)	3H , 5000	15	2.3
Unknown scintillator additive, added by manufacturer (?)	SiO_2 DF-O, Camag (?)	3H , 5000	34	2.3
Unknown scintillator additive, added by manufacturer (?)	SiO_2 N-HR, Macherey, Nagel & Co. (?)	3H , 5000	32	2.6
Unknown scintillator additive, added by manufacturer (?)	SiO_2 TLC-7F, Mallinckrodt (?)	3H , 5000	6	2.8
Gypsum, Tengsareid (50)	SiO_2 7736 H, Merck (50)	3H , 5000	61	2.4

The relative intensities given in Table IV are obtained from measurements of anode current (high voltage = 1500 V). Also, the pulse count rate was measured at the same high voltage but with a second photomultiplier tube. All data were corrected for detector noise which had a level of 30 current units or 130 counts/sec. In the last column of Table IV the ratios between the count rates and current values are given in arbitrary units. These ratios are seen to vary considerably from one sample to another, showing that the two methods of measurement may yield different values for the relative efficiencies. Measurements performed with a pulse-height multichannel analyzer² support the view that such variations in the count rate to current ratios may be due to multiphoton pulses in the photomultiplier (for fast efficient scintillators). As stated earlier, the current measurement technique is the more reliable method for comparing scintillator efficiencies.

The higher ratios in Table IV probably correspond to larger scintillator decay times (photons arriving singly at the photocathode). An increased amount of scintillator will not change this ratio. A decreased absorption of light in the sample will give the same effect as an increased efficiency, namely to lower the ratio, provided the decay time is small enough to cause multiphoton pulses in the photomultiplier. This latter point is shown clearly for anthracene (Table IV), for which the count rate to current ratio ranges from 1.0 to 2.3. The higher of these ratios is obtained for an old sample, in which the aging effect (to be discussed) has caused a marked decrease in luminescence intensity.

Importance of the layer thickness

In a particular experiment the reproducibility might depend on several parameters related to the layer thickness, *e.g.* the depth profile of radionuclide adsorption, the β -particle range, the scintillator microdistribution, and finally the absorption and scattering of the emitted luminescence within the layer. This is particularly the case for short-range β -emitters. The scattering and absorption again are dependent upon the reflection and absorption coefficients of the grain components in the layer for the emitted luminescence. These relationships have been thoroughly discussed recently¹². In anthracene the self absorption is known⁵ to be very substantial at wavelengths below 410 nm, even for thicknesses of a few microns.

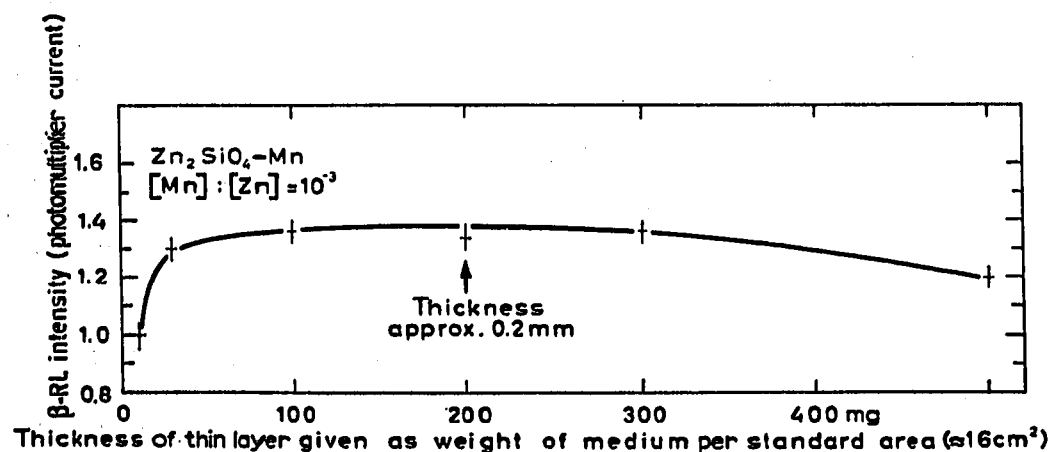


Fig. 2. The β -RL intensity as a function of thin-layer thickness for layers of pure scintillator ($\text{Zn}_2\text{SiO}_4\text{-Mn}$). Spots of 453 nCi of ^3H were applied.

