

DETECTION OF WEAK BETA EMITTERS BY LIQUID SCINTILLATION COUNTING TECHNICS, II

SOME PHENOMENA OBSERVED IN THE PRESENCE OF GASES IN LIQUID
SCINTILLATION SYSTEMS

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(Received March 8, 1968)

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Introduction

By investigations carried out to qualify the photomultiplier and to determine the optimal counting parameters — discussed in a former paper [7] —, we wanted to clear the limits between which our instruments fulfil the requirements of the liquid scintillation counting technique.

In the second part of our work the other main source of the counting technique problems: the liquid scintillation system, the scintillation solution and the sample, was investigated. The sample is to be dissolved in the scintillator solution — except some heterogeneous methods — in such chemical forms and concentration that are not hindering considerably the mechanism of the scintillation, that means without quenching effect. Usually the active sample to be measured does not comply with these requirements, in which case it must be transformed (with some kind of reactions) into a “neutral”, toluene soluble, and a well-defined compound.

According to SCHRAM [13] the preparative, transforming operations, applicable at homogeneous methods, can be placed in four categories.

a) Oxidation or reduction

The methods described in literature are carried out to transform various biological samples, because in this way the below detailed counting technics of HTO, $^{14}\text{CO}_2$ or $^{35}\text{SO}_2$ can be used, instead of the frequently coloured compounds of dubious composition.

b) Salt formation

Several toluene-insoluble substances, liable to form salts, can be dissolved in that solvent by the use of organic acids or bases of high molecular weight readily soluble in the scintillation media. Generally two bases are used:

1) Hyamine 10-X ([p-diisobutylcresoxyethoxyethyl] dimethylbenzylammonium chloride monohydrate). It is commercially available in salt (chloride) form, which is to be converted before use to hydroxide form. The efficiency varies as a function of the amount and purity of the Hyamine. It is usually used in methanolic solution (0.5 mol/l), 1 ml of which is blended with 10 ml scintillator. Hyamine 10-X is suggested e. g. by ТЫКВА [14], RADIN [11]. At $^{14}\text{CO}_2$ determination the efficiency ranges from 33 to 67 % according to the amount of the amine. To reduce the solvent losses EISENBERG [2] applied a closed absorption vial instead of pressing the active gases through the scintillator.

2) RADIN [12] suggested Primene 81-R (mixture of amines with an average molecular weight of 191, containing a primary amino group) for the determination of active sulphuric acid. One mole of Primene will trap — similarly to Hyamine 10-X — about one mole of carbon dioxide. [9]

JEFFAY [5] applied the mixture of dimethylformamid and ethanol. The use of 2-phenylethylamine and ethanolamine is suggested by DOBBS [1] and KALBERER [6], respectively. According to GORDON [3] the quenching observed in the presence of the hydroxide form of Hyamine 10-X is larger as that of its salt, therefore the H_2^{35}S was dissolved directly in toluene (max. 3 ml $\text{H}_2\text{S}/40$ ml scintillator).

For the detection of gas chromatography curves POPJAK [10] proposes to inject the chromatographic vapor into the scintillator, leading to differential or integral type records according to the solubility of the gases.

c) Synthetic methods

This wearisome procedure is only applied for the detection of low radioactivity levels, e.g. for radiocarbon dating. (Benzene or toluene is produced from the test sample by oxidation and synthesis, and used further as solvents.)

d) Modification of the solubility relations

A frequent method — besides these above mentioned — is based upon the modification of the solubility relations. For the incorporation of aqueous solutions special solvents are needed, as toluene does not blend with water, and at the same time the quenching action of water cannot be neglected. Small quantities of water can be added to toluene in the presence of methanol or ethanol, greater volumes may be dissolved in scintillator mixtures containing dioxane.

It was shown by FÜRST that with the addition of naphthalene the quenching action of water can be compensated [13].

OKITA [8] suggests the following scintillator for counting samples of low water content: 20 ml abs. ethanol, 28 ml toluene, 100 mg PPO, in which 2.1 ml solution can be incorporated.

In the mixture of naphthalene, PPO, POPOP, methanol ethylene glycol and p-dioxane 1 ml aqueous solution per 10 ml scintillator can be dissolved. The efficiency is 10–15% for tritium and 60–70% for carbon-14. (It is worth mentioning that recently the modification of solubility relations has often been used, instead of salt formation.)

