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TRACK REGISTRATION BULK TRACING METHOD

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ABSTRACT OF THE DISCLOSURE

A bulk tracing technique using track-registration materials is disclosed. This technique has exceptional sensitivity and a unique ability to discriminate over background. Basically, this method detects the distribution of added particulate fissionable matter dispersed in a fluid by collecting a sample of the fluid with the dispersed matter therein. The dispersed matter is concentrated and placed adjacent to a solid material which is susceptible to the formation of radiation-damage tracks by charged particles. The concentrated matter is irradiated with neutrons to generate charged particles which penetrate the material and leave radiation-damage tracks that indicate the presence of the added matter.

This invention relates to methods for analyzing for the presence of small amounts of materials added for tracing purposes.

It has recently been discovered that energetic charged particles, such as alpha particles and fission fragments from the heavier atoms, leave tracks of radiation damage in various types of materials. Such tracks can be seen with an electron microscope, but can also be made visible in an optical microscope if the material in which the tracks are made is selectively attacked by chemical reagents in the radiation-damage tracks. Such materials are called "solid-state nuclear track detectors," and are described in an article entitled "Track Registration in Various Solid-State Nuclear Track Detectors" by Fleischer, et al, published in Physical Review, volume 133, Number A, Mar. 2, 1964. Solid-state nuclear track detectors will not yield tracks when irradiated with beta or gamma rays or neutrons.

When certain isotopes of given elements are bombarded with neutrons, the atoms of these elements capture neutrons and produce charged particles with various energies. For example, boron-10, on capturing a neutron, emits an alpha particle and a lithium-7 ion. These relatively lightweight charged partices leave a damage track in cellulose nitrate about 8 microns long. Uranium, on the other hand, fissions into much larger and more energetic fragments which leave tracks about 20 microns long in a variety of solid-state nuclear track detectors.

The solid-state nuclear track detectors make it possible to detect matter which produces charged particles when irradiated with neutrons, with a sensitivity about one million times greater than the best previously-available chemical or physical techniques. For example, the chemist requires at least about 10^{-6} grams of a sample of matter to determine its presence, and even the best techniques with an emission spectrometer require 10^{-8} or 10^{-9} grams of sample. As few as thirty million atoms (about 10^{-15} grams) of plutonium 239 (Pu^{239} can be detected by the formation of radiation-damage tracks in solid-state nuclear track detection to determine the distribution of matter producing charged particles when irradiated with neutrons dispersed in a fluid at a dilution many times greater than that previously possible with any prior analysis techniques.

In addition to high sensitivity, the detection method of this invention can be performed at low cost because such small amounts of material are required. Moreover, there is no radiation hazard in the system under analysis because it is not necessary to have radioactive elements in the system analyzed.

Briefly, the method of this invention detects the distribution of added matter dispersed in a fluid by collecting a sample of the fluid with the dispersed matter in it. The dispersed matter is concentrated and placed adjacent to a solid material which is susceptible to the formation of radiation-damage tracks by charged particles. The concentrated matter is irradiated with neutrons to generate charged particles which penetrate the material and leave radiation-damage tracks that indicate the presence of the added matter.

In the presently-preferred method, the matter is in the form of finely-divided particles, preferably in the range of about 0.1 to about 10 microns. A micron is 10^{-6} meters or 10,000 angstrom units. Some of the elements which are useful in the method of this invention are boron, uranium, plutonium, and lithium. Certain isotopes of these elements undergo nuclear reaction when bombarded with neutrons and emit fragments which leave radiation damage in solid materials such as cellulose nitrate, Lexan (a trademark for a polycarbonate resin such as bisphenolacetone carbonate), mica, Mylar (a trademark for a film of polyethylene terephthalate), and Lucite (a trademark for methacrylate ester polymers). These materials have different characteristics for recording damage tracks. For example, an alpha particle leaves a radiation-damage track in cellulose nitrate but not in Lexan. Heavier fragments, such as those from uranium fission, leave tracks in both cellulose nitrate and Lexan. Since solid-state nuclear track detectors are insensitive to beta and gamma rays and neutrons, a nuclear reactor may conveniently be used as a neutron source.

