United States Patent

Bird

[15]   **3,704,952**

[45]   **Dec. 5, 1972**

[54] **FLUID MEDIUM SOURCE TRACER METHOD**

[72] Inventor: **Douglas Bird**, Schenectady, N.Y.

[73] Assignee: **Environment/One Corporation**, Latham, N.Y.

[22] Filed: **Dec. 29, 1969**

[21] Appl. No.: **888,747**

[52] **U.S. Cl.** ....356/87, 23/230 L, 23/230 PC, 23/232 E, 260/2.2, 260/80.78, 260/88.2, 356/187

[51] **Int. Cl.** C08f 27/04, G01j 3/30

[58] **Field of Search** ....23/230 PC, 253 PC, 230 L, 23/232 E, 254 E, 230 US; 252/408; 356/87, 187; 250/218, 43.5; 73/40.7

[56]   **References Cited**

UNITED STATES PATENTS

|			
2,664,779	1/1954	White	356/187
2,730,005	1/1956	Vonnegut	23/253 PC X
2,999,383	9/1961	Bryan	356/187 UX
3,330,960	7/1967	Rich	23/232 EX

Primary Examiner—Joseph Scovronek
Attorney—Charles W. Helzer

[57]   **ABSTRACT**

A fluid medium source tracer method and materials is described which employs specially prepared particulate materials containing bound identifier elements in known fixed ratios and dispersed in a fluid medium to be labeled. Test samples of a fluid medium (either liquid or gas) are burned in a flame emission spectrometer which measures simultaneously one principal spectral emission band from each of the bound elements in any single particle that passes through the flame of the spectrometer. The method is applicable to studies in water, air contamination, or other liquids and in studies of air flow. It allows a number of different unique, characteristic "finger prints" to be dispersed into fluid mediums to be identified at some subsequent point in space and/or time as a suspected source of contamination by use of the specially prepared particulate material containing bound elements in known fixed ratios as the "finger prints." In liquids, the additive particulate materials can be used at average levels as dilute as 1 part per billion by weight (and possibly less), and yet the technique is capable of deriving spectral emission signals generated in the flame emission spectrometer by the labeling particulate materials which are at least one or two orders of magnitude greater than emission signals produced by background noise or other naturally occurring interference. The labeling particulate materials and the method of their preparation also is disclosed.
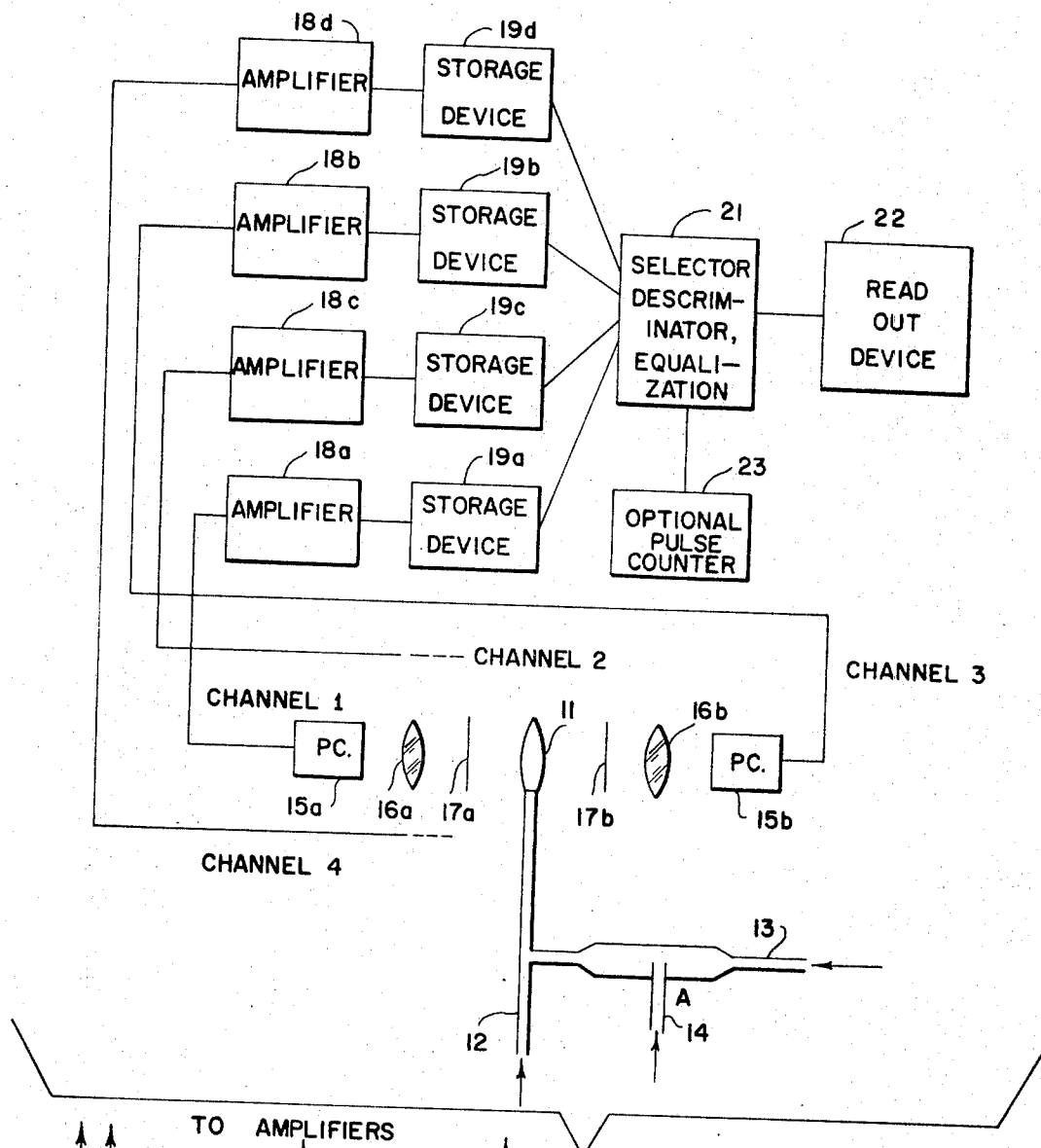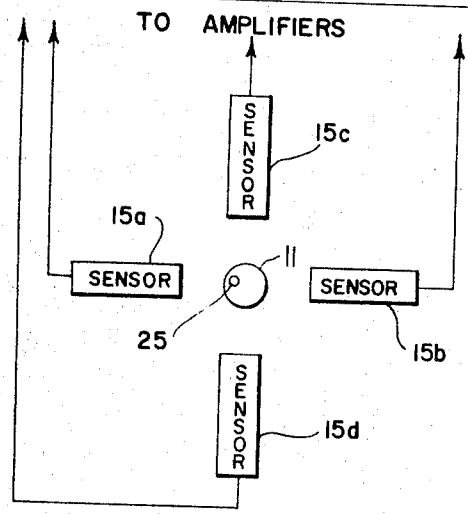
7 Claims, 3 Drawing Figures