For our practical purpose, only one control experiment was done. As is shown in Fig. 2 the overall efficiency showed a broad maximum when the thickness was varied. (The sample layers were made from pure zinc silicate scintillator of standard type, but with a Mn-Zn ratio of 10^{-3} .) Errors in the results due to variations in thickness when keeping close to 0.2 mm seem improbable in view of the broad maximum observed (no important change in the range 0.05 to 0.3 mm). The area of the applied spots (for a constant volume of added solution) varied, however, with the thickness, growing slightly larger as the layers were made thinner.

To what degree systematic differences occur between the various media in the "depth distribution" of activity within the sample is not known. Furthermore, the drying procedure might also leave a glucose deposit of systematically different magnitude for grains of the different components, *i.e.* SiO_2 , Al_2O_3 , $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and Zn_2SiO_4 -Mn or anthracene. Such a mechanism might partly explain the differences found in Part I (Fig. 1) between the emission spectrum of β -RL and that of X-ray-induced thermoluminescence observed in 1092 GF alumina. The enhancement of the gypsum peak in the β -RL spectrum could thus be due to a tendency for the glucose to concentrate on the CaSO_4 particles or in their close vicinity.

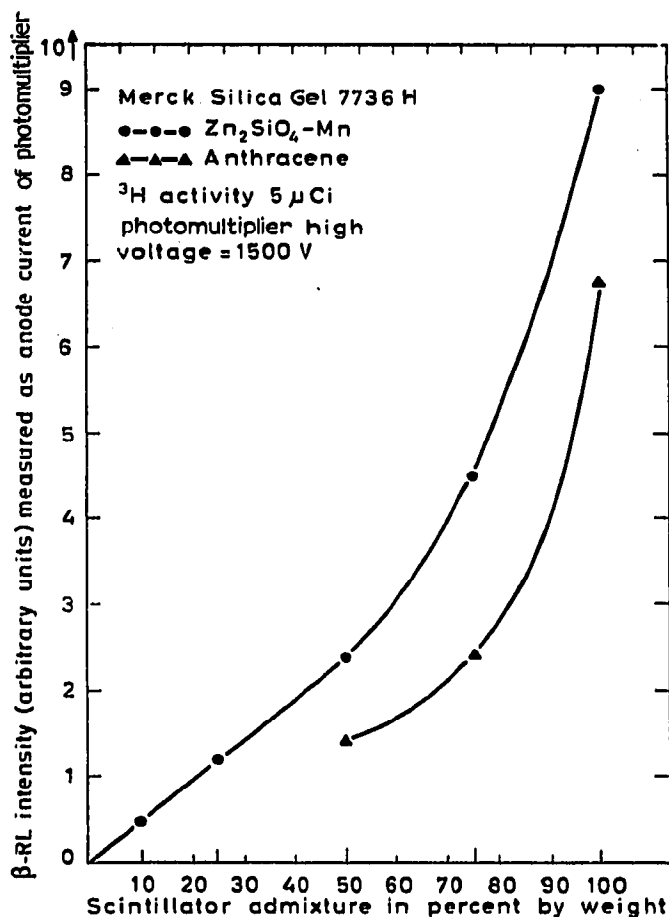


Fig. 3. The β -RL intensity for various percentages (w/w) of scintillator added to Silica Gel 7736 H (Merck). The Zn_2SiO_4 -Mn values were obtained for an activity of 0.83 μ Ci ^3H but have been correspondingly increased.

Variation in detection efficiency with the amount of scintillator

In Fig. 3 are shown curves for β -radioluminescence measured from samples containing various percentages of either zinc silicate or anthracene scintillator added to SiO_2 (7736 H). Anthracene was found to be inferior to zinc silicate. Impurities introduced in the anthracene microcrystals formed in the samples (*e.g.* due to the applied solvent) might, however, have reduced the efficiency with as much as 2/3 (ref. 5).