Many of the fluids which are to be analyzed for the added matter may contain a naturally-occurring "background" of the matter used in the analysis. In such cases, the sensitivity of the analysis is increased in accordance with this invention by dispersing the added matter in partculate form which is of limited solubility so that it can subsequently be filtered from a sample of the fluid and thus separated from the dissolved background matter.

An alternate technique for improving the sensitivity of the method when there is a natural background of the fissionable matter used in the detection system is to combine two elements in single particles composed of a compound such as uranium boride or a glass containing uranium and boron. These particles are then dispersed in the fluid to be traced or analyzed. The particles are subsequently collected, concentrated, and placed adjacent a solid-state nuclear track detector such as a cellulose nitrate film. Thereafter, the particles are irradiated with neutrons. The coincidence of heavier fission-fragment tracks from the uranium and alpha tracks from the boron uniquely distinguishes the dispersed particles from the material which occurs naturally in the fluid. Moreover, since the boron and uranium are combined stoichiometrically or in a fixed ratio in all particles, the alpha and heavy fission-fragment tracks appear in a definite ratio regardless of particle size.

The fissionable matter dispersed in the fluid may also occur naturally, such as uranium particles dispersed in a stream of water or air. In this case, the particles are collected, concentrated, and analyzed to determine the location of a uranium ore body.

The detection method of this invention is useful for studying flow rates, flow distribution, concentration distribution, dilution-mixing data, leakage and recharge rates, meteorology, ore prospecting (10^{-14} grams of natural uranium can be detected), alloy analysis, biology, control of uranium-plutonium contamination, smog control and analysis, and wear tracing such as in bearings and other moving parts.

These and other aspects of the invention will be more fully understood from the following detailed description and specific examples.

Example I.—Sewage effluent tracing

A typical sewage plant for a large city discharges 10^9 liters per day of effluent in the ocean. It is desired to determine the presence of the effluent at a dilution factor of 10^5, which is at least one hundred times better than the existing methods which measure either water salinity or bacteria content. It is then necessary to trace $10^9 \times 10^5$ or 10^{14} liters of water. A 0.5 micron diameter particle of natural boron weighs about 1.5×10^{-13} grams. Such a particle yields about 7 tracks at a relatively low neutron exposure of 10^{12} neutrons per square centimeter. Approximately 10 particles of boron per liter are needed for the quantitative determination of dilution (with approximately 30% error). This then requires 10^{15} particles per day of natural boron (added as a source of fissionable matter to the effluent from the sewage plant). The weight of boron is, therefore, $10^{15} \times 1.5 \times 10^{-13}$ or 150 grams. Thus, only 150 grams of boron per day added uniformly to the effluent are sufficient to trace the effluent in the ocean to a dilution factor of 10^5. Boron is a good element to use for such tracing work because it is relatively inexpensive, and has a large capture cross section for neutrons to produce alpha particles.

The "plume" or distribution of the sewage effluent is determined by collecting 1-liter samples at various locations offshore at the point of effluent outfall. Ocean water contains a substantial amount of dissolved boron which acts as a background and tends to mask the presence of the particulate boron added to the sewage effluent distribution. The boron in each liter sample is concentrated by either evaporation or filtration. In the case of evaporation, the dissolved boron and the added particulate boron are present together. The tracks produced by the particulate boron appear in clusters as compared to the relatively scattered single tracks produced by the dissolved boron. Thus, it is possible to distinguish the added from the naturally-occurring boron. This distinction is not necessary in using filtration to concentrate the boron particles added to the sewage effluent. In this case, the filter passes the dissolved boron but retains the particulate boron. In either case, the concentrated boron particles are placed adjacent a film of cellulose nitrate, or other suitable solid-state nuclear track detector, and irradiated with neutrons for a total exposure of about 10^{12} neutrons per square centimeter. The boron atoms which capture neutrons produce charged particles (alpha particles and Li^7 ions) which form tracks in the film. These tracks, which are about 8 microns long and 20 to 100 angstrom units wide, are too small to be seen except with an electron microscope. Since examination with an electron microscope is time consuming and expensive, the cellulose nitrate film with the radiation-damage tracks is immersed in a solution of 6 N sodium hydroxide at 25° to 60° C. for 1 to 30 minutes. The sodium hydroxide selectively attacks that portion of the cellulose nitrate film which has been damaged by the alpha particles and Li^7 ions and enlarges the tracks to a width of between about 0.5 to about 20 microns, which can be observed with a conventional optical microscope. The tracks are counted, or the image through the microscope photographed, to provide a permanent record, if desired. The number of track clusters indicates the amount of tracers boron particles present, and thus indicate the amount of sewage effluent in the sample.