FIG. 1

FIG. 2

F/G. 3

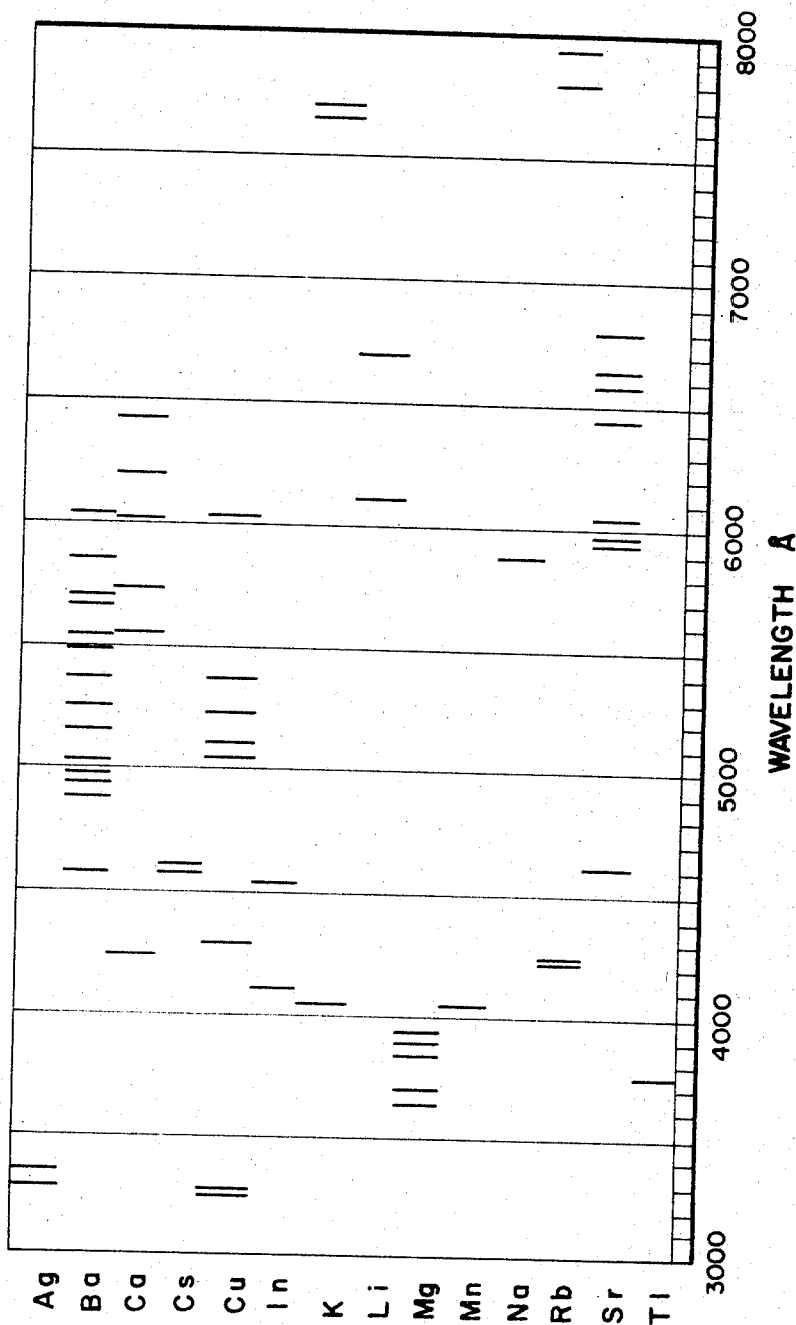EMISSION SPECTRA OF METALS IN THE AIR—HYDROGEN FLAME

WAVELENGTH Å
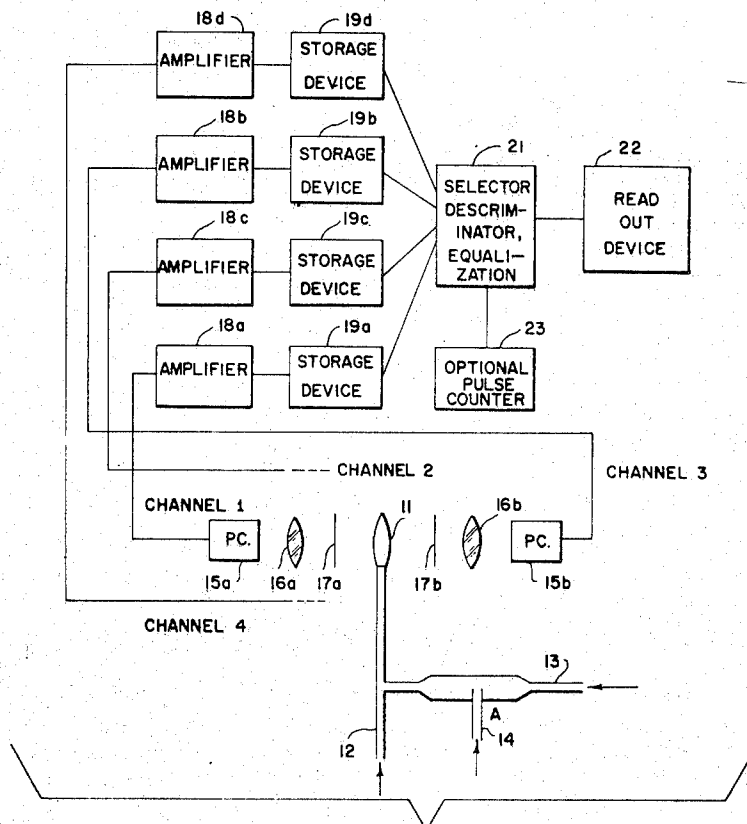
INVENTOR

DOUGLAS BIRD

BY *Charles W. Helzer*

ATTORNEY

FLUID MEDIUM SOURCE TRACER METHOD

BACKGROUND OF THE INVENTION

1. Field of Invention

This invention relates to a new and improved method 5
of labeling fluids (either liquid or gas) for subsequent
identification either as a source of contamination, to
establish owner claims, etc.

More particularly, the invention relates to such a
fluid medium tracer method, and to novel, specially 10
prepared, tracer particulate labeling materials for
dispersal into fluid mediums to be identified and to the
method of preparation of such particulate materials.

2. Prior Art Problem

The established need for mankind to clean up his en- 15
vironment (both the air and water) has given rise to a
need for techniques, materials and instruments for trac-
ing the flow of liquids or gases, and to be able to identi-
fy the source and path of an unwanted, contaminated
fluid medium such as smoke cloud or oil spill. For ex- 20
ample, such techniques are badly needed in connection
with studies on water stream flow, checking the passage
of an effluent down stream, monitoring the presence of
stack emissions at various distances from a smoke 25
stack, determining the origin of smoke in the at-
mosphere, determining the origin of oil spills, me-
terological studies of large and complex air move-
ments, and the like. In the past, flow paths have been
traced by adding to a fluid medium being analyzed, 30
some specific identifiable material which can be mea-
sured at very low concentrations. At present, the
known techniques for accomplishing this are quite
limited due to their complexity, and limited applicabili-
ty. For example, radio-active compounds have been 35
used in tracer work since they permit detection and
measurement at very low levels, but they are limited to
only three characteristic emissions (alpha, beta and
gamma radiation) and the specific measuring
techniques for detecting these emissions are both dif- 40
ficult and time consuming, and require expensive, hard
to use measuring equipment. Additionally, the use of
radio-active material as tracers in the environment, is
restricted (and rightly so) by stringent regulations.
Other tracer techniques have employed fluorescence 45
spectra to follow the movement of additive materials
which, when excited, exhibit a typical visible
fluorescent spectrum. This technique, while also very
sensitive and capable of detecting additive tracer
materials in the one part per billion by weight range, 50
nevertheless involves the use of a broad band emission,
and the presence of many naturally occurring
fluorescent materials in a number of environments
which may interfere with the measurements, limits the
usefulness of this technique. 55

It is most desirable to have available a technique em-
ploying a number of additives all of which can be used
at the same time, and yet each of which provides a
unique analytical "finger print." Additionally, it is 60
desired that all of such additives be capable of being
detected and analyzed by a single, simple to operate
and inexpensive instrument which is universally ap-
plicable to the monitoring of a number of different flow
patterns all characteristically marked with particular 65
additives.