In the diagram the light output is plotted *vs.* % (w/w). The curve shapes cannot easily be explained in detail, but the following simple model may clarify the situation somewhat. Let us suppose the tritiated sugar solution to be deposited evenly with no discrimination between adsorbent or scintillator grains (being of equal size). Furthermore let us suppose that the effective stopping volumes (for the β -particles) of air and the sugar itself are negligible. Then a rough assumption will be that the light output (I) is proportional to the fraction of the total sample volume made up by the scintillator, *i.e.*

$$I \sim \frac{V_s}{V_s + V_a} = \frac{P_s/\sigma_s}{P_s/\sigma_s + P_a/\sigma_a} = \frac{P_s}{P_s + \sigma_s P_a/\sigma_a}$$

where V_s , σ_s , P_s , and V_a , σ_a , P_a are the volume, density and weight of the scintillator and adsorbent, respectively.

This expression gives a curve shape similar to the observed ones, but somewhat less linear. Starting with a good agreement, I_{exp} becomes increasingly smaller than I_{theor} for larger contents of the scintillators. However, no attempt is made to introduce pertinent modifications in the above expression to account for varying grain sizes, light scattering and absorption and, for anthracene, possible quenching effects as well. Reabsorption occurs readily at wavelengths below 410 nm (see ref. 5).

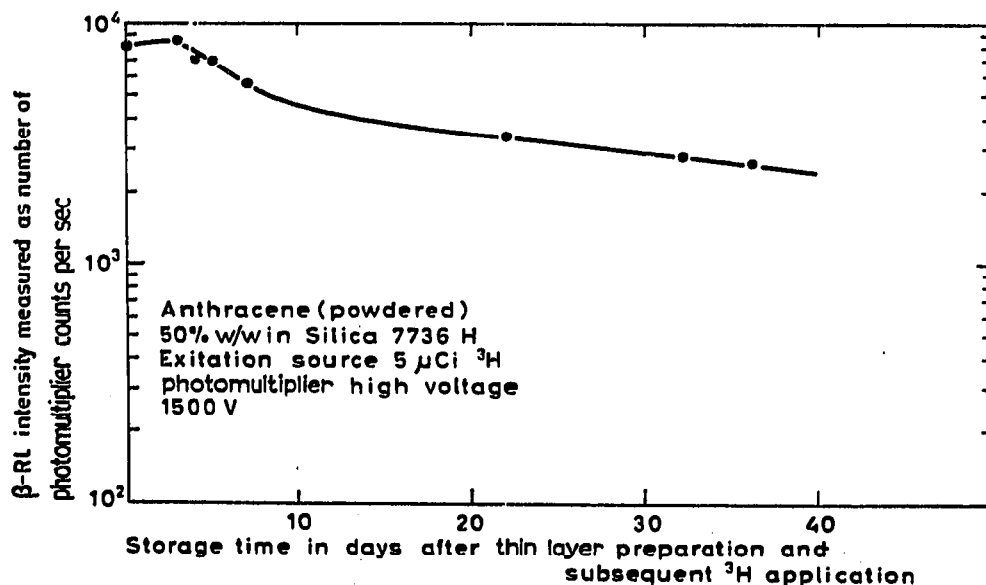


Fig. 4. The decay of anthracene β -RL efficiency during storage of the radiochromatogram.

Changed β -radioluminescence efficiency upon storage

Fig. 4 shows how the anthracene efficiency decreases upon prolonged storage. The fact that pulse counting is applied here means that the changes in scintillation intensity (representing the number of photons produced per disintegration) might be slightly larger than reflected in the curve shown but cannot be smaller. The effect might be due to a decomposition or oxidation of the anthracene, possibly light stimulated, and is followed by the formation of a brownish substance. This formation occurs much faster for anthracene stored in a powder mixture with the SiO_2 7736 H than for pure powdered anthracene, when both are exposed to air and light. Both the color change and the decrease in efficiency may be substantially slowed down by storage in a vacuum and by excluding the light. The β -radioluminescence deterioration seems not to depend very much on the applied ^3H activity. To check this point two identical samples were measured after several weeks of storage in darkness, the one having been tritiated prior to the storage and the other just before being measured. Almost identical intensities were observed.

