United States Patent Office

3,526,768
Patented Sept. 1, 1970

3,526,768

2-SUBSTITUTED NAPHTH(1,2)OXAZOLE SCINTILLATORS

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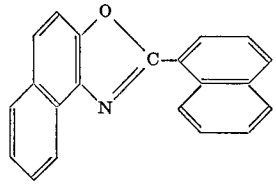
No Drawing. Filed Mar. 6, 1964, Ser. No. 350,079
Int. Cl. G01t 1/20
U.S. Cl. 250—71 13 Claims

ABSTRACT OF THE DISCLOSURE

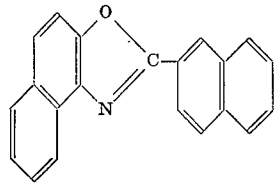
The invention covers a method of measuring the beta particle emission from a radioactive sample. The radioactive sample is contacted with a scintillator solution containing a primary and/or secondary solute of the type 2-substituted naphth(1,2)oxazole. Beta bombardment of the solute molecules cause such molecules to emit one or more primary photons. If a secondary solute is also employed, the primary photons are absorbed by the secondary solute and re-emitted. The primary and secondary photons are measured with a photomultiplier-recorder to reveal the relative beta particle emission rate.

DESCRIPTION OF THE INVENTION

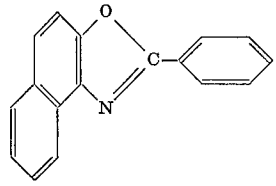
This invention relates to a new class of compounds; namely, naphthyl substituted oxazoles and naphthoxazoles to include



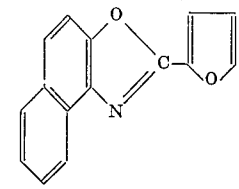
2-(1-naphthyl)-naphth(1,2)oxazole



2-(2-naphthyl)-naphth(1,2)oxazole (NNO)



2-(phenyl)-naphth(1,2)oxazole



2-(2-furyl)-naphth(1,2)oxazole

In accordance with this invention, it has further been discovered that the foregoing compounds act as primary and/or secondary scintillator solutes and, accordingly, one aspect of this invention relates to a process of enhancing the sensitivity of a system to radiation by incorporating in the system a small amount of the foregoing compounds.

The method of this invention includes the determination of the radiation emission of a radioactive sample by conducting such determinations in the presence of a solute consisting of a compound or mixture of compounds as aforedescribed.

Accordingly, it becomes a primary object of this invention to provide as new compounds 2 - (1 - naphthyl)-naphth(1,2) - oxazole, 2 - (2 - naphthyl)-naphth(1,2) oxazole, 2 - (phenyl) - naphth(1,2) oxazole and 2-(2-furyl)-naphth(1,2)-oxazole.

Another object of this invention is to provide a method of enhancing the sensitivity of a system to radiation by incorporating therein a small amount, i.e., about 0.01 to 10 g. per liter, of 2 - (1 - naphthyl) - naphth(1,2)oxazole, 2 - (2 - naphthyl) - naphth(1,2)oxazole, 2-(phenyl)-naphth(1,2) - oxazole, 2 - (2 - furyl)-naphth(1,2) oxazole and mixtures thereof.

Another object of this invention is to provide a process wherein the pulse heights and scintillation effects of solutions are enhanced for measurements of these qualities by the incorporation of a small amount, preferably within the range of about 0.01 to 10 g. per liter, of 2-(1 - naphthyl) - naphth(1,2)oxazole, 2 - (2-naphthyl)-naphth(1,2)oxazole, 2 - (phenyl) - naphth(1,2)oxazole, 2 - (2 - furyl) - naphth(1,2)oxazole, and mixtures thereof, either as a primary or secondary solute.

Still another object is to provide solvent compositions for beta ray emission activity measurements comprising the compounds disclosed herein and mixtures of same.

These and other objects of this invention will be described or become apparent as the specification proceeds.

