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Barringer

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[54] **METHOD AND APPARATUS FOR GEOCHEMICAL SURVEYING**

[75] Inventor: **Anthony Rene Barringer,** Willowdale, Ontario, Canada

[73] Assignee: **Barringer Research Limited,** Rexdale, Ontario, Canada

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[51] **Int. Cl.** **G01n 1/00,** G01j 3/00, G01j 3/30

[58] **Field of Search** .... 356/36, 38, 74, 81, 356/82, 85, 87, 96; 250/83 SA, 83.6 S; 23/230 M, 230 PC, 230 EP; 73/28

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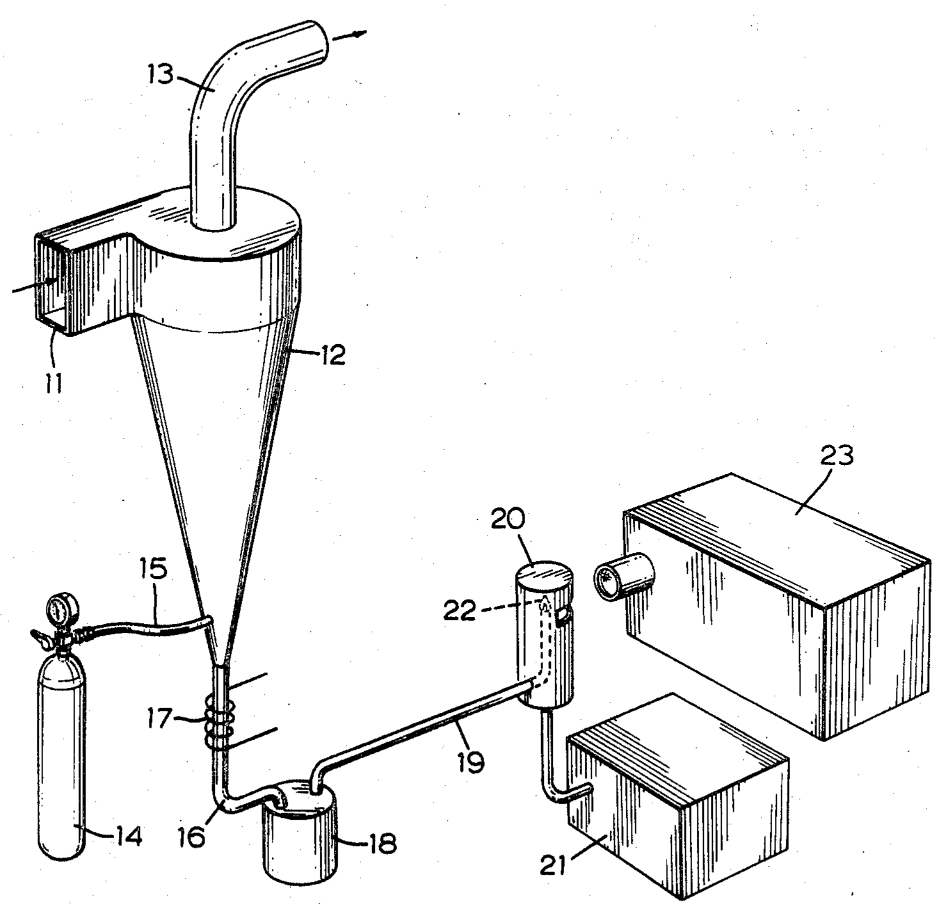
Primary Examiner—David Schonberg
Assistant Examiner—V. P. McGraw
Attorney—David M. Rogers et al.

[57] **ABSTRACT**

A method and apparatus for performing a rapid geochemical survey over an area of the earth consisting of collecting and concentrating atmospheric particulates, preferably transferring the particulates into a stream of an inert carrier gas, heating the particulates to break down organic particles into particles of smaller size and vapours, removing from the stream inorganic particles which generally are of relatively high mass, and then analyzing the remaining organic particles and vapours to detect the presence of elements or compounds indicative of underlying geological conditions.

