

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

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INTRODUCTION

Several methods have been used for the detection of tritium in radiochromatography, most of which are covered in review articles¹⁻⁴. It is well known that gas-flow GM tube detection in the case of tritium has a low efficiency of measurement (c.p.m./d.p.m.), at most about 3%. This is because of the low β -energies ($E_{\max} = 18.5$ keV, $E_{av} = 5.7$ keV) which implies a very short range in the chromatographic medium (about 1 mg/cm²). As a consequence only a few of the emitted electrons are capable of emerging from the chromatogram surface to be counted, the larger part of the electrons being absorbed in the sample itself. One way of overcoming this detection limit is to apply radioluminescence (fluorography, scintillation autoradiography) to tritium measurements. This technique employs a scintillator (embedded in the chromatographic preparation) giving off light upon absorption of the β -particles. As the samples are translucent the tritium activities may be registered by film or photomultiplier with the sensitivity being very much increased as compared to that for direct β -particle detection.

The first application of scintillation detection was reported by WILSON⁵ in 1958. Whereas he used a liquid scintillator solution of *p*-diphenyl benzene for film detection of tritium on paper chromatograms⁵, JOLCHINE was the first to apply solid scintillator detection of tritium in thin-layer chromatography⁶. Solid scintillator detection by photomultiplier on paper-chromatogram strips had, however, already been reported by SELIGER AND AGRANOFF⁷ in 1959, a year after the first report from WILSON. A scintillation strip scanner (DMSL-3) for thin-layer radiochromatograms impregnated with scintillator is now commercially available*. It is obvious that a careful examination of known cathodoluminophors (electron scintillators) should be undertaken to improve radioluminescence detection as far as possible.

Anthracene has been used as a scintillator, either in a benzene solution for paper impregnation⁸ or as a powdered admixture (as much as 50%) to commercial silica gels⁹. The last-mentioned experiments were performed by LÜTHI AND WASER⁹ who apparently used the Merck preparation 7731 G which is a silica gel containing about 13% gypsum as a binder. They reported a great enhancement of sensitivity to tritium by X-ray film detection upon addition of anthracene and, further, a thirty-fold reduction in the necessary exposure time upon cooling the sample from 277°K

* Available from S.A.I.P., 38 Rue Gabriel Crie Malakoff, Paris, France.

to 203°K. However, WILSON AND SPEDDING³, who noted that Silica Gel G itself is a scintillator (though very poor for the pure silica, according to our results), found only a doubling of sensitivity when sprayed with anthracene.

In a search for effective β -scintillators we have investigated¹⁰ several Merck media for thin-layer chromatography, all of which showed luminescence upon tritium incorporation, but with great differences in efficiency. Additional spraying with anthracene gave little increase in sensitivity for the most effective ones. (Due to the short range of the tritium β -particles, however, the physical state of the medium and the method of adding the scintillator would seem to be of great importance to the efficiency.) It is supposed that the inorganic and completely insoluble components of the Merck preparations are preferable to organic scintillators such as for example anthracene. We shall report here upon the spectral composition of the β -induced luminescence and on the efficiency of the scintillation detection of tritium.

EXPERIMENTAL

The chromatographic media discussed* are the following: 1085 H, 1090 G, 1094 HF, and 1092 GF (Merck aluminium oxides) and also 7736 H, 7731 G, and 7730 GF (Merck silica gels). Some specifications are given¹¹ as follows:

The H preparations are pure ones, either aluminium oxides or silica gels, containing no gypsum.

The G preparations contain gypsum as a binder (10% for the aluminium oxides and 13% for the silica gels).

The F preparations contain 1.5% of Zn_2SiO_4 -Mn which is the most efficient β -scintillator known to us.

Impurities are less than 0.03% iron and 0.05% chloride.

Tritiated glucose solution was pipetted on to the samples in volumes of 10 μ l from a standard solution** containing an activity of 1 mCi per ml. For sensitivity comparisons sample activities of 10 μ Ci were used. For the study of the spectral composition of the emitted light activities as much as 100 or 200 μ Ci were applied.