In order to demonstrate this invention, the following examples are given. In these examples a photomultiplier tube (PMT) of the end-window type manufactured by the Radio Corporation of America and bearing identifying No. RCA6655 was connected through a preamplifier manufactured by the Tracerlab Corporation bearing Tracerlab Type p-20D. The instrument was set at full gain and connected to a pulse or count scaler having an input sensitivity of 0.25 volt. The PMT photo-cathode was cooled to +10° C. to −15° C. to reduce noise pulses.

The solutes to be tested were dissolved in toluene to concentrations of about 4 gm./liter and 0.5 ml. portions of these solutions were placed in 1 ml. beakers containing 0.1 ml. of a standard solution of a radioactive isotope of iodine (I-131) in toluene. The approximate specific activity of the radioactive solutions thus produced

was 0.01 microcurie/ml. Solutions of toluene (0.6 ml.) and a mixture of 0.5 ml. of toluene and 0.1 ml. of the standard radioactive iodine solution were also placed in one ml. beakers for comparison. The solutions were then placed, in turn, on the light sensitive window of the PMT, and the pulses counted. The results are shown in the following table.

TABLE I

Run No.	Source sample	Primary solute	Secondary solute	Scintillation count, c.p.m.	
1	Standard, comm. primary.	p-Terphenyl, 4.0 g./l.	None	35,237	33,440
2	Comm. primary and secondary.	do	POPOP, 0.5 g./l.	51,431	48,980
3	Comm. secondary	None	POPOP, 1.0 g./l.	21,042	
4	do	do	POPOP, 0.5 g./l.	2,163	
5	2-(2-naphthyl-naphth-(1,2)oxazole (NNO).	NNO, 4.0 g./l.	None	22,837	
6	NNO plus comm. secondary.	NNO, 4.0 g./l.	POPOP, 0.5 g./l.	30,154	30,113
7	Comm. primary, NNO as secondary.	p-Terphenyl, 4.0 g./l.	NNO, 0.5 g./l.	50,723	48,950

The foregoing results shows scintillation tests run on NNO used as a primary solute compared to p-terphenyl and NNO as the secondary solute compared to POPOP (a commercial secondary solute). A comparison of Run 2 with Run 7 reveals that NNO is equal to POPOP when used as a secondary solute with p-terphenyl. A comparison of Run 1 with Run 5 shows that NNO is equal to 65 percent by weight of p-terphenyl when tested as a primary solute alone. Further comparison of Runs 2 and 6 shows that NNO as the primary solute is equal to about 60 percent of p-terphenyl as the primary solute when both have POPOP as the commercial secondary solute.

The foregoing experiments bring up another advantage of this invention. It was found that the solubility of POPOP in toluene is limited to about 1.0 g. per liter but the solubility of NNO in toluene is well over 4 g. per liter and extends up to 6 to 8 g. per liter. This makes NNO superior to POPOP as either a primary solute or a secondary solute because the increased solubility in toluene allows scintillation measurements to be made under conditions of low temperature or low solubility.

It is often necessary to make such measurements at low temperatures, for instance in the upper atmosphere during experiments conducted in the exploration of space or in arctic regions where extremely cold conditions are encountered. The increased solubility of NNO in the primary solvent toluene, or in other primary solvents such as xylene, anisole, dioxane, 1,2-dimethoxyethane and ethylene glycol monoethylether extends to temperatures as low as −100° C. The advantages of solubility also extend to mixtures of primary solvents such as 6 parts of dioxane, 1 part of anisole and 1 part of 1,2-dimethoxyethane, or 5 parts of dioxane and 1 part of ethylene glycol monoethylether.

The method of this invention is carried out using the new compounds of this invention as solutes for enhancing the pulse heights and scintillation effects in liquid scintillation or liquid phosphor counting techniques. These techniques are relatively new, having been developed in the past few years for the determination of beta activity of compounds, e.g., carbon 14 and tritium counting.

One of the main problems has been overcoming the factors which prevent the radiation from reaching the detector because of self-absorption, geometry, scatter, and absorption by air and counter windows. Three basic requirements for good counting results are (1) the radioactive sample must be in good contact with the scintillator, (2) the scintillator must emit a strong flash of light, and (3) the counting mixture must be reasonably transparent to the light flashes.