Heterogeneous counting methods (suspension and gel counting, scintillating plastics, counting with dispersed fluors, or on filter paper etc.) are not discussed in this paper.

The number and type of these preparatory operations are determined by the characteristic of the sample. In our case, for the detection of ^{14}C and ^{35}S , the starting point was carbon dioxide and sulphur dioxide. As we wished to apply some homogeneous measuring method, and 10–20 ml scintillator does not absorb these gases in a detectable amount, salt formation or solubilization had to be used. The counting of aqueous solutions is disadvantageous, as water exerts a rather strong quenching action, and the preparative processes (absorption, neutralization) are tiresome. Furthermore data about solubilization agents were inconsistent and purification difficulties arose, so method b) was selected.

According to data found in literature, and considering the apparatus/es/ and chemicals at our disposition the use of Hyamine 10-X seemed to be the most advantageous.

$^{14}\text{CO}_2$ counting by the means of Hyamine 10-X

The working solution of 0.5 mole Hyamine in methanol was diluted from the originally 1 mole solution (product of the Packard firm) in order to reduce viscosity and to increase the volume of absorptive solution.

For absorption via the flow system absorption trap — suggested by ТУКВА [14] — was applied, because at a slow flow rate and little gas volumes the solvent losses were negligible, and the counting period was shorter than with closed absorption systems. The Hyamine quantity was 1 ml throughout, sufficient to absorb 0.45 mmol of CO_2 , if absorption efficiency is taken at 90% [14].

$^{14}\text{CO}_2$ was produced with the combustion of benzoic acid. Its application is advantageous, as it is a practical model-substance, easy to oxidize catalytically and the specific activity may also be determined by liquid scintillation counting technique. (Below a concentration of 3 mg benzoic acid per 10 ml scintillator the quenching effect is negligible.)

Co_2O_3 and CuO were used as oxidatic catalysts. The sulphur and halogen impurities were fixed with silver wool, and copper turnings were applied

to reduce the nitrogen oxides and the excess of oxygen. The thus obtained gas mixture was dried with $\text{Mg}(\text{ClO}_4)_2$ before the CO_2 absorption. The combustion was carried out in an air current of 10 ml/min, dried with $\text{Mg}(\text{ClO}_4)_2$ and natron-asbestos.

The influence of pure Hyamine on the efficiency was examined before investigations were carried out with active carbon dioxide. By our counting parameters without the base (10 ml scintillator/0.1 ml standard*) 67% efficiency was observed**, which decreased after the addition of 1 ml Hyamine to 33–37%. Because of the decomposition of Hyamine this value decreased to 28% in two weeks. Upon absorbing carbon dioxide (0.4 mmole) produced by the combustion of inactive acetanilide, the efficiency increased to 38–39%.

After these informatory tests, investigations were carried out with active benzoic acid in order to determine the influence of the Hyamine's quenching action on the reproducibility, and accuracy.

The combustions carried out with samples of different activities failed to give reproducible results, the activities — counted with efficiencies determined by the internal standard method — did not agree with the true activities. Deviations ranged from -9% to +17%.

The thus observed 26% limit of error pointed to the fact, that some — up to the present neglected — parameters must be taken into consideration.

The error, or at least the overwhelming part of it, obviously cannot originate in the losses occurring at combustion and absorption, as no positive deviation can thus be interpreted. Further investigating into the reason of this deviation it appeared, that at the same time the efficiency varied between 28–60%.

For this reason the following step was to clear up, if the free base to salt ratio i.e. saturation differences are responsible for this efficiency fluctuation. Therefore its value was determined after saturating the Hyamine with inactive, dry carbon dioxide. According to our experiences the thus obtained values, after some initial deviation, were stabilized and remained constant within 24 hours.

Comparing these results with those of GORDON [3] it can be stated, that they agree with them, namely the quenching action of the free base differs from its salts form. The observed efficiency difference of 32%, however cannot be explained in this way, as in the case of free base, 90% saturation and completely saturated Hyamine efficiencies of 33–37%, 38–39% and 37–39% were obtained, respectively.

* The data of the scintillators and internal standards are discussed in our former paper [7].