As mentioned previously, the soluble boron naturally present in the seawater tends to interfere with the tracer measurement just described. Accordingly, the tracer boron is combined with another element or elements to make it relatively insoluble. This material is finely divided to the right particle size so that it remains suspended in the water during the time requirer for the tracing of the flow of the sewage effluent. Ordinarily, a "life" of about 1 week for the particles is sufficient. Conveniently, boron silicate glass is grouped to particle size between about 0.1 and about 2.0 microns. The particles are carefully graded so that they have uniform size and, therefore, remain uniformly suspended in the sewage effluent and surrounding seawater. The boron silicate glass particles gradually settle or dissolve in the seawater so they do not remain indefinitely present and produce interferring background for subsequent measurements. Other examples of boron compounds which can be used for tracing are B_6Si, B_3Si, B_4C, BP, and BN. Lithium can also ve used as a tracer. Examples of suitable lithium compounds for tracing are Li_4SiO_4 and Li_2SiO_3 and various types of lithium glasses. In this case, neutron irradiation produces alpha particles and tritons from the lithium-6 isotope.

For optimum results, the particles are of a chemical and physical nature such that they do not react with their environment and disperse uniformly in the fluid being traced, do not cohere with each other or with other solids that might be present in the system, and do not undergo selective adsorption in the system under analysis. Preferably, the particles are relatively insoluble in the fluid when there is a background problem, such as boron naturally in sea water.

From the foregoing description it will be seen that the particulate tracer material can be made to match the bulk fluid density of the medium in which it is dispersed. Since the sub-micron particles do not settle rapidly in the fluid, this method now makes the tracing of large quantities of fluids possible with small amounts of material and without the concurrent hazards of radioactive tracing. It also avoids the disadvantages attendant with the use of dyes, which must be used in enormous amounts to achieve tracing not nearly as accurate as the present technique provides, and which may react chemically with the environment.

Example II.—Tracing with mixed elements

Particulate tracing such as that described in Example I above is made even more specific and less subject to interference from possible natural background by the use of mixtures or chemical compounds, such as uranium borosilicate glasses or uranium boride particles, which are relatively insoluble, and which contain known proportions of elements that each undergo reaction with neutrons to produce separate distinctive charged particles. The uranium boride is reduced to a selected particle size and dispersed in the sewage effluent as described in Example I. Samples of the effluent and ocean water in which it is discharged are collected. The particulate uranium boride particles are concentrated by filtration or evaporation, placed adjacent a cellulose nitrate film, and irradiated with neutrons as previously described. At those locations where the uranium boride particles are located, there is a coincidence of fission-fragment and alpha tracks. The fission of the uranium on capturing a neutron produces fission-fragment tracks about 20 microns long in the cellulose nitrate. The boron produces alpha tracks only about 5 microns long in the cellulose nitrate. The boron which occurs naturally in the sample, i.e., not associated with uranium, creates only alpha tracks in the cellulose nitrate film. Thus, the tracer boron is easily distinguished from the naturally-occurring boron. Moreover, the definite ratio of uranium-to-boron in the tracer produces a definite ratio of alpha tracks-to-fission-fragment tracks so the measurement is independent of the particle size of the uranium boride. This facilitates tracing a plurality of comingling streams by the use of tracers which have elements combined in different proportions, and in different compounds.

Example III.—Air Tracing

One thousand cubic feet of air is readily filtered and analyzed for its particulate boron content, which can be in any of the forms described above in Example I. Substantially all of the air over a given surface of the earth is under a height of 20 kilometers. Then particles of boron per 1000 cubic feet of air is easily detected as described above for Example I. The following Table 1 shows the amount of boron needed to place 10 particles of boron per 1000 cubic feet in the atmosphere over different areas to a height of 20 kilometers.