The best contact between the radioactive sample and the scintillator is obtained when both the sample and scintillator are dissolved in the same solvent, called the primary solvent. However, only a few substances have been found which act as scintillators, and only a few solvents are known having the ability to dissolve or suspend the sample and act to transfer the energy absorbed from the beta particles to the scintillator. Also a great many substances, known as "quenchers," if present in the scintillating solution, inhibit this transfer of energy. Some of the primary solvents used are toluene, xylene, anisole, dioxane, 1,2-dimethoxyethane and ethylene glycol monoethylether. Mixtures of these primary solvents are also used, e.g., 6 parts of dioxane, 1 part of anisole and 1 part of 1,2-dimethoxyethane, or 5 parts of dioxane and 1 part of ethylene glycol monoethylether. These solvents can be used in the process of the instant invention.

The two essential ingredients of the liquid scintillator are (1) the solvent or primary solvent which functions to absorb the beta radiation and transfer it to (2) the scintillator or solute as it is also called. The literature on the solvents and solutes is often confusing both as to terminology and the effectiveness of various solutes or scintillators. This invention is based on the discovery of a class of compounds which act as primary solutes or as secondary solutes for liquid scintillation or liquid phosphor counting.

A large number of liquid scintillator solutions have been investigated and disclosed in the art, including the combination of p-terphenyl in toluene and such solutes as oligophenylenes, fluorenes, phenanthrenes, furans, benzoquinolines, 2-pyrones, oxazoles, thiazoles, benzoxazoles, pyrazolines, phenanthrolines, 1,3,4-oxadiazoles, the tetrazines, organometallics, esters of anthranilic acid and various other heterocyclic compounds. Review of these prior art disclosures leaves much to be desired in the selection of a scintillator because the methods of evaluation are not standardized, different experimenters use different techniques and different instrumentation. Accordingly, this art is highly empirical and the selection of a good primary or secondary solute or scintillation agent cannot be made on the basis of chemical structure and physical or chemical properties alone.

Furthermore, the technique is often difficult where weak beta emitters are being counted and the background emission level is high. In liquid scintillation tests the procedure is to place a radioactive sample in a vial containing a solvent such as toluene. A scintillating agent is added which has the property of emitting light in the visible or near ultraviolet spectrum upon excitation from the radioactive sample. The vial is placed adjacent the entry port of an instrument designed to transform a light signal to an electrical signal, such as a photomultiplier tube. Low temperatures are used to reduce background emission along with lead shielding and low counting volume. Under these conditions, at each emission of the radioactive particle of the sample the scintillating agent emits a pulse(s) of visible light which is changed to an electrical pulse by the photomultiplier tube. The signal

from the photomultiplier tube (PMT) is passed to a suitable measuring instrument such as a scaler to indicate and/or record the time and magnitude of the PMT signal.

A secondary solute, such as 1,4-di[2-(5-phenyloxazolyl)]-benzene, which compound is known as POPOP, may be added for the purpose of transforming the emitted light from the scintillating agent, which may be 2,5-di(4-biphenylyl)-oxazole, known as BBO, to a wave length detectable by the PMT. In these determinations the role of the scintillation solute is to emit a pulse of photons for each radioactive emission which deposits energy in the solution and the solvent must absorb energy and transfer it to the solute. A scintillation solute must, in addition to being available and economical, be an efficient light emitter, produce a photon spectrum which in a conventional scintillation detector will be eventually transmitted and reflected in the optical system and converted into electrical energy by the PMT, and be compatible with solubility restrictions imposed by the composition of the counting solution and by the temperature at which the counting is performed.

The best light emitters and scintillating agents form emission spectra of too short wave lengths to produce a photon spectrum which is eventually transmitted and reflected and accordingly, it is conventional practice to employ a two-solute combination comprising a primary solute to insure a large number of emitted photons and a secondary solute which becomes the actual emitter and agent for control of the spectrum of the photons.

In accordance with this invention, pulse heights and scintillation effects of solutions have been found to be enhanced for measurements by the incorporation of a small amount, preferably within the range of about 0.01 to 10 gm./liter, of 2-(1-naphthyl)-naphth(1,2)oxazole, 2-(2-naphthyl)-naphth-(1,2)oxazole, 2-(phenyl)-naphth (1,2)oxazole, 2-(2-furyl)-naphth(1,2)-oxazole and mixtures thereof.