** Counting parameters: amplifier gain: 100 %, discriminator: 750–∞, unless other data are given.

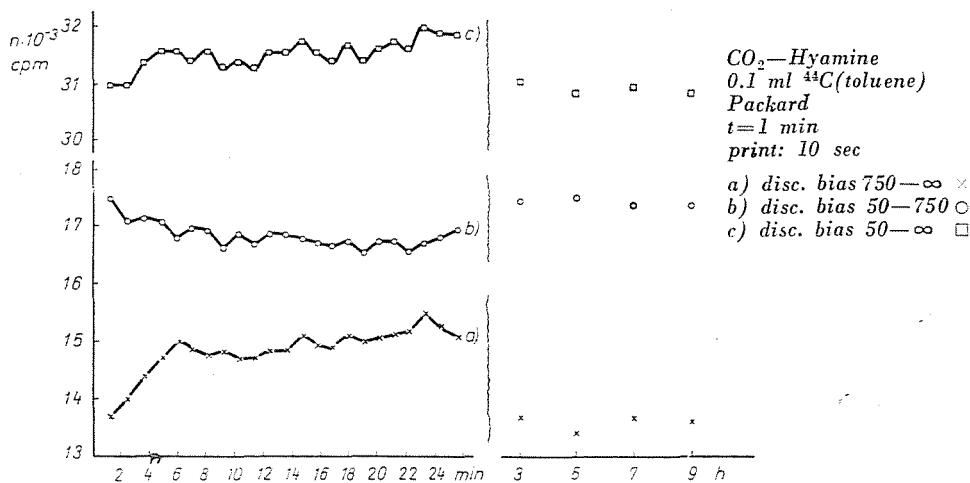


Fig. 1

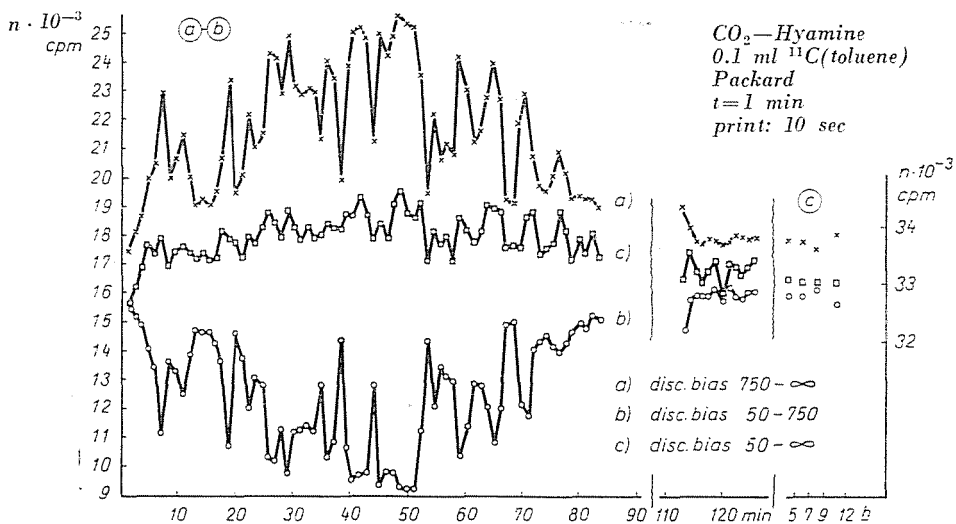


Fig. 2

For further checking hydrogen sulfide gas was also measured with Hyamine 10-X. The hydrogen sulfide was produced by the pyrolysis of methionine on platinum contact in hydrogen current. Purification and drying process agreed with the above discussed. The observed counting rate, however, was constant at least for four hours. $\sim 28\%$ efficiency was observed without H_2S , which increased to 30–34% after absorption, that is the efficiency increase, due to "salt effect", was also but 4–6%.

On the basis of these observations it is presumable, that the above-mentioned initial efficiency deviations are responsible for this problem, as

substances other than carbon dioxide were not dissolved in the sample, but neither the duration of absorption, nor the periods between the scalings were fixed.