TABLE 1

Area	Air volume, cu. ft.	Total Particles needed	Total weight of source (g).
Earth	3.5×10^{20}	3.5×10^{18}	[1] 520
California	1.7×10^{17}	1.7×10^{15}	260
San Francisco Bay area	7×10^{14}	7×10^{12}	1

[1] Kg.

It is clear from Table 1 that relatively small quantities of source material can label very large air masses. In any application to local or general meteorology where it is desired to trace the direction and dilution of a given moving air mass, more mass with a given source up to a point of dilution to the total volume shown in the above Table. For example, Table 1 shows 1 gram of boron particles dispersed as a particulate tracer source (0.5 micron in diameter) in 1000 cubic feet of air, the marked 1000 cubic feet of air can be detected to a dilution factor of 7×10^{14}.

The tracing technique of this invention permits tracing and following the movement of large air masses for either gross or micrometeorological studies. The sensitivity is further enhanced by collecting more air sample or increasing the neutron radiation time over that given in Example I.

Similar calculations show the value of the method of this invention in oceanography for the study of currents and mixing phenomena, the study of surface and ground water for conservation and control, the displacement of large oil deposits with gas or water in secondary recovery operations, the tracing of pipelines, and any studies of large-scale mixing in industry such as steel, cement, or numerous other chemical processes.

This invention, in effect, replaces radioactive tracers in many of their applications and extends the use of tracer techniques in areas where radioactive hazards make radioactive tracers inapplicable.

Example IV.—Uranium prospecting

The sensitivity of the analytical method of this invention is well demonstrated in uranium prospecting. Uranium compounds found in ore bodies are usually relatively insoluble. Erosion of each ore body by water and air gives rise to water-borne and air-borne particulates characteristic of the ore containing uranium. The particulates are carried away from the ore body by air currents or water streams. The ore body is located by collecting air or water samples at a plurality of locations spaced from each other and the ore body, concentrating the particulates from the ore body by filtration, placing the concentrated particulates in contact with Lexan or equivalent material, and irradiating them with neutrons to form radiation tracks in the material due to the fission fragments occurring when the uranium atoms capture neutrons. The Lexan film is then etched as described in Example I and observed to determine the particulate density of a given sample. Where there is a gradient of uranium concentration, there is an indication that the samples have been carried from an ore body bearing uranium, and the ore body is located by following the gradient in the direction in which the uranium concentration increases.

Example V.—Wear studies

Another example of practical use of the method of this invention is in wear tracing. In the past, bearings or other parts which were to be tested for wearing were made to incorporate radioactive particles which were abraded off in the lubricating fluid (usually oil) during the testing operation. Thereafter, the radioactivity of the lubricating fluid was measured to determine the amount of wear of the part. Wear tracing with the method of this invention is much more sensitive, and does not require the use of radioactive materials during the running of the part under test. For example, boron-10 is included in the material of which wear is to be tested, but in amounts which have no effect on the properties of the material. Typically, the material is made into a bearing, piston, or the like, which is lubricated by oil. After appropriate time of test, the lubricating fluid is filtered, or the boron particles which may have been abraded off into the fluid are otherwise suitably concentrated, and then analyzed for track etching as described above in the foregoing examples.

From the foregoing description, it is apparent that this invention provides an inexpensive, highly-sensitive method for tracing without radioactive hazards. The technique can be used to study flow rates, flow distribution, concentration distribution, dilution-mixing problems (e.g., sewage plants), leakage and recharge rates (ground water studies), meteorology (hurricanes and other storms), ore prospecting, alloy analysis, control of uranium and plutonium concentration, smog control wear tracing, and numerous other systems.

I claim:

1. A method of detecting the distribution of particulate fissionable matter dispersed in a fluid, the method comprising collecting a sample of the fluid with the dispersed matter in it, concentrating the matter in the sample, placing the concentrated matter adjacent a solid material which is susceptible to the formation of radiation-damage tracks by charged particles emitted when the matter reacts with neutrons, and irradiating the concentrated matter with neutrons to generate charged particles which penetrate the solid material and leave radiation-damage tracks that directly form a permanent record indicating the presence of the fissionable particulate matter.