For the other scintillators no systematical investigation of luminescence deterioration was made. At least for $\text{Zn}_2\text{SiO}_4\text{-Mn}$, however, it can be stated that no systematic decrease was prominent.

To establish the practical usefulness of the suggested method, some further conditions would need to be elucidated, and for this reason the effect of (a) light exposure during sample preparation, and (b) vacuum and humidity, have been investigated. Results from the humidity tests are given in Table V.

A luminescence could be observed from anthracene-loaded as well as from zinc silicate-loaded thin-layer adsorbents after exposure for 5 min to sunlight. For the latter scintillator the decaying luminescence (leakage thermoluminescence) could be followed for several hours. However, after handling in subdued light from an incandescent lamp or when using a red safelight no important anthracene background remained after 5 min. For media loaded with zinc silicate, a practical procedure should include some care in the arrangement of the safelight system or a short period of storage in darkness prior to the β -radioluminescence measurements.

The experiments indicated that storage at a high level of humidity or in a vacuum (better than 10^{-4} mm Hg by using an oil diffusion pump) reduced the β -radioluminescence for all scintillators. The deterioration mechanisms for the various substances are not known. From Table V it is seen, however, that there is a tendency for the samples to recover when they are allowed to stand in dry air after the humidity exposure. A direct comparison between the media is made somewhat difficult by the different ^3H activities and amounts of scintillator additives. As mentioned in the foregoing section, the actual changes might be somewhat larger than those observed by the pulse-counting techniques.

Effect of lowered temperature on the β -radioluminescence efficiency

We have found no important increase in efficiency for samples loaded with either anthracene, PPO, or NE 901 glass scintillator when lowering the temperature even down to that of boiling nitrogen¹³. This fact does not corroborate some results reported earlier for the former two systems^{9,14}. In these investigations, however, scintillation autoradiography on film materials cooled down together with the samples had been applied. Experiments are in progress to unravel the discrepancies.

TABLE V

SCINTILLATOR HUMIDITY TEST

In all the count rates, obtained at 1500 V high voltage, corrections are made for photomultiplier noise count rates and dead-time losses.

Scintillator loaded TLRC medium		Acti- vity (nCt of ^3H)	Relative luminescence intensities (photomultiplier count rates, sec^{-1} , after successive pretreatments of one and the same sample (of each type))						
Scintillator (%)	Adsorbent (%)		Normal 20-35% H_2O (rel.)	2 days 100% H_2O (rel.)	1 day normal	2 days normal	4 days normal	2 days with P_2O_5	2 week vacuum 10^{-4}m Hg
Zn ₂ SiO ₄ -Mn, standard (75)	SiO ₂ 7736 H, Merck (25)	453	100	74	86	90	91	92	92
Zn ₂ SiO ₄ -Mn, standard (75)	SiO ₂ 7736 H, Merck (25)	238	100	64	85	92	92	94	94
Anthracene (50)	SiO ₂ 7736 H, Merck (50)	5000	100	64	104	104	104	106	102
Gypsum, Tengsareid (50)	SiO ₂ 7736 H, Merck (50)	5000	100	44	71	76	95	100	78
Unknown scintillator additive, added by manufacturer (?)	SiO ₂ , Macherey, Nagel & Co. (?)	5000	100	71	100	124	124	159	112
Unknown scintillator additive, added by manufacturer (?)	SiO ₂ , TLC-7F, Mallinckrodt (?)	5000	100	50	120	120	130	170	120
NE 901 (50)	SiO ₂ 7736 H, Merck (50)	5000	100	45	85	90	88	92	87
Anthracene, method of of impregnation, see ref. 13 (?)	Eastman K301R2, prefabricated layer (?)	5000	100	52	83	81	80	80	72

For samples frozen down after impregnation with liquid scintillators, on the other hand, a rather great enhancement in the efficiency has been observed¹³, this being mainly in and below the temperature range of solidification. Some of the results are shown in Fig. 5. We believe our measurements with the photomultiplier to be much more reliable than film exposures for establishing the quantitative relationship between β -radioluminescence efficiencies and the temperature¹⁵.