One recent disaster involving the leakage of oil in the
Santa Barbara Channel off of California, dramatizes

the serious effects on the environment of oil spills in
coastal waters. However, the problem of oil spills is not
confined to such large, well publicized incidents where
the source of the oil spill is obvious, but also is of seri-
ous concern in a wide number of inland and coastal
water ways where oil is being stored and shipped con-
tinuously. In many of these smaller leakages, the source
of oil pollution is not obvious, and under present condi-
tions there is no easy way of tracing the source and as-
signing responsibility for the oil spillage. The most
practical way for solving this problem is to employ a
labeling technique in which each consignment or
tanker of oil is given a unique "finger print" by the ad-
dition of some synthetic material to the oil. In a similar
manner, emissions from a smoke stack can be similarly
labeled with a "finger print" from synthetic material
added to the oil, coal, etc used in the combustion
chambers of boilers, furnaces, etc.

SUMMARY OF THE INVENTION

It is therefore a primary object of the invention to
provide a new and improved method of labeling fluids
(either liquid or gas) for subsequent identification.

Another object of the invention is to provide such a
fluid medium tracer method, as well as novel, specially
prepared tracer particulate materials for dispersal into
fluid mediums to be identified, and to the method of
the preparation of such materials. The provision of the
tracer particulate material makes available a range of
specially prepared labeling compounds which can be
dispersed in fluid mediums such as crude oil at low con-
centration (less than 20 parts per billion by weight) and
which will permit a multiplicity (up to several hundred)
possible, unique, analytical patterns ("finger prints")
for identification of specific fluid mediums.

In practicing the invention, a method of specially
identifying a given fluid medium is provided which
comprises dispersing into a given fluid medium parti-
cles of matter which are insoluble in the given fluid
medium. The insoluble particles have bound thereon a
multiplicity of different, known identifier elements
each having a characteristic spectral emission. Test
quantities of the fluid medium thus labeled are col-
lected at a different point in space and/or time and are
subjected to a flame spectral analyzer for detecting the
characteristic emissions of the several different identifi-
er elements. Only dilute amounts of the insoluble parti-
cles are dispersed in a given fluid medium to be labeled
(on the order of 20 parts per billion by weight or less)
and yet provide relatively high localized identifier ele-
ment concentrations within the insoluble particles on
the order of 10 percent (10^5 parts per million) by
weight for spectral analyses purposes. The flame spec-
tral analyzer employed in the method responds to a plu-
rality of different known identifier elements bound in
the insoluble particles employed as a labeling com-
pound.

The labeling, insoluble particles used to label the
fluid medium in the method described briefly above
preferably comprises a particulate synthetic mixed
metal-polymer salt having a plurality of different metal-
lic elements bound to a solid polymer with the different
metallic elements each having a characteristic spectral
emission which does not interfere with or overlap the
spectral emission characteristics of other of the metal-

lic elements comprising the mixed metal-polymer salt. The mixed metal-polymer salt is of predominantly hydrocarbon structure in which a specific ratio of metal atoms are maintained within the particle by bonding of the metals to the cross-linked polymer matrix in which the metal atoms comprise on the order of 10 percent by weight (10^5 parts per million by weight) of the particle. The metals preferably are from the class consisting of lithium, rubidium, cesium, barium, strontium, silver, copper and potassium and the polymer may consist of methacrylic or acrylic acid in the range from 10–99 percent, divinyl benzene in the range from 0.1–5 percent and the remainder copolymer of styrene.

In addition to the above features, the invention provides a method for producing particulate synthetic insoluble trace particles of a mixed metal-polymer salt having a multiplicity of different known identifier metals bound in a predominantly hydrocarbon structure which comprises treating an already formed porous particulate cation-exchange resin, prepared by the standard methods known to the art, with solutions containing mixtures of soluble salts of the metals which are to be bound into the polymer structure. The preferred resin starting materials for these preparations are strong acid cation-exchange resins in the free acid form. In this case the reaction between the metal ions in the mixed salt solution and the resin is cation exchange, and results in the desired mixed metal polymer salt and some soluble acid residue. The soluble acid residue is removed by thorough rinsing of the metal bonded exchange resin particles with water which has been distilled or otherwise de-ionized.

Because of selectivity effects which occur to some extent with all ion-exchange resins, that is the tendency of the resin to bind some cations (metal ions) more readily than others, the ratio of metal atoms in the solution of mixed salts will most likely not correspond exactly to the ratios in which they will be bound into the resin particles. To obtain a desired ratio in the resin, the ratio of metal atoms (ions) in the mixed salt solution, the concentration of the salts in the solution and the temperature conditions of the exchange reaction will have to be adjusted empirically.

It is to be understood that if the particles of the ion-exchange resin used in this process are too large for the purposes of this invention, which will frequently be the case, they will be ground and screened before carrying out the exchange reaction just described, to give particles having sizes in the desired range, i.e. 0.5 to 5 microns diameter.

In order to prevent the ratios of bound metals in the particles from being altered by subsequent uncontrolled ion-exchange reactions in the environment in which they are used, it may be necessary to seal them against movement of ions in or out of the particles. This will be achieved by impregnating the mixed metal-polymer particles, prepared as described above, with styrene or some other monomer which forms a water-insoluble polymer, and polymerizing this monomer within the particles. This polymerization may be carried out with the particles plus monomer suspended or emulsified in water, or in a hot fluidized bed in which the fluidizing gas is saturated with monomer vapor, or by other appropriate methods of polymerization. In these reactions catalyst such as benzyl peroxide may be added to the monomer to accelerate the polymerization.

A second method of producing these synthetic metal labelled insoluble polymer particles comprises mixing styrene in 60–69 parts by weight, methacrylic or acrylic acid in 39–30 parts by weight, divinyl benzene in 1 part by weight, distilled water in 200 parts by weight, ammonium persulfate in 0.3 parts by weight and non-ionic emulsifier in 4 parts by weight, heating the mixture to a temperature of 50°–60° C. under nitrogen for 8 to 24 hours to 95 to 99 percent conversion of monomers, vacuum stripping of traces of residual monomers, mixing a solution of hydroxides of desired identifier metal in the proportions necessary to yield the desired identified metal ratios, adding the mixed metal hydroxides to the polymer latex and heating the mixture to a steady pH value of 8 to thereby substantially neutralize the mixture, and drying the resultant mixed metal polymer salt to produce an insoluble polymeric powder containing a multiplicity of metals bound to the polymer matrix in fixed known ratios. Optionally, if it is desired to seal the particles against inadvertent ion-exchange, after addition of the mixed metal hydroxides and neutralization of pH of 8, further styrene, an additional 5 to 20 parts by weight, may be added to the latex, and a second polymerization carried out before drying. The metal hydroxide mixtures preferably are formed from the hydroxides of the class of metals consisting of lithium, rubidium, cesium, barium, strontium and potassium.