The measuring equipment and its calibration are discussed in detail elsewhere¹². A sensitive photomultiplier (E.M.I. 9558 AQ) was used in combination with either a grating monochromator or a set of eight optical filters. The transmission profiles of these had previously been checked. The light-measuring system can be said to be a very sensitive one. The sample temperature could be regulated as desired.

MEASUREMENTS AND RESULTS

Previously we had observed¹³, for the above-mentioned substances, a very intense thermoluminescence (TL) when samples were heated after X-irradiation at low temperature (78°K). The energy transfer to the irradiated substances occurs mainly through the secondary electrons and the application of tritium would also be expected to introduce β -TL during storage at low temperature. This was found to be the case, only the intensity was very faint as compared to the X-TL that could be introduced by a few mR of irradiation dose.

* Obtained from E. Merck AG, Darmstadt, Germany.

** Obtained from The Radiochemical Centre, Amersham, Buckinghamshire, England.

The steady-state radioluminescence due to tritium application (β -RL) was in all substances of much greater value for detection than the β -TL. A lowering of the temperature from 295°K to 95°K resulted in a ten-fold increase in intensity of luminescence for the 1085 H and 7736 H samples and a five-fold increase for the 1090 G and 7731 G samples. The luminescence was at all temperatures about ten times more intense in 1090 G than in the other three. The temperature effects were less prominent in the F media.

When comparing (for F media) the β -TL and the β -RL we find that the total β -TL emitted during heating, following storage for one or several hours at liquid-air temperature, is only about 3 % of the light emitted as β -RL during the storage time. Thus, only the latter seems to be of interest for tritium detection. For both types of luminescence it was found that the presence of the fluorescence indicator Zn_2SiO_4 -Mn resulted in a strong enhancement as measured by the E.M.I. 9558 AQ photomultiplier. For F media one may work at room temperature as there is no significant sensitivity increase upon cooling. In a single experiment a 1092 GF sample (aluminium oxide) was sprayed with anthracene (in benzene solution). The sensitivity was about doubled. This result may be comparable to that of WILSON AND SPEDDING³ for silica.

When discussing the composition of the β -RL one may, as a first approximation, suppose that each component in the medium (alumina or silica, gypsum and zinc silicate-Mn) is emitting light independently. That this is more or less correct is demonstrated in the TL glow curves as well as in the spectra by peaks being specific for the components.

It is not easy to obtain spectra of the β -RL. The emission is too faint to allow good spectrophotometric registration. Instead one can simulate very large β -exposure by X-irradiation. While we could not perform measurement of X-RL during irradiation it was possible to obtain good spectra of X-TL during warming. In this way the problem of the low intensity was overcome. Although it is somewhat hazardous to suppose that the X-TL spectrum is identical with the β -RL spectrum. Therefore we applied large activities of tritium and used a set of eight broad-band optical filters placed one at a time in front of the photomultiplier.

In Fig. 1 are shown for comparison the spectra of the aluminium oxides 1094 HF and 1092 GF for the induced X-TL and β -RL. Curves 1 and 2 represent good spectra, carefully corrected. These were obtained from measurements with a grating monochromator at large light intensities. The spectra 3 and 4 are constructed from eight measured values for filters with known transmission profiles. The measurements, done at low luminescence intensities, may be considered somewhat crude, mainly because of the few points measured. The spectra have two major components (530 nm and 650 nm). Gypsum is seen to be responsible for the 650 nm band in curve 2. From curve 3 the β -RL is seen to have a component not present in the X-TL (curve 1) of the same medium, 1094 HF. This component coincides with the 650 nm gypsum peak of the X-TL in 1092 GF. Curve 4 shows that the 650 nm component dominates the β -RL emission of the last medium. None of the investigated media showed any ultraviolet emission.

Spectral measurements of the β -RL in silica gels have not been performed, but the spectra of X-TL are very similar to curves 1 and 2 showing that Zn_2SiO_4 -Mn and $CaSO_4$ are the most effective in the silica as well as in the alumina preparations.