The importance of Mn doping in Zn₂SiO₄-Mn

As mentioned in Table II the standard Mn content in Zn₂SiO₄-Mn was about 3%. It is clear from Fig. 6 that no important increase in efficiency can be expected from making the concentration larger than 3%. Curve 2 represents the luminescence intensity remaining when the value for zero Mn content was subtracted (from curve 1). Since measurements of the photomultiplier current were applied and zinc silicate is a "slow" scintillator, the curves are quite reliable. Whether the small distances between the Mn centers (if evenly distributed within the crystal lattice) or an Mn cluster formation at higher concentrations¹⁶ is responsible for the limited increase in the luminescence is not known.

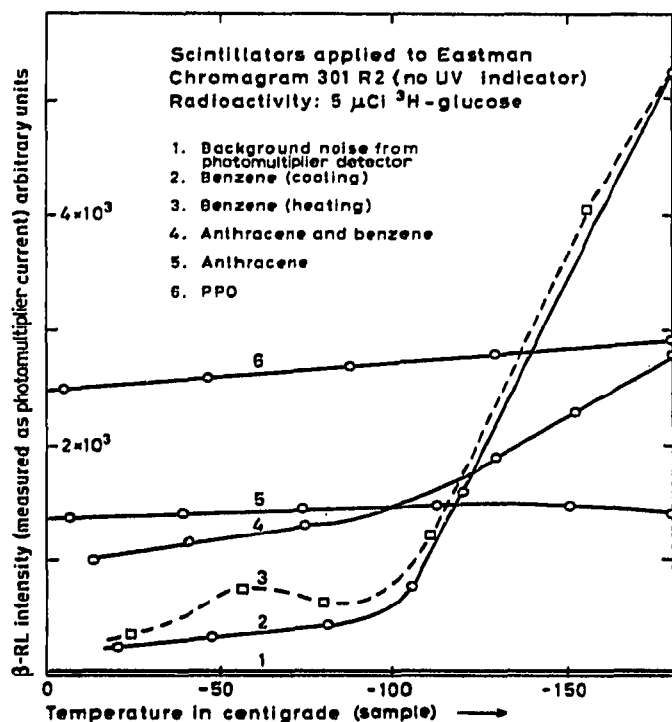


Fig. 5. The effect of lowered temperature on the β -RL efficiency. The different behavior of solid and liquid scintillators is clearly seen.

The luminescence level found at zero concentration might still be due to Mn traces or other impurities. No control of emission spectra has been attempted. At the present stage these relationships will not be studied any further.