BRIEF DESCRIPTION OF DRAWINGS

Other objects, features and many of the attendant advantages of this invention will be appreciated more readily as the same becomes better understood by reference to the following detailed description, when considered in connection with the accompanying drawings, wherein like parts in each of the several figures are identified by the same reference character, and wherein:

FIG. 1 is a schematic block diagram of a particle emission spectrometer suitable for use in practicing present invention;

FIG. 2 is a schematic block diagram of the particle emission spectrometer shown in FIG. 1, and illustrates the geometric arrangement of the sensor units of the spectrometer about a flame source of emission; and

FIG. 3 is a plot of the emission spectra of metals in an air-hydrogen metals identified on the lefthand margin of the figure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Overall Fluid Medium Labeling and Source Tracer Method

In practicing the novel fluid medium labeling and source tracer method made available by the invention, it is necessary to provide a variety of specially prepared label compounds which can be dispersed in a fluid medium such as crude oil, stack gas, et at low concentrations (less than 20 parts per billion by weight) and which will permit a large number (possibly up to several hundred) unique analytical spectral emissions to be derived. The method further requires an analyzer instrument in the form of a particulate emission spec-

trometer which burns small test samples of the fluid medium (less than 10 grams in the case of oil) and subsequently analyzes the spectral emission pattern produced as a result of the combustion process of the particulate labeling compound previously dispersed in the medium. It is also necessary to provide some means for assuring adequate dispersal of the specially prepared additive particulate labeling compound into a fluid medium to be subsequently identified.

In practicing the novel method of the invention, the specially prepared, particulate labeling compounds are dispersed into a given fluid medium, and are of such character that they are insoluble in the particular fluid medium into which they are dispersed. These insoluble particles have bound thereon a multiplicity of different known identifier elements such as metal each having a characteristic spectral emission. It is preferred that the multiplicity of different known identifier elements bound on the individual insoluble particles each emit light having a different spectral frequency than other of the indentifier elements employed in forming the insoluble particles. The labeling, insoluble particles thus comprised then are dispersed into the fluid medium to be later identified by suitable dispersing techniques and apparatus to be described more fully hereinafter.

At some later point in space or time when it is desired to identify reliably a particular given fluid medium, such as an oil spill, a sample of the oil spill is obtained and is burned in a particulate emission spectrometer. The essential features of a suitable, multiple channel particulate emission spectrometer (hereinafter referred to as a PES) are shown in FIGS. 1 and 2 of the drawings. The particular PES shown in FIG. 1 and 2 is designed to specifically identify the spectral emission of four different metals which are considered to be adequate for purposes of the instant disclosure. More or less channels could be added by duplication or elimination of sensors and amplifier channels with a consequence increase or decrease in cost and complexity as the case may be.

In operation the retrieved sample of the fluid medium to be identified (here assumed to be an oil spill) is sprayed into a filtered air stream supplying the flame maintained at the center of the spectrometer shown in FIG. 1. Each of the labeling insoluble particles which enters the spectrometer flame will generate a brief light pulse which contains emissions having a characteristic frequency due to each of the identifier metals bound within the insoluble labeling particles. The particulate emission spectrometer includes appropriate light filters, as will be described more fully hereinafter which pass only the frequency of a principal emission of one of the identifier metals in the labeling insoluble particles. Each channel of the particulate emission spectrometer therefore selects out the principle emission of one of the metals, and supplies the light therefrom through a collimating lens to a photo multiplier tube. The output from each of the photo multiplier tubes then is amplified and subsequently stored or applied to a recorder for analysis and identification purposes. Because the particular fluid medium under examination had dispersed therein an amount of previously recorded labeling insoluble particles having different elements bound therein, and whose characteristic spectral emission readily can be identified, it will be ap-

preciated that the labeling insoluble particles therefore serve as a unique, characteristic "finger print" for the particular fluid medium under examination. Thus, in the case of an oil spill, the source of the spill readily and reliably can be identified for corrective action.

One of the most important features of the present technique lies in the distinction between the average concentration of the labeling metals, obtained by dividing the known weight of the metals in the added label compound by the total weight of the fluid medium in which they are dispersed, and the localized metal concentration within the particle which can be as high as several per cent. It is this latter mentioned high local concentration of metals that determines the strength of the emission signal produced when a labeling insoluble particle passes through the flame of the particulate emission spectrometer. The emission signal is in the form of a very brief light pulse whose intensity will completely override any emissions due to natural trace metals or other elements in the environment. Another feature that contributes to the sensitivity and reliability of the method, is that the particulate emission spectrometer will respond to practically every particle that enters the flame so that only a very few labeling insoluble particles will have to be present in the sample to enable an unequivocal identification to be made.

The following calculation will illustrate the sensitivity of the proposed method. For the purpose of illustration, assume that 1 kilogram of additive labeling insoluble particulate material is provided which contains 10 percent bound metal identifier elements in each of the insoluble particles which are on the order of 0.5 microns in diameter. This additive labeling material is then dispersed into 26 million gallons of liquid having a specific gravity equal to one and hence a weight of 10^{11} grams. The average concentration of the metal in the liquid is given by $10^2/10^{11} = 10^{-9}$ or 1 part per billion by weight (1 ppb).

In contrast to the above concentration, the concentration of metal identifier elements within any one insoluble particle (which is what the particulate emission spectrometer sees) is 10 percent by weight or 10^5 parts per million by weight. Also, each particle of this size of specific gravity equal 1, will weigh about 10^{-13} grams and will have 10^{16} powder particles in 1 kilogram or 10^{16} in the 10^{11} grams of liquids. Accordingly, if dispersion is uniform it is expected that there will be $10^{16}/10^{11}$ or 10^5 particles per gram of liquid. Since, even 10 particles passing through the particulate emission spectrometer would be enough to effect an analysis and unequivocal identification, the test samples probably could be diluted by one or two orders of magnitude and still make effective measurements possible.

A second important feature of the proposed method is that it enables many possible different tracer labels to be established and used simultaneously. For example, if four different metals can be bound in an insoluble particle at four levels (four different weights), then because the size or weight of a particular metal determines the level of intensity of its emission, some 256 different analytical combinations are theoretically available. To enable it to use this capability, the particulate emission spectrometer would have to have four channels able to look at the emission from four different metals, and also be capable of resolving four

levels of concentration in each emission band. The design of particulate emission spectrometers having six, eight, or even more channels is feasible but of necessity would result in greater complexity and expense because of the short duration of each emission light pulse. This factor when added to the possibility of improving the peak height resolution of the instrument so that up to 10 levels of concentration of a given identifier metal, could be separated and identified, makes available some several hundred different analytical patterns or "finger prints" which readily could be identified with the proposed method.

From the foregoing description, it will be appreciated that the proposed labeling method is applicable to studies of fluid mediums either liquid or gas. It provides several hundred different, analytical patterns or "finger prints" to be established and used with different fluid mediums to be identified through the use of additive, labeling insoluble particles, all of which can be read by a single instrument. In liquids, the additive labeling insoluble particles can be used at average levels as low as one part per billion by weight, and yet the technique is such that the signals generated in the analytical instrument by the labeling material should be at least one or two orders of magnitude greater than any produced by background or naturally occurring emission sources.