To support this hypothesis Hyamine was saturated with inactive, dry carbon dioxide, the scintillator and active standard were added directly after absorption to the sample, and the counting rate was detected in function of

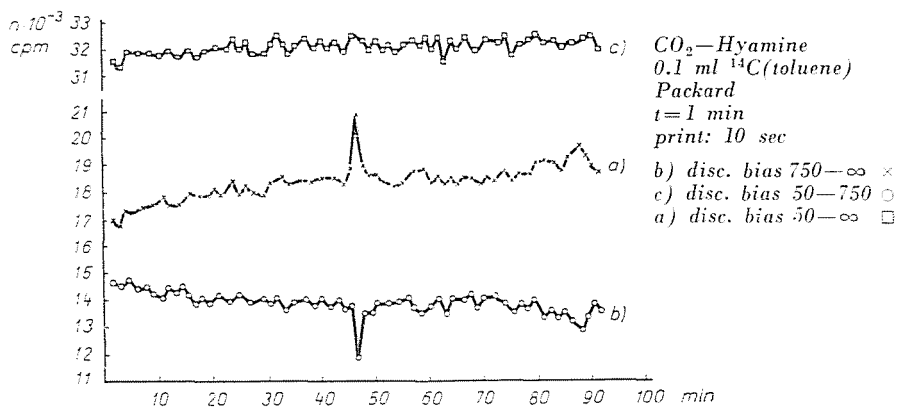


Fig. 3

time. Significant differences were observed between the shapes of the obtained curves. Figs 1 to 3 are representing the three main types, among which several transitory forms were observed. The most general and frequent is the form seen in Fig. 2, and this is the basis of the following reflections.

The curves seen in each figure were simultaneously measured with a Packard Tri-Carb spektrometer. Curves *a*, *b*, *c* represent the counts obtained in the "carbon", "tritium" and "total" channels, i.e. with discriminator bias: 750— ∞ , 50—750 and 50— ∞ , respectively. Counts detected in channel "total" differ by 0.3—0.6% from summarized value of channel "carbon" and "tritium" because of adjustment slip.

Examining these data it is obvious that the max. change of counts in curve *c* is 1250 cpm., only 3.7% (3.5 times the standard deviation), therefore it cannot be the cause of a deviation about $6.5 \cdot 10^3$ cpm observed on *a* and *b* curves. (The initial efficiency increase is due to the cooling of the sample, therefore in spite of decaying phosphorescence the counting rate increases.) Furthermore it can be stated that curves *a* and *b* are antipodes, images of each other.

On the basis of these facts it is unambiguous that:

a) the observed phenomenon is not chemiluminescence. Though SCHRAM [13] mentioned that in Hyamine solutions chemiluminescence was observed, but only in presence of organic substances,

b) the counting rate and efficiency fluctuation is caused by the pulse height i.e. luminescent efficiency deviation, and not by variable losses of counts (impulses),

c) the effect is observed only in the presence of CO_2 .

About the discussed phenomena we did not find data in literature. To interpret it a hypothesis was set up.

The efficiency deviation, up to 30—35%, indicates, that in the beginning, for 0.5—2.5 hours, the system is in a metastable state. Within this period some, up to now unidentified process or processes are taking place. Further on the deviation does not exceed the standard deviation, but the "final" efficiency value is markedly influenced by the antecedents, and it is badly reproducible. In our investigations its value ranged from

curve <i>a</i> :	28,5	to	36,8% ("carbon" channel)
curve <i>b</i> :	32,5	to	36,8% ("tritium" channel)
curve <i>c</i> :	65	to	70 % ("total" channel).

According to our conception the metastable state and efficiency fluctuation is connected with various "chemical bonds" and compounds of carbon dioxide. It is not yet cleared up whether Hyamine forms only acid salt, or if neutral salt is also present, as well as the steps from which the final product originates. It is possible for example that at first — before some chemical reaction — Hyamine acts only as solubilization agent.

The origin of the discussed transitional efficiency increase and deviation could be explained with the above stepwise mechanism scheme, by accepting that chemical intermediate or intermediates interact in the energy transfer. (This last assumption is based on experimental data, detailed in the next paragraph.)

Summing up the precedings it can be stated that

a) Hyamine 10-X suits for H_2S counting, but

b) in the initial 1.5—2.5 hours of CO_2 counting the scintillation system is in metastable state, the possible cause of which is some interaction between Hyamine and carbon dioxide, — up to now unknown for us, and

c) because of this reason for unambiguous counting rate determinations three hours "decay period" is needed after absorption.

