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(54) IMPROVEMENTS IN AND RELATING TO
SPECTROCHEMICAL ANALYSIS

(71) We, BARRINGER RESEARCH LIMITED, a company incorporated under the Province of Ontario, Canada, of 304 Carlingview Drive, Rexdale, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to the art of chemical analysis, and in particular to a method of analyzing particulates, powdered samples or any other material that can be formed into a thin layer. The invention is applicable to the analysis of samples of soils, minerals, food stuffs or other solid or liquid materials.

According to the invention, there is provided a method of analysing samples of material for predetermined chemical parameters, comprising depositing a sample of said material in a thin layer on a substrate, irradiating said sample with a laser beam, the wavelength and intensity of said laser beam and the thickness of said sample being such that at least a portion of said sample is vapourized by said laser beam, said substrate being made of material which is substantially non-absorbent of energy at the wavelength of said laser beam and being substantially free of chemical parameters which would interfere with the analysis of said predetermined chemical parameters, and analysing the vapourized sample for said predetermined chemical parameters.

According to the invention, there is also provided apparatus for analysing samples of predetermined materials for predetermined chemical parameters, said samples being deposited in a thin layer on a tape which is substantially free of chemical parameters which would interfere with the analysis of said predetermined chemical parameters and which is substantially non-absorbent of energy when irradiated by a laser beam having a predetermined wavelength and

intensity, the apparatus comprising means for supporting the tape and for moving it along a predetermined path, means operative when the tape supports each sample in a predetermined position in the said path to irradiate the sample with a laser beam having the predetermined wavelength and intensity, said irradiating means including means for directing said laser beam on the sample at the predetermined position, the said predetermined wavelength and intensity of the laser beam being such in relation to a predetermined sample thickness that at least a portion of the sample is substantially completely vapourized by the laser beam, and means for analysing the vapourized sample for said predetermined chemical parameters.

Figure 1 is a diagrammatic perspective view of the apparatus, partly broken away;

Figure 2 is a front sectional view of a vaporization cell in the apparatus; and

Figure 3 is a side sectional view of the vaporization cell shown in Figure 2.

Referring to the drawings, and in particular to Figure 1, samples of particulate material are deposited as spots 11 on an adhesive tape 12 that can be transported from a storage reel 13 past a vaporization cell 14 to a take-up reel 15. As the tape 12 is moved from the storage reel 13 to the take-up reel 15 a cover tape 16 is stripped off the tape 12 and is wound up on a take-up reel 17. A similar cover tape 18 which may be made of a relatively inert synthetic resin such as polytetrafluoroethylene which is stored on a reel 19, may be applied to the tape 12 as shown in Figure 1 so that the tapes 12 and 18 are wound up together on the take-up reel 15. In this manner, any samples remaining on the tape after analysis may be stored for subsequent reanalysis.

The samples 11 are positioned so that they are subject to irradiation from a laser beam of which passes through a