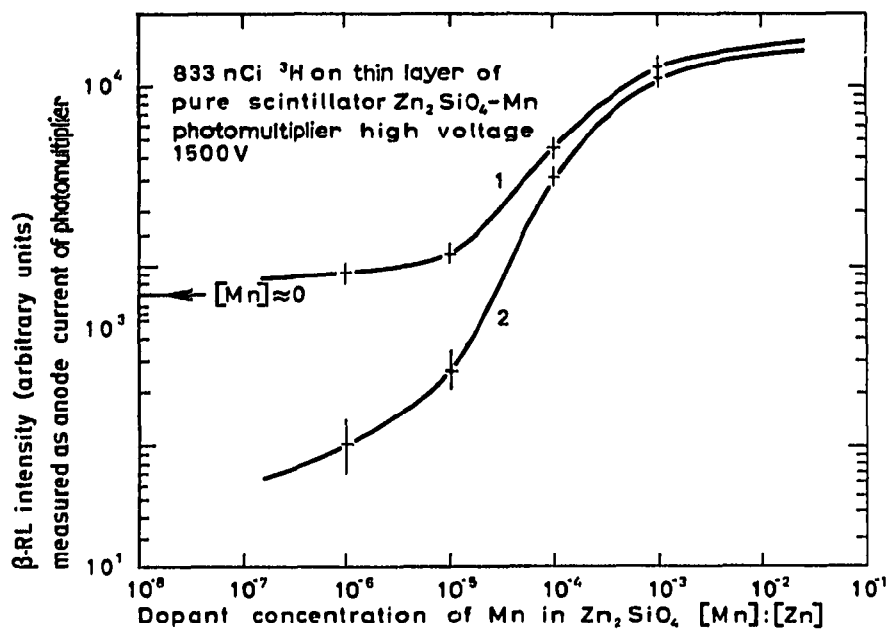


Fig. 6. The variation of β -RL intensity with dopant concentration of Mn in the pure scintillator $\text{Zn}_2\text{SiO}_4\text{-Mn}$. The intensity for zero Mn content is indicated. Curve 2 is the Mn luminescence obtained when the above zero level is subtracted from curve 1.

DISCUSSION AND CONCLUSION

The essential result of these investigations is the general establishment of the method of photoelectric detection of radionuclides in TLRC by means of adding solid scintillators. Experiments show that for most chemical systems, the separation can probably be performed even when large amounts of scintillator have been added to the layer. It is beyond doubt that for systems not being harmed by scintillator admixtures, β -radioluminescence detection is to be preferred for its high sensitivity (especially for low-energy radionuclides) and simplicity. The detailed working conditions of the photoelectric detection system are not stated and will in fact be determined by the type of scintillator (efficiency, decay time) and its amount in the adsorbent mixture, by the level of radioactivity to be detected, and finally by the type of detection (single-spot counting or scanning) and the instrumental design. With a suitable scintillator it is clear that spot activities smaller than 1 nCi ^3H or 0.05 nCi ^{14}C may easily be detected within about 2 sec. At this activity level uncertainties smaller than 10% may be reached within 200 sec.

Some commercial thin-layer media already containing a small amount of scintillator were studied. In addition, anthracene and manganese-doped zinc silicate were more thoroughly investigated. The latter system seems to have a slightly larger luminescence yield and, with a large decay time, is the scintillator best suited for photomultiplier pulse-counting techniques. Its light sensitivity, however, is a drawback. The use of a red safelight substantially reduces the inconvenience.

A warning must be made against taking the relative scintillation efficiencies established here to be strictly valid for film exposure. Recent results seem to indicate that the exposure efficiencies are also dependent on the scintillator decay times, so that long decay times give a decreased efficiency¹⁵.

In the method described a linear relationship exists between the activity and the detected signal. Variations in layer thickness are not of very great importance for the reproducibility, at least not for the zinc silicate type of scintillator. The light output (per disintegration) is found to be strongly related to the scintillator content in the applied adsorbent layer and no important deviations from expected results are found due to uneven scintillator distribution in the produced thin-layer plates.

As concerns the standard type $\text{Zn}_2\text{SiO}_4\text{-Mn}$ (UV indicator for TLC adsorbents produced by Merck), no important increase in its electron-induced luminescence could be obtained by a further increase of the Mn content.

As reported elsewhere¹³ no important increase in luminescence efficiency upon cooling was achieved for zinc silicate, anthracene, PPO or NE 901. It is evident from our measurements that nearly all the investigated scintillator preparations are sensitive to humidity, even if a partial restoration of the luminescent efficiency occurs when the sample is again placed in a dry atmosphere.

For anthracene a decay is also found during storage in a normal atmosphere. Briefly, the process responsible for the luminescence deterioration seems to be accelerated by air and light and might perhaps involve an oxidation. A possible trivial explanation for the decreased luminescence efficiency found after exposure to vacuum for gypsum and the Mallinckrodt and Nagel scintillators might be a deposit of a film of vacuum oil, as no oil trap was applied. This was not tested any further. However, it is still possible that a true luminescence deterioration was observed.

Even if this study has promoted the understanding of several relationships involved in the β -radioluminescence processes, additional knowledge might still be gained for the various scintillators from multichannel pulse-height analysis experiments. Such investigations are in progress and will be reported soon².

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