26 Claims, 4 Drawing Figures



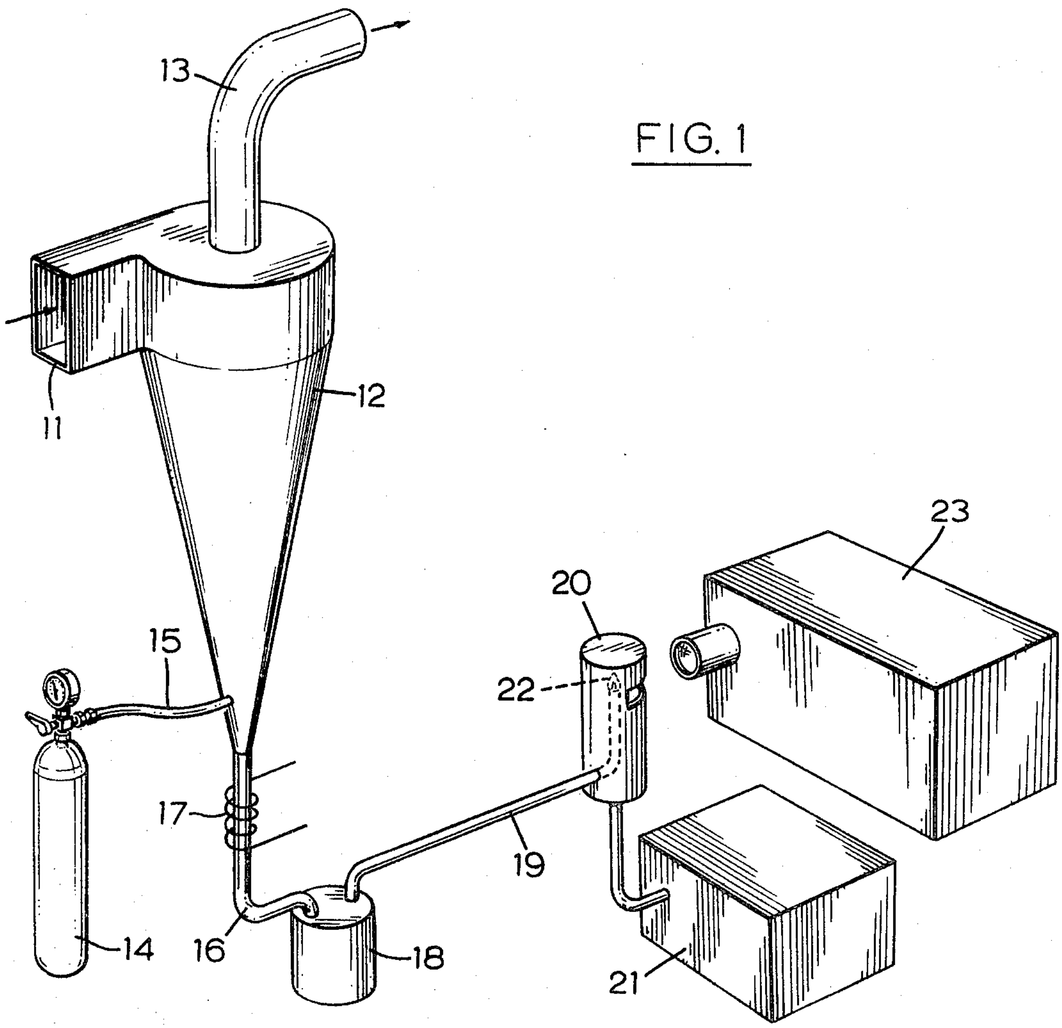


FIG. 1

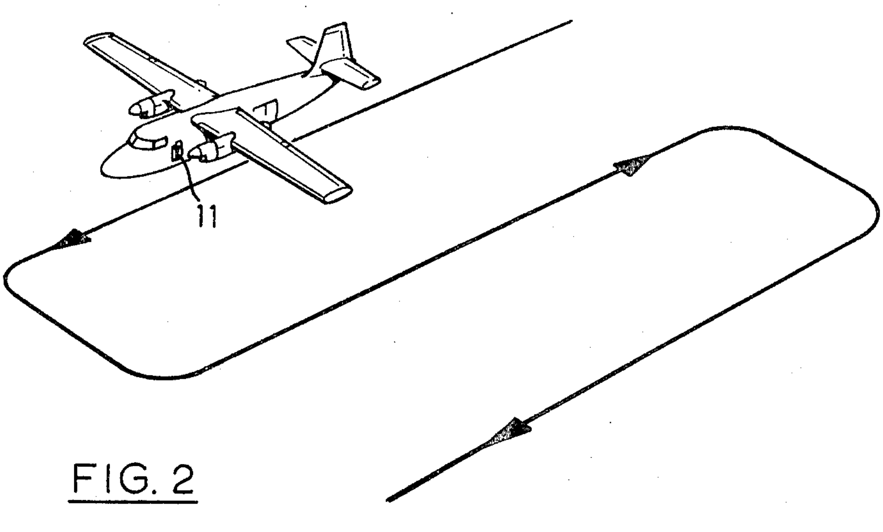


FIG. 2

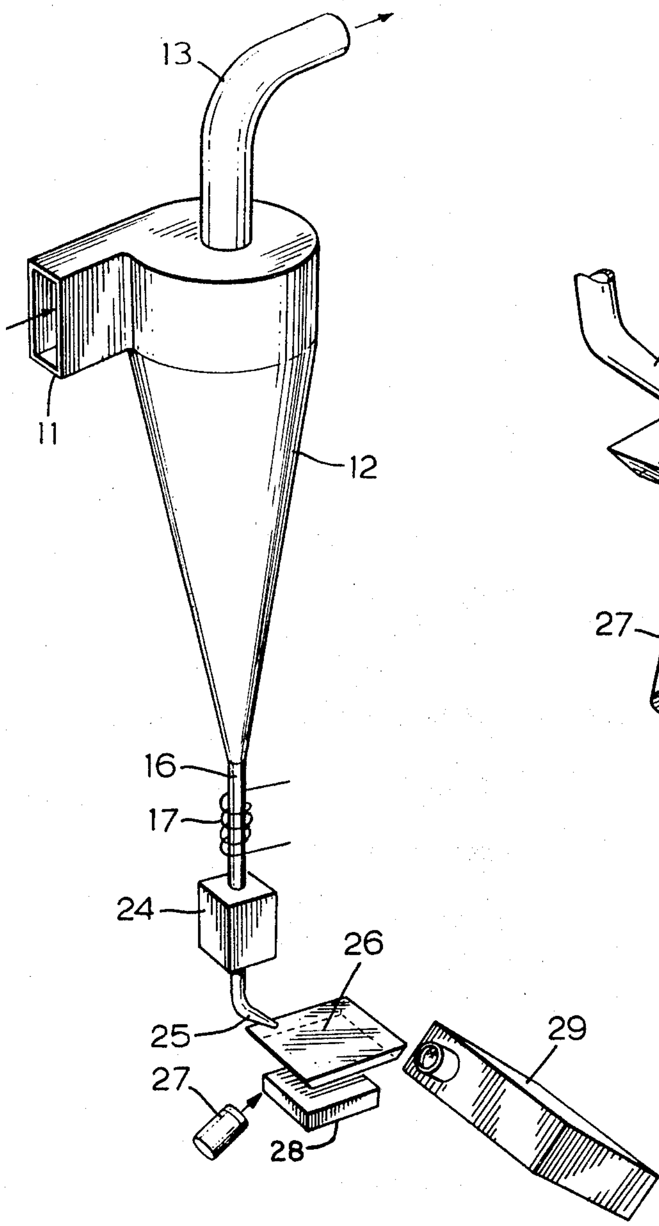


FIG. 3

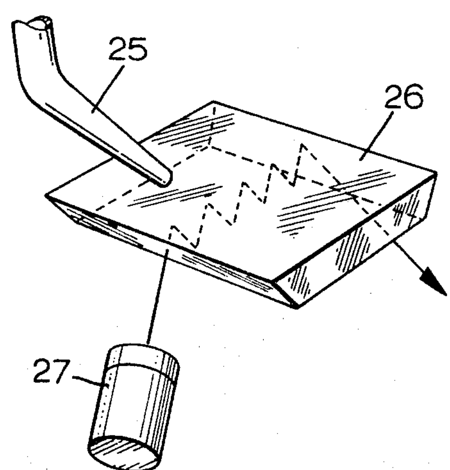


FIG. 4

METHOD AND APPARATUS FOR GEOCHEMICAL SURVEYING

This invention relates to the art of mineral exploration and geochemical mapping, and in particular to a method and apparatus for geochemical analysis of atmospheric particulates from a moving vehicle such as an aircraft.