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- control iris 21 and enters a housing 22, which encloses the tape mechanism, through a window 23. The laser beam is deflected by means of mirrors 24, 25 down through a focusing lens 26 which serves the function of focusing the laser beam at a point just below the plane of the tape 12. The laser beam passes through a window 27 in the vaporization cell 14. An inert carrier gas such as argon is introduced into the vaporization cell 14 through a pipe 28 via a control valve 29, and the inert carrier gas leaves the vaporization cell via a pipe 30. The vaporization cell is provided with an elongated inlet pipe 31 and outlet pipe 32 which respectively are attached to the pipes 28 and 30. The vaporization cell consists of an outer shell 33 and an inner shell 34 spaced inwardly from the outer shell 33 to define an annular space 35 which communicates with the inlet 31. The shell 34 defines an inner region 36 which is aligned with the window 27 and which is in communication with the outlet 32. The vaporization cell 14 is open at its lower end which is adjacent to the tape 12 so that the regions 35 and 36 of the vaporization cell 14 are open to the tape 12.
- When a laser pulse is fired, vaporization of the sample occurs at the point where the laser beam strikes a sample spot 11. The sample spot 11 may be positioned accurately by automatic electro-optical means which may be adapted, for example, to sense the location of registration marks on the tape. The laser beam is sufficiently defocused at the surface of the tape 12 to provide a spot of between about 2 and 4 millimeters in diameter, thus allowing a sample of reasonable size to be vaporized.
- The power of the laser, which typically is of the order of 1 joule, is adjusted to be adequate to vaporize a predetermined amount of the sample material without significantly vaporizing the tape.
- Some of the inert carrier gas introduced into the vaporization cell 14 from the pipe 28 escapes into the interior of the housing 22 so that the housing 22 becomes filled with the inert carrier gas. The pressure inside the housing 22 is preferably kept slightly above atmospheric pressure as observed on a manometer 37. A valve 38 is provided to permit a controlled leakage of the inert carrier gas from the housing 22 in order to maintain the pressure within the housing 22 at a predetermined level.
- Referring now to Figure 2, it will be observed that the vaporization cell preferably is positioned slightly above the surface of the tape 12, e.g. of the order of 1 millimeter above the surface. Some of the inert carrier gas escapes from the region 35 of the vaporization cell 14 and enters the interior of the housing 22, from which it eventually escapes through the valve 38. The remainder of the inert carrier gas passes into the region 36, from which it passes via outlet 32 into outlet pipe 30. Materials released from the surface of the tape 12 by the laser beam are carried up to the interior of the vaporization cell 14 and out through the pipe 30 into a separate analytical system. By maintaining a steady leakage of inert carrier gas at the surface of the tape 12, any air present in the housing 22 effectively is prevented from becoming entrained in the main flow of gas through the pipe 30 into the analytical system.
- The aerosol formed by vaporization of the sample matter by the laser beam and any recondensation of such matter passes out through the pipe 30 into a suitable analyzer, such as an inductively coupled plasma the emission spectra of which is measured by means of a conventional spectrometer.
- By way of example, a carbon dioxide laser operating at 10.6 microns may be chosen using a pulsed mode of operation such as that provided by a transverse excited TEA laser. At 10.6 microns most materials, both organic and inorganic, absorb energy strongly, whereas it is possible to chose a substrate such as thin polymer film made of polyethelene, that has a negligible absorption at 10.6 microns. Adhesive tapes are manufactured of this material, such as type 480 manufactured by The Minnesota Mining and Manufacturing Company of St. Paul, Minnesota, U.S.A., which employs a polyethelene base with an adhesive which also exhibits very little absorption at 10.6 microns. Particulate matter that is made to adhere to such tape may be vaporized off the tape with a carbon dioxide laser with little or no vaporization of the tape. Furthermore, the tape as manufactured contains only small traces of elements other than the basic elements of carbon, oxygen and hydrogen. Thus, any vaporization of the substrate which might occur would in any case cause little or no contamination of the sample when the sample is being analyzed for elements other than those that are the basic constituents of the tape.
- In some cases, it may be desirable to employ a laser the wave length of which is deliberately chosen to vaporize only a selected portion of the sample. Thus, if a ruby laser is employed having a wave length of 6943 angstroms in the visible spectrum, then organic materials containing cellulose, starch and protein will absorb very little energy. On the other hand, any inorganic materials that may be mixed with such organic materials will show strong absorption at such wave length. Thus, analyses of such mixed powders or particulates carried out on the vapours formed by irradiating the sample with a ruby laser at 6943 angstroms

will be dominated by the composition of the inorganic constituents with very little effect from the organic constituents. If the same sample is vaporized with a carbon dioxide laser at 10.6 microns, all constituents will absorb energy strongly and the analysis will be indicative of the total composition. From a study of the analysis obtained from both kinds of lasers, it is possible to compute the distribution of various elements between the organic portion that fails to absorb energy at 6943 angstroms and the inorganic portion that absorbs energy at both 6943 angstroms and 10.6 microns.