Labeling Materials And Method Of Preparation

The additive materials employed to label specific fluid mediums comprise insoluble dispersable particulate materials having an average diameter in the 0.2 to 5 micron range and which contain 2–8 metals chemically bound within the particle in a fixed ratio. These insoluble, particulate labeling materials will be prepared in such a way that the ratio of metal contents that serve as the identifier elements will be constant from one particle to another, regardless of particle size. Suitable identifier metals for this purpose should satisfy the following requirements.

i. The metals used should form chemical bonds, by complexing, salt formation or otherwise with the particulate material.

ii. The metals should have characteristic flame emission bands which do not interfere with each other or with the emission bands from metals common in the natural environment such as sodium, aluminum, magnesium and iron.

iii. The metals employed should not themselves be major constituents of the environment to be studied. Thus, sodium should not be used for tracer studies in connection with sea water.

iv. It is desirable, although not always essential that the metal compound be of low toxicity.

Considering the above list of desirable characteristics, it will be seen that for the example in mind, namely the labeling of the source of an oil spill, the additive labeling insoluble particles should satisfy several requirements. They should not impair the usefulness of the oil, be non-volatile and insoluble in water, be disperable in crude oil, be easily, differentiated from constituents of the oil, be of reasonable cost, and they should be susceptible of preparation into large numbers of different compositions, each with unique analyzable emission characteristics.

The above set forth list of specifications can best be met by a family of particulate synthetic polymers, of predominantly hydrocarbon structure, in which a specific ratio of metal atoms will be maintained within the particle by bonding of the metals to the cross-linked polymer matrix. This can be done, for example, by preparing an emulsion of a cross-linked acidic polymer which is then neutralized with mixtures of metal hydroxides or basic oxides, as will be explained more fully hereinafter; or with greater difficulty, by preparing particles of cross-linked polymers which will form stable complexes with mixtures of metals.

As will be demonstrated more fully hereinafter, the proposed method of labeling requires that the additive labeling material be in the form of small particles from 0.2–5 microns in diameter and which are readily dispersible but not soluble in the fluid medium to which they are to be added, for example oil. In the case of polymer-metal compound additive, such particles are in the form of latex, and are the normal product of emulsion polymerization of vinyl monomers containing some difunctional (divinyl) compound which is the preferred method of fabricating the additive, labeling insoluble particles. If the glass transition temperature of the polymer is above about 70° C. and the particles are substantially cross-linked, the latex particles will remain as discrete spheres forming a dusty powder when the latex is dried in an oven or by spraying.

With regard to the question of not impairing the usefulness of the fluid medium (oil) the following calculation is instructive. Assume that there are **100,000** tons of oil in a tank which it is desired to label. 100,000 tones equals $10^5 \times 2 \times 10^3 \times 454$ grams or about 10^{11} grams. If to this amount of oil 1 kilogram of labeling polymer-based insoluble particles are added there will be 10^3 over 10^{11} equal 10^{-8} grams of polymer per gram of oil or about 10 parts per billion by weight of polymer, most of which is hydrocarbon.

In the typical labeling insoluble particulate material to be described more fully hereinafter, about 10 percent of the particle would be metal giving a total metal concentration in the example cited above of about 1 part per billion. This concentration of additive is not likely to cause any problem in the end use of the oil. More importantly, while the average metal concentration in the oil is about 1 part per billion by weight and is so low that it would be difficult, if not impossible, to detect such amounts with conventional forms of trace analysis such as flame ionization, atomic absorption or fluorescence spectromety without great difficulty in the measurements. However, the localized metal concentration within each particle is 10 percent (or about 10^5 parts per billion by weight) which is a very high level by the standards of trace analyses. This distinction between the average and localized metal concentration is the key to the successful analysis of the additive labeling insoluble particulate materials with minimal interference from the tracer elements in the natural environment.

The analytical method herein proposed preferably will measure chosen mixtures of metals within mixed polymer-metal particles without the necessity for complex separation or concentration procedures. As an example of the simplicity and elegance of the method, consider that each of the particles has a diameter of 0.5

microns and a specific gravity equal to 1 with a mass of about 10^{-13} particles per grams. If again 1 kilogram of the additive labeling particulate material is added to 10^{11} grams of oil (1,000,000 tons) there will be $10^3/10^{-13} = 10^{16}$ particles in 10^{11} grams of oil. There are a number of flame ionization spectrometers which will respond to almost all particles of this nature which enter its analyzer flame. See for example U.S. Pat. No. 3,330,960 and 2,730,005 for a description of such known flame ionization spectrometers. In a normal test procedure seeking to identify a given mass of oil, a fraction of a gram of oil will be diluted about ten fold with benzene and a solution sprayed into the air stream leading to a hydrogen-air flame of a flame particulate emission spectrometer. Each particle that enters the flame will emit a light pulse having emission bands which are characteristic of the metals bound within the particle. Peak intensity should be proportional to metal concentration. If three or four metals are present in a sensed particle, the instrument can be designed to look simultaneously at one strong band for each metal by means of four narrow pass filters and suitable photo detectors deployed around the flame.

To operate satisfactorily in the above proposed analyzing system the choice of labeled metals employed is important and is governed by the following considerations:

i. The label metals should have the ability to be detected by flame ionization. Metals having strong emission bands which are clear of interfering bands with such common elements as sodium, magnesium and calcium, should be employed. Obviously, there shold be no cross-interference between the metals if more than one metal is used in a given particle. Since the metal will be quite concentrated within the particle, high absolute flame ionization sensitivity may not be essential.

ii. The metals should facilitate preparation of polymer-metal salts or complexes both readily and efficiently.

iii. The metals should have a reasonable cost balanced against fairly low natural abundance in oil, sea water or the environment in which it will be employed as a labeling identifier element.

Table 1 lists the natural abundance of metals and metals of low abundance available in the sea water and the earth's crust in parts per million by weight. Table II lists some of the characteristics of possible metals of interest by their ease of salt formation with the acidic polymer, potential interference with other metals at ±30 A., their relative abundance in the sea and in the earth's crust, and their relative cost. Table III lists some additional properties of potential label metals of interest in connection with the presently proposed method of labeling. From a consideration of tables I–III and a comparison of the various metals, it appears that lithium, rubidium, cesium, barium, strontium, silver, copper and possibly potassium would serve as suitable label metals. The ability to form polymeric salts with these metals has been judged from the availability of acetates of the metals; however, to make the salts easily by direct neutralization of an acid polymer latex, the hydroxides of these metals should be water soluble. This further consideration immediately narrows the choice to six metals K. Li, Rb, Cs, Sr, and Ba as shown in Table II. If, for example, four of these metals can be cross-linked in a polymer at four different levels, it is possible to set up 256 (4^4) combinations of wave lengths and intensity in the emission spectrum of particles produced with these metals.