Effect of gases dissolved in scintillator solutions

For several reasons it became necessary to investigate the effect of dissolved gases in scintillator solutions.

a) Searching the reason of the efficiency variation of Hyamine solutions containing carbon dioxide, it was important to clear up the influence on the

efficiency of carbon dioxide dissolved in pure scintillator. Only in possession of these data can be decided what part of the variation of the quenching action of carbon dioxide is due to its compounds formed with Hyamine.

b) GORDON [3] detected H_2S trapped directly in the scintillator, and continuous detectors were worked out by the Packard firm for measurements of active gases injected or absorbed in the scintillator. For this method, besides of the solubility data, the quenching actions must be known, especially at the detection of gas mixtures.

c) Except for the classical example of oxygen [13] no relevant literature data are available. However in this way useful knowledge could be obtained about the mechanism of scintillation too. The investigations were carried out with the following gases.

a) O_2 . About its quenching action detailed data are in literature, therefore it is a practical reference substance.

b) H_2 , N_2 . Gases considered neutral from the point of view of the scintillation mechanism.

c) CO_2 , SO_2 . Acid anhydrides.

d) CH_4 , C_2H_4 . Saturated and unsaturated hydrocarbons.

e) NH_3 . Base anhydride.

5 ml scintillator was saturated with previously exsiccated gas. Saturation time and flow rate were selected so as to achieve total saturation. The purities of N_2 , O_2 , CH_4 , C_2H_4 and CO_2 were controlled by gas chromatography. In the first four gases no impurities were detectable, while carbone dioxide contained N_2 and CH_4 , but ethylene was not observed.

The sample — saturated with gas — had been spiked with 0.1 ml standard, and after half hour cooling the counting rate was determined, in comparison with the efficiencies of the unsaturated sample (blank test).

First, toluene- ^{14}C was used as standard. The obtained data are compiled in Table 1.

Table 1

Sample	blank	CO_2	O_2	N_2	H_2
Efficiency %	49.7	50.4	45.3	49.4	49.6
Standard deviation	of the counts: ± 0.65 %.				

Data in Table 1 give answer to one of the questions. The formerly only presumed fact can now be unambiguously established, namely, that in the Hyamine system the efficiency increase observed in presence of carbon dioxide must be interpreted with the presence of Hyamine- CO_2 complexes.

Apart from the "oxygen" sample, the some tenth per cent differences between the others are in the order of the standard deviation. For this reason further investigations were carried out to examine these efficiency fluctuations

for which purpose tritium standard (0.1 ml, standard deviation: $\pm 0.4\%$) was applied because of its low energy radiation.

The efficiency of the blank test was not constant in the various experiments, therefore the experimental results are grouped according to the investigated gases.

It was discussed in a former paper [7] that "pro anal" toluene was used as scintillation solvent. For this reason — beside of testing the quenching action of the dissolved oxygen — the influence on the efficiency of water, dissolved in the toluene, had to be determined too.

These experiments were carried out in two ways applying: scintillator saturated with water; toluene distilled from sodium.

Saturating the scintillator with water, the efficiency variation was in the order of the standard deviation (see Table 2).

Table 2

Blank	29.2%	28.4%	28.5%	29.0%	29.9%
Blank saturated with water	29.6%	29.0%		28.7%	29.7%

Applying toluene distilled from sodium metal the efficiency increased to 32%, and did not vary after addition of water. Consequently the water content of the toluene does not influence markedly the efficiency, but during the distillation from sodium some quenching agents are destructed. We wish to stress this fact, as toluene purified by direct chemical treatment with Reanal chemicals (e.g. extraction with sulphuric acid, exsiccation with calcium chloride) is unfit as scintillation solvent.

Data obtained by the use of oxygen, nitrogen and methane are presented in Table 3.

Table 3

Blank	N ₂	O ₂	CH ₄
24.6%	25.0%	19.0%	24.5%
32.0*%	31.6*%	25.0*%	

The thus obtained efficiencies are constant for 12 hours. Marked* values are those obtained with toluene distilled from sodium metal.

In accordance with data found in literature we found oxygen to cause 21—22% efficiency decrease, but its amount dissolved from the air during storage does not alter considerably the efficiency. For this reason the removal of oxygen by bubbling argon or nitrogen through the solution seems to be unnecessary. It can be stated that methane does not influence the counting rate, so that in this respect it is a neutral gas.

On the basis of these results the experimental methods could be simplified: neither toluene had to be distilled from metallic sodium, nor oxygen had to be removed by nitrogen bubbling.

On the other hand with samples saturated with *ethylene* considerable efficiency increase could be measured (Table 4).

Table 4

Blank	24.1%	29.2%	28.4%	30.0%	32.0*%
Samples saturated with ethylene	32.1%	31.5%	32.6%	32.5%	33.5*%

Within 12 hours and even after addition of water, these data are constant.