2. The method according to claim 1 in which the matter is particulate and in the size range of about 0.1 micron to about 100 microns.

3. The method according to claim 1 which includes the step of forming the matter into finely-divided particles, and dispersing them in the fluid.

4. The method according to claim 1 in which the matter is relatively insoluble in the fluid.

5. The method according to claim 4 in which the matter has a solubility of less than about 0.1 part per 100 parts of the fluid.

6. The method according to claim 1 in which the matter is boron.

7. The method according to claim 1 in which the matter is uranium.

8. The method of detecting the distribution of particulate matter dispersed in a fluid, the matter being a combination of one element which produces charged particles in one range of energy and mass and another element which produces charged particles in a substantially higher range of energy and mass, the method comprising collecting a sample of the fluid with the dispersed matter in it, concentrating the matter, placing the concentrated matter on a solid material, the solid material being susceptible to the formation of radiation-damage tracks by fragments emitted from either of the fissionable elements in the matter, the tracks formed by fragments from each of the fissionable elements being distinguishable, and irradiating the concentrated matter with neutrons to generate fragments which pass through some of the solid material and leave radiation-damage tracks that directly form a perma-

nent record indicating the presence of the matter and the ratio of the elements combined.

9. The method according to claim **8** in which the solid material is selected from the group consisting of cellulose nitrate, cellulose acetate, and cellulose acetate butyrate.

10. The method according to claim **1** in which the solid material is selected from the group consisting of cellulose nitrate, cellulose acetate, cellulose acetate butyrate, polycarbonate resin, mica, polyethylene terephthalate, and methacrylate ester polymers.

11. The method according to claim **1** which includes the step of selectively etching the radiation-damage portion of the solid material to enlarge the size of the tracks and make them visible under an optical microscope.

12. The method according to claim **1** which includes the step of filtering the sample of fluid to concentrate the dispersed matter in the sample.

13. The method according to claim **1** in which the fluid is liquid, and including the step of evaporating the liquid to concentrate the matter in it.

14. The method according to claim **1** in which the matter is selected from the group consisting of B_6Si, B_3Si, B_4C, BP, BN, boron glass, Li_4SiO_4, Li_2SiO_3, lithium glass, uranium glass, uranium boride, plutonium glass, and plutonium compounds.

15. The method of detecting the presence of a uranium ore body from which particles of uranium are dispersed by natural forces in a naturally-occurring ambient fluid such as water or air, the method comprising the steps of collecting samples of the ambient fluid at a plurality of locations spaced from each other and from the ore body, placing the uranium particles from the samples adjacent a solid material susceptible to the formation of radiation-damage tracks by charged particles emitted when the uranium particles react with neutrons, and irradiating the uranium particles with neutrons to analyze each sample for its uranium content and thereby indicate the presence of the uranium ore body.

References Cited

UNITED STATES PATENTS

2,874,303	2/1959	Lane	250—83
3,149,233	9/1964	Wilson et al.	
3,227,881	10/1962	Gordon.	
3,242,338	3/1966	Danforth et al.	
3,002,091	9/1961	Armstrong	250—106 X
3,254,210	5/1966	Schmitt	250—43.5
3,335,278	8/1967	Price et al.	250—83.1

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250—43.5

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,486,027 Dated December 23, 1969

Inventor(s) Henry W. Alter

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 68, line omitted after the word "track", should be --detectors. (new paragraph) This invention uses solid-state nuclear track--. Column 3, line 73, "tracers" should be --tracer--. Column 4, line 6, "requirer" should be --required--; line 9, "grouped" should be --ground--. Column 5, line 8, "Then" should be --Ten--; line 27, line omitted after the word "more", should be --than 10 particles per 1000 cubic feet will be found in such a--. Column 6, line 72, delete the comma after "distinguishable".

SIGNED AND SEALED DEC 15 1970

(SEAL)
Attest:

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