TABLE I

Natural Abundance of Metals

| | Metals of Low Abundance | |
Element	In Sea Water ppm	In Earth's Crust ppm
Sr	13	300
Rb	0.2	310
Li	0.1	65
Ba	0.05	250
Zn	0.014	132
Cu	0.09	70
Mn	0.01	1000
Pb	0.005	16
Sn	0.003	40
Cs	0.002	7
Ga	0.0005	15
Ni	0.0005	80
Hg	0.0003	0.5
Ag	0.0003	0.1
In	—	0.1
Tl	In Marine Organisms	0.6

	Metals of High Abundance	
Na	10,560	28,300
Mg	1,272	20,900
Ca	400	36,300
K	380	25,900
Al	1.9	81,300
Fe	0.02	50,000

TABLE II

Characteristics of Some Metals of Interest

Metal	ease of salt formation with acidic Polymer (1)	potential interfering metals at ±30 A (3)	sea abundance ppm	average earth abundance ppm	cost
Ag	2	Cu	0.0003	0.1	high
Ba	2	Ca, Cs, Cu, Sr	0.05	250	low
Ca	2	Ba	400	36,300	low
Cu	2	Ag, Ba	0.09	70	low
Cs	1	Ba, Sr	0.002	7	high
In	3	none	—	0.1	high
K	1	Mn	380	25,900	low
Li	1	none	0.1	65	low
Mg	2	none	1,272	20,900	low
Mn	3	K	0.01	1,000	low
Na	1	none	10,560	28,300	low
Rb	1	none	0.2	310	high
Sr	1	Cs	13	300	low
Tl	?	none	—	0.6	high

Notes

(1) In this column 1 indicates easy formation via water soluble hydroxides, shows acetate salts known, 3 indicates salts unknown or probably difficult to prepare.

(2) The metals Ca, Mg and Na are included to show the lack of serious interference with possible indicator metals.

(3) With allowance for relative band strength.

TABLE III

Properties of Some Potential Label Metals

| | | hydroxide/oxide | estimated dollar |
principal		solubility	per lb.

metal	atomic weight	flame emission A	g./100 ml. water at 10°C	metal (see note 2)
Ag	107.9	3280 3384	0.0013	100
Ba	137.4	5535	5.6	1.25
Cu	63.5	3247 4555	insoluble	2.50
Cs	132.9	8521 (1) 7665	395	200
K	39.1	7699 (1)	107	4.00
Li	6.9	6707	12.7	14
Rb	85.5	4202 4215	180	150
Sr	87.6	4607	21.8 (3)	12

Notes
(1) Will need special photo-multiplier for detection at this wavelength.
(2) Tentative estimates based on small lot quotations from chemical specialty houses. It would be reasonable to expect reductions of 25–50% for bulk purchase.
(3) At 100°C.

The above discussion should not in any way limit the applicability of the proposed technique to two, four or any specific number of metal identifier elements plus various combination of levels of intensity. In citing the combination of four metals plus four levels of intensity, it is assumed that the particulate emission spectrometer will not be able to distinguish fractional changes in peak heights and widely spaced increments of metal concentrations such as 1, 2, 4, 8 percent by weight. By appropriate design and development of the instrument, it is quite likely that much smaller differences in intensity can be resolved. This would be highly desirable since a choice of say 10 levels of intensity would allow one to obtain 100 different labeling spectra ("finger prints") with only two metals. This would permit substantial savings in the cost of the label polymer since inexpensive lithium and barium could be used alone as the metal identifier elements. It would also allow considerable expansion of the number of spectra available with four metals, etc. Another option in the labeling method involves the use of mixtures of labeled particles. For example, two types of particles, each type with a different two-metal spectra could be employed. In an analysis employing such a mixture, it would then be necessary to run only enough of the sample to establish that both types of particles were present in order to make a positive identification.

From the standpoint of cost, it is considered that the additive labeling insoluble particulate material would not be significant factor in practicing the presently proposed method. Assuming an average level of 10^5 particles per gram of fluid medium (oil) it is quite probable that the dose of additive labeling material can be reduced by a factor of 5–10 depending upon how effectively one can disperse the additive labeling particulate material in the fluid medium under test. This factor places some importance on the effective disperal of the additive labeling insoluble particulate material in a test fluid medium.

With respect to the question of dispersion, a worst case example is posed by the need to disperse additive labeling particulate materials in oil. If the additive labeling particulate material is prepared by emulsion polymerization, followed by neutralization and drying, its final form will be a dry, free-flowing powder, probably somewhat dusty because of the small particle size. The manner in which this material is added to the oil will depend upon circumstances. For dispersion it should be added to flowing oil in a pipe line where it can be added directly as a powder by a simple vibratory feeder. Alternatively, the polymer powder could be dispersed in any liquid which did not swell the particle, for example heptene, kerosene or some low melting paraffin wax. In the case of wax dispersion the solid composition could be extruded as a ribbon into the oil to be dispersed by solution of the wax. In an extension of this concept, label insoluble particles could be dispersed in small pills of hydrocarbon wax or oil soluble polymer and could be distributed over the surface of a large tank by using a device such as an air gun adapted for the purpose. Such a technique would be particularly valuable in cases where the oil surface was accessible through only one or two small openings in the top of a tank.

Although good dispersion of the additive labeling insoluble particulates in the fluid medium (oil) is desirable, the sensitivity of the proposed analytical method is such that probably only two or three particles would have to pass through the flame of the particulate emission spectrometer in order to establish the identity of the labeled fluid medium. For example, with 1 kilogram additive labeling insoluble particulates in 100,000 tons of oil giving an average of 10^5 particles per gram, a considerable amount of non-uniformity in the dispersion of the labeling particles can be accommodated and still obtain satisfactory identification if a number of test samples of the fluid medium (oil) under examination are taken at random from the mass of the medium.

Synthesis Of Additive Labeling Insoluble Particulate Polymers

The simplest type of polymer that appears suitable as a matrix to bond the metal atom to form a mixed metal-polymer salt is a copolymer of styrene, methacrylic acid and divinyl benzene. The styrene, which is present in the largest proportions, will provide the necessary hydrocarbon affinity (and hydrophobic character) to insure easy dispersion in the oil. The methacrylic acid will provide the carboxylic acid function for metal binding and divinyl benzene wild cross-link the polymer as it is formed so that the final polymer shows minimal swelling in hydrocarbons. These monomers will be polymerized in emulsion using a non-ionic emulsifier and a metal-free initiator.

A typical example of a suitable recipe for forming the above briefly described mixed metal-polymer salt is as follows:

Components	Parts (Weight)
Styrene	60–69 (Distilled)
Methacrylic Acid	39–30
Divinyl Benzene	1
Distilled Water	200
Ammonium Persulfate	0.3
Emulsifier	4.0

The above set forth mixture would be heated at 50° C. under nitrogen with mild agitation until polymerization is about 95–98 percent complete. Any traces of unreacted acid are then stripped out by vacuum stripping. The resultant emulsion will have a pH of about 3 and the particles will have a diameter in the required range, averaging about 0.5 microns.

A solution of metal hydroxides is then prepared, mixing the hydroxides to give the desired ratio of metals. The solution of metal hydroxides is then added to the latex which may be heated until a steady value of pH of about 8 is reached. Even at a pH of 8 it is not likely that 5 all of the polymeric acid groups will be neutralized due to the incomplete penetration of the particles. However, the ratio of the metals bound to each particle will be defined by the hydroxide mixture and should not vary from particle to particle. Drying of the latex in 10 shallow trays, or by spraying then yields an insoluble, mixed metal-polymer salt containing the metals bound to the polymer matrix in a fixed ratio. In a final step the powder is washed with distilled water to remove mechanically held salts, and then redried. 15
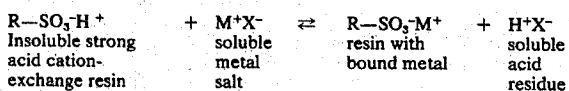
If it is found necessary to eliminate ion transport across the particle boundary, this can be accomplished by carrying out a second polymerization after neutralization which would form an impermeable sheath around each particle. This second polymeriza- 20 tion could be done, for example, by adding to the neutralized latex 10–30 percent (on original polymer) of acrylonitrile, styrene or other neutral monomer which forms a water-insoluble polymer, and polymeriz- ing it without further addition of emulsifier. When the 25 polymerization is complete the latex is dried as before.