The scintillating agents of this invention are used in apparatus designed to measure electromagnetic or corpuscular radiation from naturally occurring or artificially produced radioactive isotopes or from machine-produced radioactive isotopes or from machine-produced radiation. The scintillation solutes of this invention comprise a class of compounds which is distinguished by the characteristic that its members lose a significant fraction of the energy from their excitation molecules by the emission of light, which is measurable by means such as photomultiplier tubes and associated equipment. The compounds of the present invention are not only effective pulse height scintillation enhancers but are easy to prepare and quite inexpensive, these factors representing an advantage over the known pulse height enhancers such as POPOP and BBO.

The compounds of this invention are used in the known manner as either primary or secondary solutes, that is they may be used with such known scintillators or primary solutes as p-terphenyl in toluene, 2,5-diphenyloxazole (PPO), 2-phenyl-5(4-biphenylyl)-1,3,4-oxadiazole (PBD), 1,4-di-[2-(5-phenyloxazolyl)]-benzene (POPOP), 2-(4-methoxyphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole, 2-(4-methoxyphenyl)-5-(4-biphenylyl)-oxazole and the like. The solvents may be toluene, xylene, anisole, dioxane, 1,2-dimethoxyethane, ethylene glycol monoethylether and mixtures thereof.

The method and solvent compositions of this invention are applicable in the determination of beta ray emission activity of any radioactive sample including, but not limited to tritium, C^{14}, H^3 and C^{14}, Na^{22}, K^{40}, I^{131}, Rb^{87}, In^{115}, Nd^{150}, Lu^{176}, Re^{187} and the like involving primarily beta ray emission, that is, the emission of negative electrons resulting from the transformation of neutrons into protons wherein there is an increase in nuclear charge by one unit, but no effect on mass number. Various samples of materials having the foregoing atoms which are characteristic beta ray emitters, include a wide variety of organic compounds, and such specific compounds as: urea, methanol, ethanol, acetylene, toluene, p-cymene, hexane, octane, acetic acid, caproic acid, phenylalanine and benzoic acid containing one or more C^{14} atoms; stilbene with an H^3 atom; cholesterol and related steroids with H^3 and C^{14} atoms, water with H^3 atoms; water in urine, plasma, and the like with H^3 atoms. Also environments containing inorganic compounds, such as, barium carbonate and sodium acetate with C^{14} atoms and potassium chloride with K^{40} atoms or salt with Na^{22} atoms can be tested using the solutes of this invention.

In these determinations the known methods of sample preparation are applied. Some scintillation samples may be solvents themselves, in which case it is only necessary to add the desired amount of solute or scintillation enhancer of this invention with or without an auxiliary solute such as POPOP, i.e., at a concentration of .05–0.3 g./l. for most determinations. Where the sample is soluble in the primary solvent, such as toluene, dioxane and the like, which should be of the best quality obtainable, at least "reagent grade," it is only necessary to dissolve the sample therein in the desired concentration to form the stock sample and place the stock sample solution in the vial of the instrument. If the sample is water or water-soluble, the procedure is to prepare the water solution of the sample and mix it with absolute alcohol in the vial or counting bottle. To this is added the stock solution of the solute in the primary solvent to form a homogeneous mixture, allowing the maximum toluene or solvent concentration consistent with the total volume desired and the amount of sample necessary for the proper testing. Any precipitates which form during this procedure are filtered off and alcohol-washed, and the filtrate is combined with the homogeneous mixture. Those samples which are insoluble in a primary solvent, water or alcohol are ground in a tissue homogenizer or a semi-micro ball-mill and washed into the vial with the stock solute solution. Agitation is necessary before counting is conducted.