Such selective vaporization is of importance, for example, in the analysis of aerosols. Such aerosols may be impacted onto a transparent adhesive tape and then selectively analyzed for different constituents. Carbonates may be selectively vaporized with a laser pulse of approximately 7 microns. Similarly, elements present as sulphates may be determined by vaporization at wave lengths at which there is strong sulphate absorption.

After each sample is vaporized, two kinds of products are produced. One is an aerosol formed by the rapid condensation of vapours generated from material having high vaporization temperatures and the second kind is vapours which either are driven off from the sample or represent pyrolysis breakdown products, which do not recondense into aerosols after they have been formed. The latter constituents can be introduced directly into vapour analyzing systems such as mass spectrometers and gas chromatographs, while the aerosols normally have to be re-vaporized (for example in a plasma) prior to analysis.

The apparatus has been described above with reference to the use of transparent adhesive tapes as a substrate. However, an alternative medium is adhesive aluminum tape which has sufficiently high reflectivity to prevent vaporization of the substrate. Furthermore, although it is convenient to use an adhesive tape for holding the samples, it is conceivable that uncoated polyethylene tape may be utilized instead, and in such case electrostatic attraction could be used to fix the samples in position. For particles in the size range of below about 5 microns, adhesive is generally not required as the particles may be impacted directly onto an uncoated plastic substrate or onto aluminum foil. In general, plastics are preferred over aluminium or other metallic foil as a tape medium since they tend to be free of trace metals to a greater extent so that minor vaporization of the substrate does not affect the analysis to any significant extent. It is comparatively more difficult, for example, to obtain aluminium foil with adequate purity. In general,

whether the substrate is a tape or else a smaller carrier such as a glass slide, the requirement is that the material of the substrate should either totally reflect the laser beam or else should be made of a material which does not appreciably absorb the laser energy.

In general, the smaller the particle, the easier it is to vaporize the particle in its entirety. Conversely, heavier particles may not be completely vaporized by a single laser pulse, and matrix effects (which lead to measurement errors) usually occur in such circumstances.

A technique which has been employed with some success in respect of heavier particles (of the order of 200 microns and greater) is to apply the laser beam successively to the same sample and integrate the results of successive analyses.

WHAT WE CLAIM IS:

1. A method of analysing samples of material for predetermined chemical parameters, comprising depositing a sample of said material in a thin layer on a substrate, irradiating said sample with a laser beam, the wavelength and intensity of said laser beam and the thickness of said sample being such that at least a portion of said sample is vapourized by said laser beam, said substrate being made of material which is substantially non-absorbent of energy at the wavelength of said laser beam and being substantially free of chemical parameters which would interfere with the analysis of said predetermined chemical parameters, and analysing the vapourized sample for said predetermined chemical parameters.

2. A method according to claim 1, in which the analysing step is carried out at a location separated from the location where the irradiating step takes place.

3. A method according to claim 2, where after said sample has been vapourized, said vapourized sample is injected into a stream of an inert carrier gas and is transported to a plasma where it is excited to facilitate spectrographic analysis.

4. A method according to any one of claims 1 to 3, wherein substantially all of said sample is vapourized with a single pulse of said laser beam.

5. A method according to any one of claims 1 to 3, wherein substantially all of said sample is vapourized with successive pulses of said laser beam.

6. A method according to any preceding claim, wherein said samples are deposited at spaced-apart locations on said substrate, and said substrate comprises a tape which is movable step-wise to expose successive samples to said laser beam.

7. A method according to any preceding claim, wherein said material is in the form of particulates, wherein said particulates are

deposited on said substrate substantially one particle thick, and wherein said particulates are below about 100 microns in diameter.

5 8. A method according to claim 7, in which said particulates are below about 50-60 microns in diameter.