In these preparations the acid content can be varied from 10–100 percent DVB percentage from 0.1–5, or one could find it advantageous to copolymerize pre- formed mixed acrylic acid-metal salts with difunctional 30 cross-linking monomers in dilute aqueous solution. It is necessary, however, to end up with a polymer which does not appreciably swell in hydrocarbons or water, and which remains unagglomerated when the latex is dried. The low water swelling requirement may have to 35 be balanced against ease of neutralization.

Another method of preparing the metal labeled in- soluble particulate materials starts with available porous strong acid type cation exchange resin beads. 40 One example of such a resin in Rohm and Hass Amber- lite 1R – 120(H) AR but other resins of this type may equally well be used.

Since the resin beads as normally supplied are too large for the purposes of this invention they are first 45 ground, using a ball mill, attrition in a fluidized bed or other appropriate means, to obtain material with parti- cles in the 0.5 to 5 micron size range.

In a typical preparation, 100 g. of the ground and screened particles with a total exchange capacity of 1 50 equivalent (10 milli-equivalents per g.) are slurried with 1 liter of an aqueous solution containing one to eight metal salts. The concentration of these metals salts is such that the total equivalents of metal present in the 1 liter solution lies between 2 and 5. The ratio of 55 metal ions in the solution will probably be fairly close to the ratio of the metals to be bound in the resin parti- cles, but the exact ratios to use in the solution will have to be determined by experiment. The reaction between the metal ions in the mixed salt solution and the resin, is 60 cation exchange, and may be represented by the fol- lowing general equation:

| R—SO$_3$H$^+$ | + | M$^+$X$^-$ | $\rightleftarrows$ | R—SO$_3$M$^+$ | + | H$^+$X$^-$ | 65 |
| Insoluble strong acid cation- exchange resin | | soluble metal salt | | resin with bound metal | | soluble acid residue | |

After allowing time for the reaction to proceed to equilibrium, the particles are filtered from the solution and washed on the filter with de-ionized water.

The particles are then sealed against further ion exchange as follows. A reactor is fitted with a stirrer, condenser, thermometer and inlet for nitrogen or other inert gas.

The reaction recipe is as follows:

	Wt. g.
Mixed metal bonded particles (prepared as above)	100
Styrene	20
Divinyl benzene (DVB)	0.2
Non-ionic emulsifier	5
Benzoyl peroxide (dissolve in the styrene-DVB mixture	0.2
Water	300

These materials are added in the following order. The water and emulsifier are first added to the reactor and the mixture stirred until the emulsifier is dissolved. The particles are next added, and stirring continued until they are smoothly dispersed in the water, without clumping. The styrene, divinyl benzene and benzoyl peroxide are mixed in a separate container and this mixtures is then added slowly, with continual stirring, to the emulsion in the reactor. When all the monomers have been added stirring is maintained, air is swept out of the vessel with nitrogen and the mixture is stirred at 50°–80 C. until conversion of the monomers is sub- stantially complete. Reaction must be continued until at least 80–90 percent of the monomers have been con- verted and the particles can then be isolated by oven or spray drying.

Although the previous examples have cited polymers as the means of binding the metal identifier elements in fixed ratios within the particles, other methods may be used. For example, metal salts may be mixed in the desired ratio, the mixture then subdivided and the par- ticles encapsulated with an insoluble sheath to hold the metal salts within the particle. In some cases, mixed metal salt compounds may be used in themselves to generate particles of known metal ratios although the number of combinations available by this means is limited. Yet another method of preparing the labeling insoluble particles is one that would be particularly use- ful in the air borne applications. In this proposed method, one could absorb mixtures of metal salts from solution onto the surface of absorbent particles such as carbon black, aluminum or silica. When desorption is possible as in an aqueous environment, such composi- tions would have to be protected by encapsulation. For most applications, however, metals bound to insoluble polymer particles are the preferred type of additive labeling insoluble particles for the purposes of practic- ing this invention.

Particle Emission Spectrometer

FIG. 1 of the drawings is a functional block diagram of a four channel particle emission spectrometer (PES) suitable for use in practicing the invention. For any par- ticular application, fewer or more channels may be added to the instrument depending upon the number of characteristic spectral emissions to be read out. For the example in mind, namely the identification of the source of an oil spill, it is believed that a four channel particle emission spectrometer is adequate.

The spectometer is comprised of a hydrogen flame source shown generally at 11 which is supplied through inlet tube 12 with hydrogen, through inlet tube 13 with filtered air and inlet tube 14 with a diluted sample such as oil to be analyzed in the spectometer. The flame 11 is viewed by an array of photo electric converters shown at 15a, 15b, etc. through a suitable lens arrangement 16a, 16b, etc. and appropriate narrow band filters 17a, 17b, etc. FIG. 2 of the drawings illustrates the manner in which the photo electric sensors which may comprise photo multipler cells, photo transistors, photo diodes or any other forms of photosensitive element for converting light energy to electric signal pulses, are arrayed around the hydrogen flame source 11. The narrow pass band filters may comprise Baird atomic interference filters which are designed to pass only one principal emission band for each of the labeling metals used in the additive labeling insoluble particulate material. FIG. 3 of the drawings is a plot of the emission spectra of metals in an air-hydrogen flame depicting a principal emission for the metals of interest in the present application, and which will identify the bandpass characteristics of the several filters 17a, 17b employed in the PES. It is to be understood that any one of the filters such as 17a will pass only the principal emission band for a single labeling metal while a second filter such as 17b would pass the principal emission band of a second different labeling metal. The output from the photosensitive detectors 15a, 15b are supplied to respective amplifiers 18a–18d, whose outputs in turn are supplied to separate storage devices 19a–19d. The storage devices 19a–19d have their outputs supplied to a suitable selector-discriminator circuit which serves to selectively read out in a serial manner the outputs of the storage devices 19a–19d and to supply the same to a read out device 22 and/or a pulse counting device 23.

In operation diluted samples of the medium under test such as oil having dispersed therein the labeling insoluble particle, is sprayed into the filtered air stream and burned in the hydrogen-air flame 11. Each particle entering the zone of the flame will generate a brief light pulse which will contain emissions due to each of the metals bound within the labeling insoluble particles as depicted in FIG. 3 of the drawings. For a more detailed description of this phenomenon reference is made to U.S. Pat. Nos. 3,330,960 and 2,730,005. When the instrument is being used to test a liquid medium, the liquid medium together with the suspended labeling particles will be sprayed into the hydrogen flame and when gaseous mediums are being analyzed, the gaseous medium together with the suspended labeling particles will be drawn from the environment with filtering of coarse particles only and then supplied to the hydrogen-air flame.