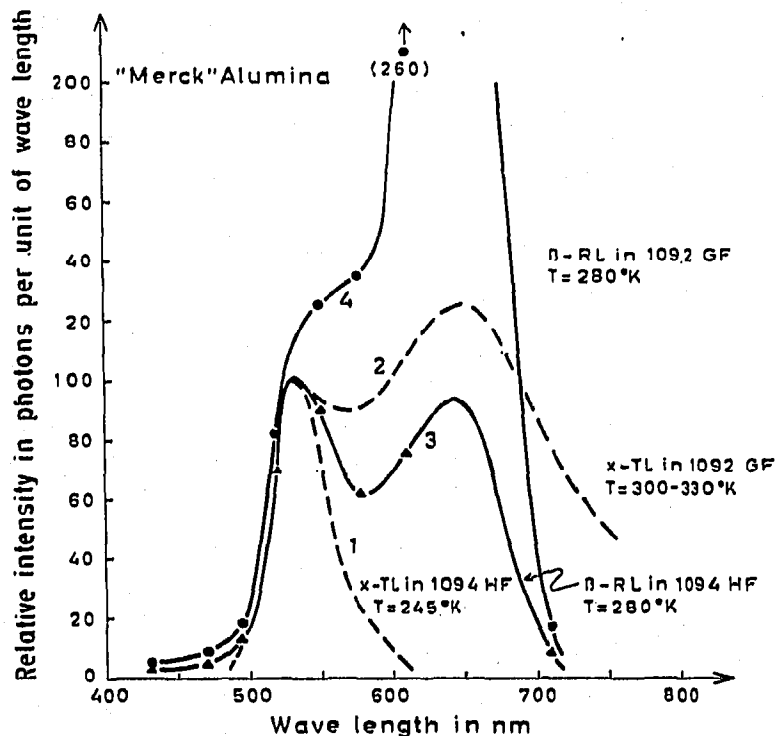


Fig. 1. Emission spectra from standard media for chromatography ("Merck" aluminium oxides 1092 GF and 1094 HF). The luminescence is either thermoluminescence due to pre-irradiation with X-rays (X-TL) or radioluminescence due to tritium application (β -RL). Curves 1 and 2 represent good spectra obtained with a grating monochromator, while the spectra 3 and 4 are drawn from measurements through eight filters and are somewhat coarser.

It seems clear from these measurements that the spectral range 500–700 nm should be covered with the highest possible sensitivity for both film and photomultiplier detection. This statement applies to all media containing $\text{Zn}_2\text{SiO}_4\text{-Mn}$ and CaSO_4 . In conclusion, the commonly used X-ray film emulsions seem to be superseded in sensitivity by emulsions sensitized for the optical region.

It should be mentioned that the efficiency of the above media could be further increased by a larger addition of zinc silicate, now present in an amount of only 1.5%. Possibly, a gypsum specially sensitized¹⁴⁻¹⁷ for TL dosimetry of X-rays (e.g., $\text{CaSO}_4\text{-Mn}$ or $\text{CaSO}_4\text{-Sm}$) would serve as a more efficient β -scintillator for tritium detection.

The efficiency of the 1092 GF (Merck) medium is illustrated by the fact that an amount of 0.5 μCi of tritiated glucose gave about 50 c.p.s. from the photomultiplier. The dark current alone gives about 20 c.p.s. and an activity of 0.01 μCi should be measurable with an accuracy of about 20% for a measuring time of 10 minutes. A higher accuracy could be obtained by increasing the measuring time as well as by an increase in the high voltage applied to the photomultiplier.

Thus, solid scintillator detection of tritium in radiochromatography appears promising. Further investigations on tritium detection on thin-layer chromatograms are in progress.

SUMMARY

The relative β -scintillation efficiencies of several thin-layer media for chromatography ("Merck" alumina and silica) have recently been determined at room and

lower temperatures. In addition, we have now investigated the spectral composition of the emitted luminescence (for the most efficient media) to obtain a basis for choosing photomultiplier or film material with appropriate spectral response for optical detection. A broad-band emission (500–700 nm) was found, where a dominant peak at about 650 nm was due to gypsum admixture (as a binder). The sensitivity for tritium detection by luminescence was estimated.

NOTE ADDED IN PROOF

Shortly more detailed measurements will be reported (in this journal). Comparisons of scintillator efficiencies (between different scintillator systems, and for different temperatures) have been performed. A more satisfactory method of measurement was applied. The resulting efficiencies are to some extent changed even if the main conclusions given in this paper are still found valid.

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