Metalliferous mineral deposits which lie beneath the surface of the earth and which are enclosed by rocks and soil, are associated with a dispersion of trace elements in the surrounding rocks and soils. Analyses of rocks and soils have been used extensively in mineral prospecting and methods of systematic sampling and analysis have become accepted in the field of mineral exploration. In addition, it has been found that oil fields are frequently accompanied by dispersions of trace hydrocarbons in the overlying rock strata and along fracturing systems extending above the oil fields. Of particular significance is the distribution of the lighter hydrocarbons in fractures such as methane, ethane, pentane, etc. Accumulations of bituminous substances and porphyrins have also been noted in distinctive patterns above oil fields in the near surface soils, and trace metals associated with oil porphyrins such as vanadium and nickel have been found to exhibit characteristic patterns of distribution in some oil field regions. Also, anomalous amounts of hydrocarbons attributable to submarine oil and gas deposits may be present in minute droplets of water or aerosols in the atmosphere above the sea, and hence would act as indicators of the presence of such submarine deposits.

Geological formations are also associated with assemblages of chemical elements which are frequently characteristic of particular rock types and a knowledge of the regional distribution of key elements can provide a valuable guide to geological mapping.

The collection of surface soil and rock samples is relatively slow and expensive, and therefore it would be advantageous to be able to ascertain the existence of trace elements or hydrocarbons remotely, e.g. from a moving aircraft. It has been proposed by Weiss in U.S. Pat. No. 3,309,518 dated Mar. 14, 1967 to collect samples of atmospheric particles (e.g. on a membrane filter) and to analyze the particles to ascertain their constituent elements. The present invention also deals with the collection and analysis of particulates, but unlike Weiss only a particular portion of the particulates is analyzed. It has been discovered that the analysis of the organic portion of the particulates and not the inorganic provides a more sensitive and more generally applicable indication of the existence of orebodies than the Weiss method, which does not discriminate between the organic and inorganic portions. Also, in the present invention the analysis may be carried out continuously and in real time, without resort to filters of the kind suggested by Weiss, which filters must of course be replaced at frequent intervals.

In the present invention, atmospheric particulates are firstly collected and concentrated by any conventional technique, such as a dust collection device known as a cyclone, the cyclone being modified to concentrate the particles into a reduced stream of air or gas. Alternatively, electrostatic precipitators could be used. The concentrated particles are then preferably transferred into a stream of inert carrier gas, such as argon. The organic particles are then separated from the inorganic

particles, for example by heating the particles to a temperature of between 100°C and 700°C depending upon the type of detection being carried out. At the lower end of the temperature range, solid or liquid hydrocarbons can be vaporized and may be anlayzed by gas chromatography, mass spectroscopy, flame ionization, etc. At higher temperatures, the organic particles or aerosols are pyrolized and break down into simpler organic compounds and water vapour or are converted to inorganic ash. The organic breakdown products can be readily separated from the mineral particulates by a gravity settling procedure or by using a miniature cyclone since the pyrolyzed organic particles are greatly reduced in size, mass and density compared with the mineral particulates which are unchanged by heating. The pyrolized and lightweight organic particulates after separation from the heavy mineral particulates are passed to the analytical equipment which may be of the optical atomic absorption type or of an optical emission type such as a microwave plasma emission spectrometer. In the latter embodiment extremely high sensitivity can be obtained since the finely divided pyrolyzed particulates are injected into a high temperature plasma where they are very readily atomized and provide very intense and specific line emissions. The pyrolized and finely divided organic particulates possess major advantages over the inorganic particulates in respect of their ease of atomization in an atomic absorption flame or microwave emission plasma, and in the fact that they are so finely divided (like smoke) that they tend to pass through the apparatus quite freely, so that frequent cleaning of the apparatus is not required.

In the drawings,

FIGS. 1 and 3 are diagrammatic perspective views showing two embodiments of the invention,

FIG. 2 is a diagrammatic view showing a typical airborne survey flight path, and

FIG. 4 is a diagrammatic perspective view of a crystal that is used with the embodiment of FIG. 3.