From the data of Table 4 it follows that using p.a. toluene as scintillator solvent ("normal scintillator") the efficiency increases to 31.5–32.5% independently of its initial value. The increase is 8–33%, and thus a saturation effect can be observed. For this reason it is presumable that the observed "ethylene action" is connected with some impurities of the toluene, their quenching action being compensated. Therefore saturating the scintillator with ethylene seems to be a possible method to increase efficiency when counting of tritium in quenched solutions.

By counting samples saturated with carbon dioxide similar anomalies were observed.

Table 5

Blank	21.1%	29.2%	29.2%	29.2%	29.2%	30.0%
Saturated with CO ₂	29.5%	29.8%	30.7%	30.5%	31.4%	31.5%

After an efficiency fluctuation of 12 hours these values are stabilised with 0.5–1% decrease. Also after addition of water, similar fluctuation could be observed.

The cause of the detected efficiency increase could be the carbon dioxide itself, or its possible ethylene (unsaturated hydrocarbon) content. This later possibility is supported by the fact that efficiencies were increased by increasing the time of saturation, though no ethylene content could be indicated by gas chromatography.

At the same time, however, the system is unstable, the efficiency fluctuates, it is influenced by the water content, and even after saturation for several hours, its value is lower than observed in samples saturated with ethylene. (It fluctuates between 102–122% of the original values.)

Besides the facts mentioned above, it is to be noted that after saturation with methane, no efficiency variation has been observed. For these reasons it is rather unlikely that this effect is caused by a possible ethylene content, and thus it is connected with the presence of carbon dioxide.

Efficiency increase of 1.5–2% (105–107%) was also observed when *ammonia gas* was absorbed. After addition of water additional ~1% efficiency increment could be detected.

Saturating the scintillator with *sulphur dioxide* it discoloured within a few minutes, and the counting rate decreased to zero.

On the basis of these experimental results the following conclusions can be drawn.

a) For liquid scintillation counting methane is a neutral gas, as are nitrogen and hydrogen.

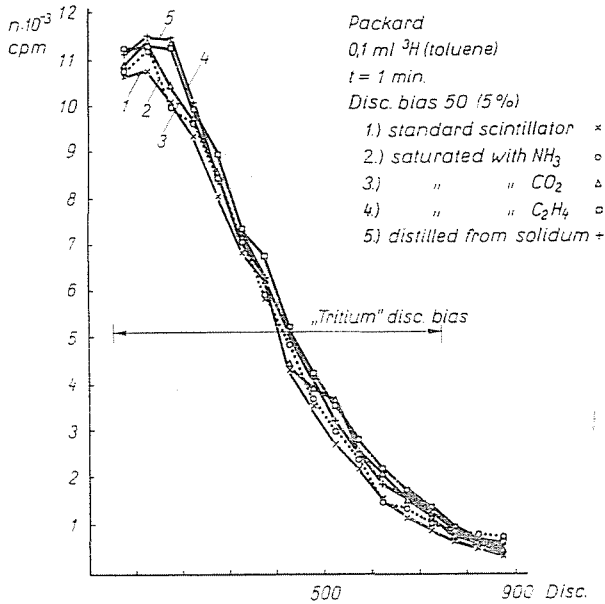


Fig. 4

Curve (1): basic state, curve (2): shaken up with water

b) In the presence of ethylene an efficiency alteration of the order of the oxygen's quenching action is observed but its sign is positive. This effect shows a solubility independent "saturation value".

c) Similar efficiency increase can be observed after absorbing ammonia or carbon dioxide in the scintillator, but its value is markedly influenced by the water content and is unstable during storage.

d) For ^{35}S counting sulphur dioxide cannot be directly dissolved in the scintillator.

These statements are supported by some beta-spectra determined with a Packard Tri-Carb spectrometer on samples spiked with tritium labelled toluene (Fig. 4).

Spectra of samples containing carbone dioxide — are shown in Fig. 5.