The four sensor units deployed around the hydrogen-air flame each contains its own characteristic narrow band width filter 17a which passes only the frequency of the principle emission of the one of the labeling metals. The collimating lens assembly 16a, 16b, etc transmits the detected light emission to the photo sensitive surface of the associated photo sensitive detector 15a, 15b that is designed to have good sensitivity at the particular wave length in question. The output electric signals derived from the photo sensitive detectors 15a–15 are then supplied through the amplifiers

18a–18 of conventional construction to suitable storage devices which may comprise capacitive storage networks, etc. Each storage signal then can be selectively picked up from the storage devices 19a–19d, equalized and supplied through a suitable discriminator network to the read out device 22. This read out device may be a high impedance voltmeter, chart recorder or it can be an oscilloscope with a persistant memory screen. If desired, suitable logic circuitry can be supplied to control the read out circuitry in a manner such that once four outputs from a single labeling insoluble particle have been received into the storage devices 19a–19d, further input signals will be blocked until the storage signals are read out and dissipated. The discriminator and equalizer circuit 21 may be designed in a manner such that it will permit adjustments to compensate for the sensitivity variation between the channels and will include leveling circuitry to accommodate variation and overall signal intensity because of difference in particle size.

In addition to the above features, in some measuring applications certain variations may be desirable. As explained earlier, the presently proposed system foregoes the ability to measure time average concentration of the labeling material in order to have available many different label combinations together with very high sensitivity and high signal to noise ratio with respect to the labeling metals contained in each labeling insoluble particle. However, in some applications it may be possible to select only one spectral pattern and to set the PES so that it will count only those particles that show the particular selected pattern. With such an arrangement it would then be possible to obtain a measure of concentration of a given labeling insoluble particle in the sample fluid stream. This can be done by inserting additional comparison and switching circuitry within the discriminator section of the PES and supplying the resultant output signal pulses to a high speed counter such as shown at 23.

Another problem of concern with respect PES is to insure that every emitted light pulse generated by a particle passing through the flame is seen equally by all of the four sensors. This problem can be appreciated by reference to FIG. 2 of the drawing wherein it can be seen that if the four sensors 15a–15d are uniformly spaced 90° apart around the flame, it is possible that a particle which flashes on the edge of the flame as shown at 25 may be seen differently by the several sensor units. For example, sensor unit 15a would view the particle flash 25 directly, while sensor unit 15b would have to view the particle flash through the full flame width. Should this cause difficulty in all four detectors sensing all of the particle emissions, a beam splitter could be employed to view the flame from a single viewing point and to supply all four photo sensitive detectors. In this manner, it would be assured that all four detectors view each particle emission sensed by any one of the detectors.

From the foregoing description, it will be appreciated that the invention provides a novel fluid medium labeling source tracer method and materials which employs a number of different additives that can be used simultaneously to imprint a unique analytical "finger print" label on a given fluid medium with all of the additives being capable of detection and analysis by

a single instrument. Hence, many different flow streams and masses of liquids and gases may be monitored by the same instrument. The technique is applicable to studies in water or other liquids as well as air and other gases. It enables several 100 unique analytical patterns ("finger prints") to be established by the use of a series of additives of differing concentrations, all of which can be read by one instrument. The additives may be used in the fluid medium in dilute concentrations having average levels of 1 part per billion by weight and possibly less, yet provide output signals generated in the analytical PES instrument by the labeling metals which are at least one or two orders of magnitude greater than any background noise or naturally occurring particle emissions. The method employs two major components comprising specially prepared additive labeling insoluble particulate materials containing bound metals in known fixed ratios and a particulate emission spectrometer which measures simultaneously one principle flame emission band from each of the bound metals in any single particle that passes through the analyzing flame of the instrument. The key to the success of the method lies in the distinction between the average concentration of the labeling metal, obtained by dividing the known weight of the metals in the additive labeling insoluble particulate material by the total weight of the fluid medium in which they are contained, and the localized metal concentration within the individual additive labeling insoluble particles which can be as high as 10 percent. It is this local concentration of labeling metals that determines the strength of the light emission signal when a particle passes through the analyzing flame of the particle emission spectrometer. Although only a very brief light pulse is emitted, its intensity is such that it will completely override any emission due to natural trace metals in the environment. Also, the particle emission spectrometer responds to practically every particle that enters its analyzing flame, so that only a very few particles have to be present in a sample fluid medium in order to enable unequivocal identification of the medium to be made. Having described certain embodiments of a fluid medium labeling source, tracer method and materials constructed in accordance with the invention, it is believed obvious that other modifications and variations of the invention are possible in the light of the above teachings. It is therefore to be understood that changes may be made in the particular embodiments of the inventions described which are within the full intended scope of the invention as defined by the appended claims.

What is claimed is:

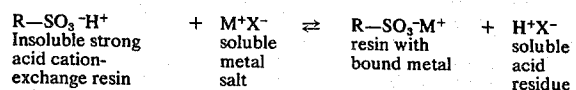1. A method of spectrally identifying a given fluid medium which comprises dispersing into the given fluid medium particles of a synthetic mixed metal-polymer salt which are insoluble in the given fluid medium, said particles comprising a plurality of different metallic identifier elements bound to a solid polymer with the different identifier elements each having a characteristic spectral emission which does not interfere with or overlap the spectral emission characteristics of other identifier elements, collecting a test quantity of the fluid medium at a different point in space and time and subjecting the test quantity of the fluid medium to a flame spectral analyzer for detecting the characteristic emissions of the several different identifier elements.

2. A method according to claim 1 wherein only dilute amounts of the insoluble particles are dispersed in a given fluid medium to be traced on the order of 20 parts per billion by weight or less yet providing relatively high localized identifier element concentrations within the insoluble particles on the order of 10^5 parts per million by weight for spectral analysis purposes.

3. A method according to claim 1 wherein the particulate synthetic mixed metal-polymer salt is polymerized and neutralized so as to be chemically non-reactive with a particular fluid medium into which it is dispersed as a trace identifier and the metallic elements comprising the mixed metal-polymer particulates are different from those naturally occuring in the fluid medium into which the particulates are dispersed.

4. A method according to claim 3 wherein the particulate synthetic mixed metal-polymer salt is of predominantly cross linked hydrocarbon structure in which a specific ratio of metal atoms are maintained within the particle by bonding of the metal to the cross-linked polymer matrix and in which the metal atoms comprise on the order of 10 percent by weight of the particle.

5. A method according to claim 3 wherein the insoluble particles are formed by the reaction between a strong acid cation-exchange resin and the metal ions of a mixed metal salt solution in accordance with the following general equation:

$$R{-}SO_3{}^-H^+ \;+\; M^+X^- \;\rightleftarrows\; R{-}SO_3{}^-M^+ \;+\; H^+X^-$$

| $R{-}SO_3{}^-H^+$ Insoluble strong acid cation- exchange resin | M^+X^- soluble metal salt | $R{-}SO_3{}^-M^+$ resin with bound metal | H^+X^- soluble acid residue |

6. A method according to claim 1, wherein a separate spectral analysis is performed for each of the different known identifier elements.

7. A method according to claim 6 wherein only dilute amounts of the insoluble particles are dispersed in a given fluid medium to be traced on the order of 20 part per billion by weight or less yet providing relatively high localized identifier elements concentrations within the insoluble particles on the order of 10^5 parts per million by weight for spectral analysis purposes.

* * * * *

60

65