Referring to the drawings, the apparatus as shown in FIG. 1 may be installed in an aircraft or other vehicle. Air containing particulates to be analyzed enters through a sampling duct 11 and thence into a cyclone 12 which causes the air to form a vortex. The particulates in the air collect on the walls of the cyclone by centrifugal action and settle towards the conical base of the cyclone 12 under the action of gravity. Relatively clean air is discharged through an outlet duct 13. An inert carrier gas such as argon is inserted into the cyclone 12 in such a manner as to capture the particulates. The argon or other inert gas may be contained within a pressurized gas cylinder 14 which is connected to the cyclone 12 by means of a length of tubing 15. At the point where the tube 15 meets the cyclone 12, the particulates are relatively concentrated and the air at this point inside the cyclone can be arranged to be at virtually zero pressure differential with the outside air. This condition is achieved by appropriate design of the cyclone with special reference to the relative cross sectional areas of the cyclone inlet and clean air outlet. By inserting a non-turbulent argon stream at the conical base of the cyclone 12, the particulates will settle into the pool of argon so formed and will be carried through the rest of the apparatus, as will be described. In effect, the arrangement described above transfers the particulates from air into an inert gas, thus considerably simplifying the subsequent analysis of the particulates. An opening is formed at the conical base of the cyclone **12** and a tube **16** is connected to the cyclone **12** at the conical base for the purpose of conveying the argon stream with the particulates from the cyclone **12.** The tubing **16** preferably is heated to a predetermined temperature such as 700°C by means of an electrical heating coil or the equivalent, for the purpose of breaking down organic particles into vapours and smaller sized particulates. The tube **16** is connected to a conventional dust trap **18** which serves to separate by gravity the relatively heavy inorganic particles from the relatively light organic particles and vapours. The organic particles and vapours are then directed from the dust trap **18** via a tube **19** into a microwave cavity **20** which is connected to a microwave generator **21.** The microwave generator **21** produces a plasma in the argon stream formed inside the microwave cavity **10.** The microwave plasma is diagrammatically indicated by reference numeral **22.**

The organic vapours and particles are excited in the plasma **22** and they will emit light which is indicative of their atomic or molecular structure, and as is well known, by spectrally analyzing the emitted light the nature of the elements and compounds in the plasma **22** can be determined. As shown in FIG. **1,** the plasma **22** is viewed by a spectrometer **23** which is capable of measuring the intensity of light at one or more predetermined wavelengths, depending upon the number of elements or compounds it is desired to observe. The spectrometer **23** has one or more output channels, depending upon the number of separate elements or compounds it is desired to measure, and electrical signals appear at the output channels in the conventional manner, from whence they may be fed to a conventional recorder.

The apparatus described above may be installed in an aircraft as shown in FIG. **2,** with the open end of the duct **11** positioned forwardly, as shown. The aircraft is flown in systematic traverses over an area to be explored, at a relatively low flying altitude and with traverse intervals varying between about one eighth of a mile and five miles depending upon the nature of the information it is desired to obtain.

The response time of a practical system for airborne geochemical sampling should be not more than six seconds, in order to localize target areas. Assuming that the analytical equipment has an absolute detection sensitivity of between about 10^{-10} and 10^{-12} grams, it is necessary to concentrate the organic particulates from the atmosphere at a collection rate of about 10 cubic meters per minute. When using cyclone collection techniques having a dust collection efficiency of at least fifty per cent (50 percent), the overall air flow capacity required is of the order of 20 cubic meters per minute.

It will be understood that other conventional techniques may be employed for receiving and concentrating the particulates, for example an electrostatic precipitator may be employed instead of the cyclone **12.** The dust trap **18** may be selected from a variety of devices capable of separating the relatively light organic particles and vapours from the relatively heavy inorganic particles. Also, although the microwave plasma technique is preferred, it will be understood that other conventional optical spectroscopic analysis techniques may be employed as well, provided they have adequate sensitivity and a sufficiently fast response time in relation to the velocity of the vehicle used in the performance of the survey. Still other methods of analysis may also be employed such as x-ray fluorescence and neutron activation and the selection of analytical techniques is a matter of choice having regard to factors of sensitivity and convenience for mobile applications.

It will also be understood that there are many alternative ways for transferring particulates concentrated in an air stream into a stream of inert gas. These include injecting the air stream into the upper portion of a horizontal tube while injecting an inert relatively heavy gas such as argon into the lower portion of the tube. By suitable design laminar flow can be induced thereby maintaining the upper and lower separation of the two gases in the tube and allowing particulates to settle into the lower inert layer of gas during transit along the tube.