The higher energy ranges of these spectra have a similar shape, significant counting rate differences cannot be observed. Considerable deviation is present only between the peak heights, and at the same time with growing efficiencies the peaks are shifted to higher energies. After addition of water only the peak

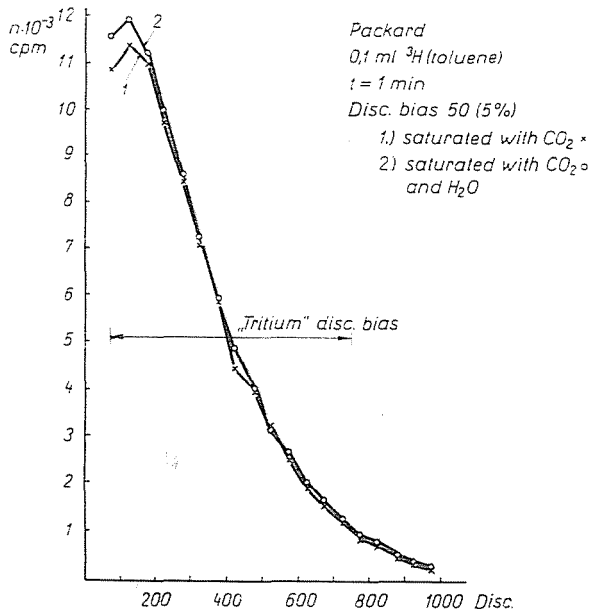


Fig. 5

height was increased in the case of carbon dioxide while in the presence of ammonia its position was shifted too. Adding water to scintillators containing ethylene or prepared with toluene distilled above metallic sodium significant deviation could not be observed.

These curves therefore support our former hypothesis, according to which these phenomena can be attributed to the mechanism of the scintillating process. The efficiency increase is caused by the *pulse height increase*, i. e. the “transforming” or quantum efficiency of the scintillator is modified.

After our conception these substances are taking part directly or indirectly in the energy migration, thus increasing the pulse heights. It is obvious that this increment — dependent on the extent of interaction — could only be well detected at low pulse heights, that is at low energy radiations.

On the basis of these considerations, the following hypothesis is to interpret the experimental data discussed above.

According to the theory of mechanism of luminescence, the radiation, in this case the beta particles, primarily excites the solvent molecules, and this excitation energy is transferred — by radiative or nonradiative way — to the phosphor or scintillator, which converts a portion of this energy into luminescent light. Even the energy of a weak beta particle of tritium (max. 18 keV) is higher by several orders of magnitude than that of the chemical bonds. Thus the scintillator molecules are partly ionized and suffer perhaps permanent chemical damage, as well as free radicals are also formed. These processes, however, are inactive, according to the present conception, the thus absorbed energy is not converted into light.

At the same time within the energy migration several transition states may also occur, the cross sections of which — and thus the luminescent efficiency i.e. the light output — are markedly influenced by the experimental conditions. As electrons excited to higher levels immediately return to the lowest excited state through a radiationless process, only those lowest energy levels are solely responsible for the observed luminescence. Thus we may say, that applying toluene or benzene as scintillation solvents 5–7 eV excitation energy — 0.5–1% of the energy of a beta particle emitted by tritium — is needed.

Taking into consideration, that the emission spectrum of PPO (primer phosphor at our disposal) has a maximum at 394 nm, which corresponds to ~ 3 eV, it can be stated that substances dissolved in the scintillator may influence the mechanism of luminescence, if their lowest electronic excitation energy is between the above discussed values.

This interaction may produce:

a) quenching action, if the molecule hinders the energy transfer; e.g. the life-time of the excited state is too small, etc. i.e. the molecule acts as an energy trap.

b) "inverse" quenching action.

On the other hand similar interactions are presumable, if the lowest electronic excitation level is with a few tenths eV higher than that of the solvent. The excitation energy of these levels can also be moved to the solvent or phosphor, in which case a cascade process is formed, or the ratio of the radiative/nonradiative energy transfer is altered. In these cases the portion of radiation energy converted into light can be increased, as its maximal value is only about 10%.

According to our conception the efficiency increase observed in presence of ethylene can be interpreted in this way. 7.5–6.4 eV energy is needed to its $\pi-\pi^*$ transition, that is the dissolved ethylene — in the case of ideal solubility 20 mg ethylene/5 ml scintillator — is also excited, and a portion of this excitation energy may also reach the phosphor. Consequently the pulse heights, and thereby the efficiency are increased, as the scaler counts only impulses with pulse heights above the lower discriminator voltage.

The situation is much more complex in the case of carbon dioxide. It is an extremely stable compound, its lowest electronic excitation energy being > 8 eV, furthermore the fluctuation of the experimental data indicates the presence of some complex phenomena.