The known procedures for scintillation counting are applied and it is not considered necessary to elucidate thereon. A wide variety of apparatus is available commercially for these determinations. Thus the sample holders and mounts may be of the type manufactured by Nuclear-Chicago Corporation, Model M2A, the scintillation detector may be Model DS5–5 and self-quenching G–M tubes or counters Models D22, D12, D50, D51 and D52, PMT devices and scalers from this source may be used, or the instruments for this purpose manufactured by Technical Measurement Corporation or Packard Instrument Company may be used. The procedures outlined or detailed in various technical bulletins published by these companies may be followed in carrying out the method of this invention using the new solutes described herein.

The advantages of the low-temperature solubility of the oxazole compounds of this invention are evidenced when scintillation measurements are made at temperatures of about 0° C. to −100° C. or under natural environmental earth atmospheric temperatures which may be as low as −60° C. Where such measurements are made in spacecraft even lower temperatures are contemplated. Laboratory bench scintillation apparatus are designated for low temperature use and for these purposes the use of the primary and secondary solutes of this invention extend the utilities to temperatures in the range of −15° C. to −100° C. as a feature of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method of determining the beta particle emission from a radioactive sample which comprises contacting said sample with a solution containing a primary solute of the group consisting of 2-(1-naphthyl)-naphth

(1,2-oxazole, 2-(2-naphthyl)-naphth(1,2)oxazole, 2-(phenyl)-naphth(1,2)-oxazole, 2-(2-furyl)-naphth(1,2)oxazole and mixtures thereof, said primary solute being present in an amount sufficient to enhance the scintillation count and measuring the photon emission rate of said solution.

2. The method in accordance with claim **1** in which said primary solute is present in a concentration of about 4.0 g./liter.

3. The method in accordance with claim **2** in which said primary solute is 2-(2-naphthyl)-naphth(1,2)-oxazole.

4. The method of determining the scintillation effect of a radioactive sample which comprises contacting said sample with a solution containing a primary solute and about 0.01 to about 10 gm. per liter of a secondary solute of the group consisting of 2-(1-naphthyl)-napth-(1,2)oxazole, 2-(2 - naphthyl)-naphth(1,2)oxazole, 2-(phenyl) - napth(1,2)oxazole, 2-(2-furyl) - naphth(1,2)-oxazole and mixtures thereof and measuring the photon emission rate of said solution.

5. The method in accordance with claim **4** in which said primary solution is toluene and said secondary solute is present in a concentration of about 4 gm. per liter.

6. The method is accordance with claim **5** in which said secondary solute is 2-(2-naphthyl)-naphth(1,2)oxazole.

7. The method of determining the beta particle emission from a radioactive sample at temperatures below about −15° C. to about −100° C. which comprises contacting said sample with a solution containing a primary solute of the group consisting of 2-(1-naphthyl)-naphth-(1,2) - oxazole, 2-(2-naphthyl)-naphth(1,2)oxazole, 2-(phenyl)-naphth-(1,2)-oxazole, 2-(2-furyl)-naphth(1,2)-oxazole and mixtures thereof, said primary solute being present in an amount sufficient to enhance the scintillation count and measuring the photon emission rate of said solution.

8. The method in accordance with claim **7** in which said primary solute is dissolved in a solvent of the group

consisting of toluene, xylene, anisole, dioxane, 1,2-dimethoxyethane, ethylene glycol monoethylether and mixtures thereof.

9. The method in accordance with claim **8** in which said solvent comprises a mixture of 6 parts dioxane, 1 part anisole, and 1 part 1,2-dimethoxyethane.

10. The method in accordance with claim **8** in which said solvent comprises a mixture of 5 parts dioxane and 1 part of ethylene glycol monoethylether.

11. A scintillator solution for beta particle emission activity measurements comprising a primary solute, a pulse height enhancing amount of a secondary solute of the group consisting of 2-(1-naphthyl)-naphth(1,2)oxazole, 2(2-naphthyl) - naphth(1,2)oxazole, 2-(phenyl)-naphth(1,2)oxazole, 2-(2-furyl)-naphth(1,2)oxazole and mixtures thereof, and a suitable solvent.

12. A scintillator solution in accordance with claim **11** in which said secondary solute is 2-(2-naphthyl)-naphth(1,2)oxazole.

13. A scintillator solution in accordance with claim **11** in which said solvent is toluene.

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U.S. Cl. X.R.

260—307