The apparatus described above is particularly intended to measure trace elements present in organic particles, such as copper, nickel, lead, etc. However, the invention is also applicable to the detection of organic particles containing hydrocarbons for the purpose of oil and gas exploration. The apparatus shown in FIG. **3** may be used for this purpose, and it will be noted that some of the components of the apparatus shown in FIG. **1** are similar to those used in the apparatus of FIG. **3**; such components are indicated by like reference numerals in FIGS. **1** and **3.** Particulates which have been concentrated in the cyclone **12** emerge at a relatively low velocity through the bottom of the cyclone **12** and then they flow through the tube **16.** In this embodiment, it is not necessary to inject the particulates into a stream of an inert carrier gas. The tube **16** may consist of high temperature ceramic material that is heated with a coiled resistance wire to a predetermined elevated termperature, for example of the order of 500°C. The resistance wire coil and the tube **16** acts as a pyrolyzer which breaks down organic aerosols and particulates containing hydrocarbons into simpler organic gaseous fractions. After passing through the pyrolyzer section of the apparatus, the heated particulates and gases pass through a heated filter and dehydrator unit **24,** the function of is to pass only those particles having a size of less than about one micron. The filter **24** contains hot dehydrating material which will combine with water vapour without adsorbing hydrocarbons, so that the output of the filter **24** will consist of heated air with organic vapours and low moisture content, and extremely finely divided particles, most of which will be organic in nature. The filter material contained within the filter **24** can readily be replaced, and alternatively the filter **24** can take the form of a miniature cyclone such as that described above. It is advantageous to limit the size of the particles emerging from the filter **24** to a low level, in order to keep the components of the system downstream of the filter **24** as clean as possible.

The heated hydrocarbon vapours which have passed through the filter **24** are directed through a nozzle **25** onto a cooled crystal plate **26** of the conventional kind used in attenuated total internal reflectance spectroscopy (ATR). Light from an infrared source **27** is passed onto a beveled end face of the crystal **26** and undergoes multiple internal reflections before exiting at the far end of the crystal **26,** as shown in FIG. **4.** A property of the crystal **26** is that if liquid film or adsorbed layers of gases are deposited on the upper face of the crystal

26, their infrared absorption spectra are picked up by the beam of light which is internally reflected from the upper surface. The crystal 26 rests upon a refrigerating plate 28 which maintains the crystal 26 at a low temperature, for example of the order of 0°C, to thereby cause a strong condensation and adsorption of the hydrocarbon gases at the upper surface of the crystal 26. The film formed at the upper surface of the crystal 26 is dynamic, in the sense that it is continually being replaced by fresh material. Flow rates and differential temperatures are arranged to ensure that the residence time of components in the surface film is not more than about six seconds, so that the entire system remains rapidly responsive to changes in the organic content of the incoming particulates. An infrared spectrometer 29 is designed to detect the presence of diagnostic absorption bands in the infrared light emerging from the crystal 26, i.e. it is adjusted to selected wavelengths corresponding to the absorption spectra of the gas or gases to be detected. Alternatively, the spectrometer 29 may be of the correlation type described in U.S. Pat. No. 3,518,002, dated July 30, 1970. A correlation spectrometer of the kind disclosed in the above patent can be programmed to preferentially detect any group of absorption bands representing either a particular organic compound such as methane or propane or a characteristic spectral pattern representing a given class or classes of organic substances.

Quantitative information can be obtained on the distribution of elements or organic compounds in the underlying terrain by means of the invention as described provided that the distribution of particulate concentrations in the atmosphere remains relatively constant. Under a given set of meteorological conditions, this situation is approximated and if, for example, a profile is flown across a mineral deposit, a clear increase in certain elements will be noted as the deposit is traversed. The change in element concentrations in the atmosphere far exceeds local variability caused by changes in particulate concentrations in the atmosphere. However, if systematic surveying is to be carried out under varying meteorological conditions, it is advisable to provide a means for compensating for changes in atmospheric particulate loading. Two approaches can be applied, one based on ratioing against the total particulate concentration in the atmosphere and the other based on normalizing against the airborne organic particulate component. In the first case a conventional optical atmospheric particulate counter can be employed similar to the kind usually used for air pollution monitoring purposes. Such device, which depends upon the measurement of light scattering of a sampled air stream passed through an optical cell, provides an electrical output signal proportional to particulate concentration. This output signal can be divided into the output of respective analyzing channels for each element or compound being measured. Thus, if the particulate loading in the atmosphere doubles, the measured values for each element or compound are divided by two. The conventional particulate counter described above can be installed on the aircraft with its own separate air intake.