9. Apparatus for analysing samples of predetermined materials for predetermined chemical parameters, said samples being deposited in a thin layer on a tape which is substantially free of chemical parameters which would interfere with the analysis of said predetermined chemical parameters and which is substantially non-absorbent of energy when irradiated by a laser beam having a predetermined wavelength and intensity, the apparatus comprising means for supporting the tape and for moving it along a predetermined path, means operative when the tape supports each sample in a predetermined position in the said path to irradiate the sample with a laser beam having the predetermined wavelength and intensity, said irradiating means including means for directing said laser beam on the sample at the predetermined wavelength and intensity of the laser beam being such in relation to a predetermined sample thickness that at least a portion of the sample is substantially completely vapourized by the laser beam, and means for analysing the vapourized sample for said predetermined chemical parameters.

10. Apparatus according to claim 9, for use where said material is in the form of solid particulates less than about 100 microns in diameter, and including a housing, and means in said housing for moving said tape step-wise to expose successive samples to said laser beam, said housing having a window through which the laser beam is directed and optical means for directing said laser beam onto each said sample.

11. Apparatus according to claim 10, wherein said housing is filled with an inert gas under a predetermined pressure, and wherein means is provided for transferring vapourized matter into a stream of said inert gas and for transporting said vapourized matter out of said housing for subsequent analysis.

12. Apparatus according to any one of claims 9 to 11, wherein the wavelength of said laser beam is 10.6 microns.

13. A method of analysing samples of materials for predetermined chemical parameters, substantially as described with reference to the accompanying drawings.

14. Apparatus for analysing samples of materials for predetermined chemical parameters, substantially as described with reference to the accompanying drawings.

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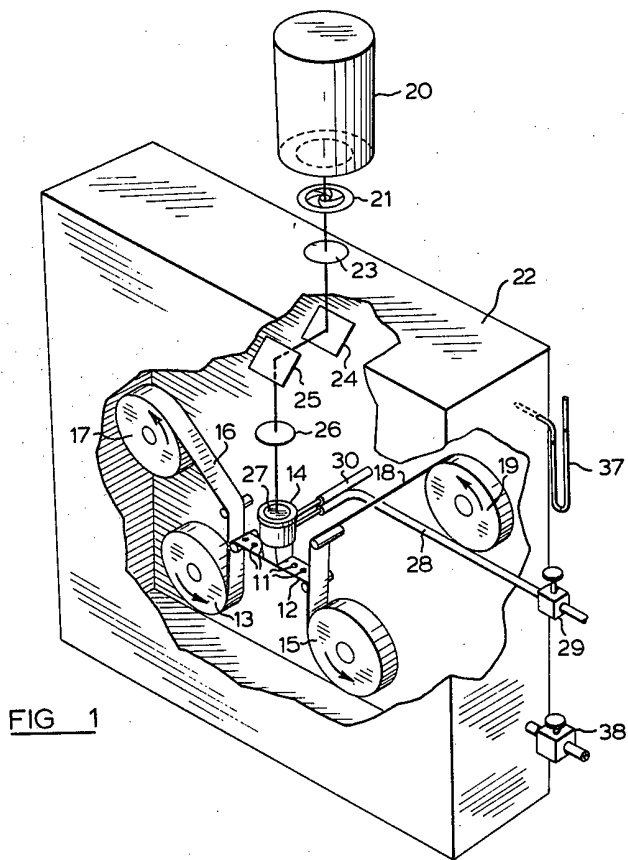


FIG. 1

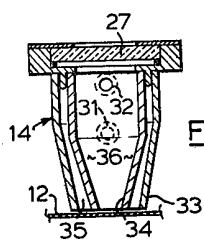


FIG. 2

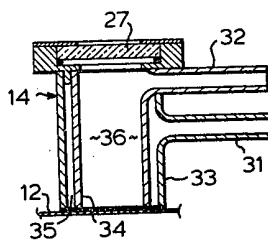


FIG. 3