After our hypothesis the observed effect can be attributed to the compounds of carbon dioxide rather than to the dissolved gas itself. According to data found in literature, absorption bands were determined at 6.2–7 eV (185–200 nm) for carbonates but for hydrocarbonates above 7 eV. The observed experimental facts should be pointed out that the water content of the scintillator system sensitively influenced the efficiency but only in the presence of carbon dioxide, as well as that Hyamine and carbon dioxide form similar instable complexes as already discussed in details in the previous chapter.

Our hypothesis is the following. In the presence of carbon dioxide the efficiency variation is caused by the formation of carbonates and hydrocarbonates. In the case of pure scintillator, carbon dioxide reacts with the water content of toluene, and carbonic acid, carbonate and hydrocarbonate ions are formed. The varying amount of water, the fluctuating ratio and amount of the carbonate and hydrocarbonate ions are causes of the efficiency deviation and increase.

This conception is in good agreement with the experimental results discussed in chapter 2, according to which similar effects but several orders higher could be observed if Hyamine saturated with carbon dioxide is investigated. It can be presumed that the primary pulse height increase is connected with the formation of Hyamine-carbonate, besides which Hyamine-hydrocarbonate and solubilized carbon dioxide are also present. After this unstable period hydrocarbonate and perhaps solubilized carbon dioxide remain only in the solution, and the efficiency decreases to its initial value. The stronger effect can be explained with the structure of the cation, because according to literature data it is probable that Hyamine decreases the excitation energy, or increases the life-time of the excitation states. Further, the larger amount of carbon dioxide must be taken into consideration too, as the scintillator solution is a poor solvent for carbon dioxide and water, but the present Hyamine can at least absorb 0.5–1 mmole of this gas.

According to this theory the shape of the curves and the considerable instability of the effect may be explained without any difficulty, and in the "total" channel the slight counting rate increase and decrease curves, *c*) in Figs 1, 2, 3, can be interpreted too.

The efficiency variation observed in the presence of ammonia could be explained in a similar way.

Summary

For the detection of carbon dioxide labelled with carbon-14 by means of liquid scintillation counting technics, Hyamine 10-X was applied. According to our experiences, the counting system is highly unstable in the first 1.5–2 hours, the deviation of the pulse heights are in the order of 30–35%. After this period the efficiency is stabilized at its starting value.

After our experiments some gases: ethylene, carbon dioxide and ammonia, dissolved in the pure scintillator, are also modifying the value of the quantum efficiency, but this effect is minor than the former.

According to our hypothesis these gases or their compounds may also be directly or indirectly excited, and thus they may take part in the energy transfer. This conception is supported by some spectroscopic data.

References

1. DOBBS, H. E.: *Anal. Chem.* **35**, N°7, 786 (1963).
2. EISENBERG, F.: *Liquid scintillation counting*. Pergamon Press London, 1958 p. 123.
3. GORDON, C. F., LUKENS, H. F., ten HOVE, W.: *Int. J. Appl. Radiation and Isotopes* **12**, 145 (1961).
4. JEFFAY, H.: *Anal. Chem.* **32**, 306 (1960).
5. JEFFAY, H., ALVAREZ, J.: *Anal. Biochem.* **2**, 506 (1961).
6. KALBERER, F., RUTSCHMANN, J.: *Helv. Chim. Acta* **44**, 1956 (1961).
7. NAGY, G. L., TÖRÖK, G., SZARVAS, T.: *Periodica Polytechnica CH* **10**, 279 (1966).
8. OKITA, G., SPRATT, J., LEROY, G. W.: *Nucleonics* **14**, N°3, 76 (1956).
9. OPPERMANN, R. A., NYSTROM, F. F., NELSON, W. O., BROWN, R. E.: *Int. J. Appl. Radiation and Isotopes* **7**, 38 (1959).
10. POPJAK, G., LOWE, A. E., MOORE, D., BROWN, L., SCHMITH, F. A.: *Biochem. J.* **73**, 33 (1959a).
11. RADIN, N. S.: *Liquid scintillation counting*. Pergamon Press London, 1958. p. 128.
12. RADIN, N. S., FRIED, R.: *Anal. Chem.* **30**, No 12, 1926 (1958).
13. SCHRAM, E.: *Organic scintillation detectors*. Elsevier, Amsterdam, 1963.
14. TYKVA, R.: *Collection Czechoslov. Chem. Commun.* **29**, 680 (1964).

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