Another approach for normalizing is to measure the total carbon concentration of particulates in the atmosphere. Most organic materials contain between 40 percent and 55 percent carbon and consequently the measurement of the total carbon content of particulates is an indication of the mass of organic material present. Such a measurement may be achieved providing an additional optical channel for the measurement of an emission line of carbon. This channel is now responsive to the organic material passing through the system and its output can be divided directly into the outputs of the other channels responsive to various other elements. A simple and accurate means is thereby provided for taking into account variations in atmospheric organic particulate loading from hour to hour, day to day and from place to place.

In applying the technique to monitoring of hydrocarbon concentrations for oil exploration, spectrographic equipment for measuring the carbon emission line may not be available as part of the system. In this case, an alternative technique for measuring carbon concentration in the particulate stream is to pass a portion of the stream through a standard flame ionization detector of the type used in gas chromatographs. Variations in carbon content can accurately be monitored by ionization effects in the flame.

The invention has been described in relation to mineral exploration and geochemical surveying including exploration for ore bodies and hydrocarbons. It will be appreciated, however, that the invention may also be applicable to other remote sensing applications such as the detection of narcotics and explosives.

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

1. A method of performing a rapid geochemical survey comprising receiving an air stream containing atmospheric particulates at a plurality of different positions, determining the geographic locations at which said particulates were collected, separating the collected particulates into a first portion consisting primarily of organic matter and a second portion consisting primarily of inorganic particulates, and analyzing said organic matter to ascertain the relative quantity of elements or compounds therein which are indicative of the presence of underlying geological conditions.

2. A method as claimed in claim 1 including, prior to the step of analyzing said particulates, the step of transferring the particulates into a stream of inert carrier gas.

3. A method as claimed in claim 2 wherein the step of separating said organic portion includes (1) heating the particulates to a predetermined temperature after they have been concentrated and transferred into said stream of inert carrier gas and before the analysis thereof, and (2) then removing particles of relatively high mass from said stream, said removed particles being primarily of inorganic origin, said predetermined temperature being insufficient to substantially affect the state of said particles of inorganic origin.

4. A method as claimed in claim 3 wherein the step of analyzing said organic portion comprises forming a plasma in said stream of inert carrier gas after particles of inorganic origin have been removed and exciting said particulates of organic origin in said plasma.

5. A method as claimed in claim 2, including the additional steps of measuring the relative quantity of carbon in said organic matter and comparing the said quantity of carbon with the said quantity of elements or compounds.

6. A method as claimed in claim 2, including the additional steps of measuring the concentration of the at-

mospheric particulates and comparing the said concentration with the said quantity of elements or compounds.

7. Apparatus for use in geochemical surveying comprising:

a. means for receiving an air stream containing atmospheric particulates, said particulates comprising organic and inorganic matter,
b. means coupled to said receiving means for continuously concentrating said particulates as they are moving in said stream,
c. means for continuously transferring the concentrated particulates into a stream of an inert carrier gas immediately after they have been concentrated as aforesaid, and
d. means for analyzing the particulates in said stream of inert carrier gas to ascertain the relative quantity of elements or compounds therein which are indicative of the presence of underlying geological conditions.

8. Apparatus as claimed in claim 7 including means for separating the inorganic and organic matter prior to the analysis thereof, and wherein only said organic matter is analyzed.

9. Apparatus as claimed in claim 8 including means for heating the particulates to a predetermined temperature after they have been concentrated, said heating means being positioned downstream of said transferring means.

10. Apparatus as claimed in claim 9 including a dust trap positioned downstream from said heating means for collecting inorganic particles of relatively high mass and separating them from the heated particles and vapours fed to the analyzing means.

11. Apparatus for use in geochemical surveying comprising:

a. means for receiving an air stream containing atmospheric particulates, said particulates including organic and inorganic matter,
b. means coupled to said receiving means for concentrating said particulates,
c. means connected to said concentrating means for separating the concentrated particulates into a first portion that primarily comprises organic matter and a second portion that primarily comprises inorganic matter,
d. means connected to said separating means for analyzing said organic origin portion to ascertain the relative quantity of elements or compounds therein which are indicative of underlying geological conditions.

12. Apparatus as claimed in claim 11 wherein said separating means includes means for heating the particulates to a predetermined temperature after they have been concentrated to break down the organic matter.

13. Apparatus as claimed in claim 12 wherein said separating means further includes a dust trap positioned downstream from said heating means for collecting inorganic particles of relatively high mass and separating them from the heated particles and vapours fed to the analyzing means.

14. Apparatus as claimed in claim 11, wherein said organic matter includes hydrocarbons and said analyzing means includes a refrigerated crystal plate of the kind used in attenuated total internal reflectance spectroscopy, said organic matter being deposited on one face of said plate, a source of infrared light directed towards an end face of said plate whereby said light undergoes multiple internal reflections in passing through said plate, and means for analyzing the infrared light which has passed through said plate.

15. A method of performing a rapid geochemical survey of an area of the earth from a moving vehicle comprising receiving an air stream containing atmospheric particulates at a plurality of different positions in said area, determining the geographic locations at which said particulates were received, concentrating said particulates, and analyzing organic matter contained in said concentrated particulates to ascertain the relative quantity of elements or compounds therein which are indicative of the presence of underlying geological conditions.

16. A method as claimed in claim 15 including, prior to the step of analyzing said organic matter, the step of transferring the particulates into a stream of inert carrier gas.

17. A method as claimed in claim 16 including, prior to the step of analyzing said organic matter and after the step of transferring, the step of removing said organic matter from the concentrated particulates by heating the particulates to a predetermined temperature, said predetermined temperature being insufficient to substantially affect the state of said particles of inorganic origin but being sufficient to volatize organic gases and vapours.

18. Apparatus for use in geochemical surveying comprising:

a. means for receiving an air stream containing atmospheric particulates, said particulates including organic and inorganic matter,
b. means coupled to said receiving means for concentrating said particulates,
c. means connected to said concentrating means for removing said organic matter from said concentrated particulates and forming a stream of said organic matter, and
d. means connected to said removing means for analyzing said organic portion to ascertain the relative quantity of elements or compounds therein which are indicative of underlying geological conditions.

19. Apparatus as claimed in claim 18 wherein said removing means includes means for heating the particulates to a predetermined temperature after they have been concentrated to break down the organic matter.

20. Apparatus as claimed in claim 19 wherein means is provided for transferring said particulates into a stream of an inert carrier gas, said transferring means being connected between said concentrating means and said removing means, whereby said organic matter is removed from said particulates while said particulates are travelling in said stream of inert carrier gas and before the analysis thereof.

21. A method of analyzing atmospheric particulates comprising producing a stream of air containing particulates to be analyzed, concentrating said particulates while said particulates are moving in said stream, transferring said particulates immediately after they have been concentrated into a stream of an inert carrier gas, and analyzing said particulates while they are in said inert carrier gas.

22. A method as claimed in claim 21 including, prior to the step of analyzing, the additional step of separating particulates that are primarily of organic origin from particulates that are primarily of inorganic origin,

and wherein the step of analyzing comprises analyzing those particulates that are primarily of organic origin.

23. A method as claimed in claim 22 wherein the step of separating said particulates includes heating the particulates to a predetermined temperature after they have been concentrated and transferred into the stream of inert carrier gas and before the analysis thereof, and then removing particles of relatively high mass from said stream, said removed particles being primarily of inorganic origin, said predetermined temperature being insufficient to substantially affect the state of said particles of inorganic origin.

24. A method as claimed in claim 23 wherein the step of analyzing said particulates further includes forming a plasma in said inert carrier gas and exciting said particulates of organic origin in said plasma.

25. A method as claimed in claim 21 including, prior to the step of analyzing, the additional step of heating the particulates to a temperature sufficient to volatize organic matter comprising hydrocarbons which may be present in said particulates.

26. A method as claimed in claim 15 including, prior to the step of analyzing, the additional step of heating the particulates to a temperature sufficient to volatize organic matter comprising hydrocarbons which may be present in said particulates.

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