(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 November 2009 (12.11.2009)

PCT

(10) International Publication Number
WO 2009/137494 A1

(51) International Patent Classification:
G01J 3/00 (2006.01)

(21) International Application Number:
PCT/US2009/042862

(22) International Filing Date:
5 May 2009 (05.05.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/126,633 5 May 2008 (05.05.2008) US

(71) Applicant *(for all designated States except US)*: **APPLIED SPECTRA, INC.** [US/US]; Applied Spectra, Inc., 46661 Fremont Blvd., Fremont, CA 94538 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **YOO, Jong, Hyun** [US/US]; Jong Hyun Yoo, 190 Rainbow Place, Milpitas, CA 95035 (US). **TRIBE, Randolph, S.** [US/US]; Randolph S. Tribe, 4271 N 1st St. SPC29, San Jose, CA 95134-1203 (US). **LIU, Chunyi** [—/US]; Chunyi Liu, 1885 Firebrick Ter., Union City, CA 94587 (US).

(74) Agent: **HAVERSTOCK, Thomas, B.**; Haverstock & Owens LLP, 162 North Wolfe Road, Sunnyvale, CA 94086 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: LASER ABLATION APPARATUS AND METHOD

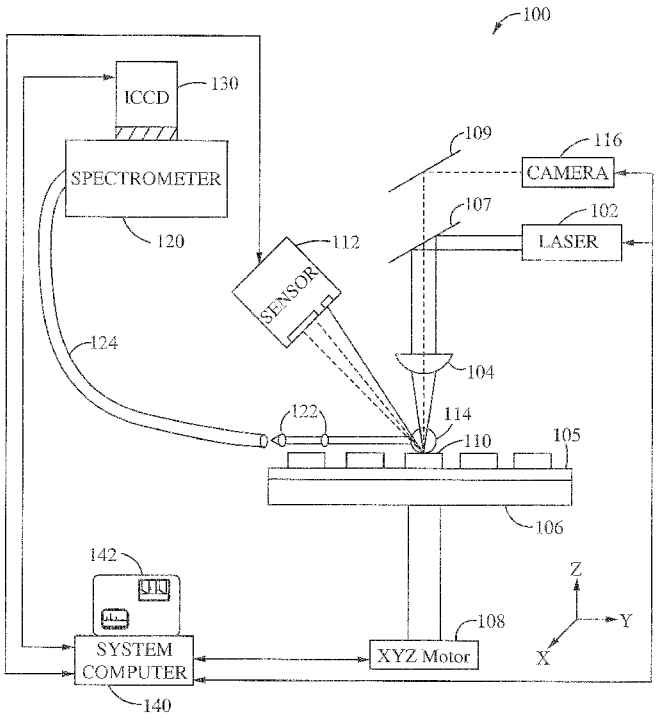

Fig. 1

(57) Abstract: Provided is a laser ablation spectroscopy apparatus and method. A pulse laser focused on the sample site to generate a plasma plume dunng a laser ablation process. The plasma plume is detected with a spectrometer and an intensified charge coupled device. A sample of matenal is coupled to a stage movable in three axes using an array of x-y-z motors. A change in the sample height is detected using a tπangulation sensor. The apparatus includes a system computer for synchronizing the movement of the stage in all directions dunng the laser ablation process. The method includes a protocol of generating one or more laser ablations per sample site. The spectral data of the total number of laser ablations for each sample site are averaged together. The protocol includes laser ablating additional sample sites and averaging the spectral data of the total number of sample sites

WO 2009/137494 A1

Published:

— *with international search report (Art. 21(3))*

LASER ABLATION APPARATUS AND METHOD

FIELD OF THE INVENTION

This Patent Application claims priority under 35 U.S.C. 119 (e) of the co-pending U.S. Provisional Patent Application, Serial No. 61/126,633, filed May 5, 2008, and entitled "LASER ABLATION APPARATUS AND METHOD ". The Provisional Patent Application, Serial No. 61/126,633 filed May 5, 2008, and entitled "LASER ABLATION APPARATUS AND METHOD " is also hereby incorporated by reference.

BACKGROUND

Restriction of hazardous substances by statutes such as the Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment 2002/95/EC (commonly referred to as the Restriction of Hazardous Substances Directive or RoHS) was adopted in February 2003 by the European Union. The state of California has passed a similar law. The directive restricts the use of six hazardous materials in the manufacture of various types of electronic and electrical equipment. The six hazardous materials include Lead, Mercury, Cadmium, Hexavalent chromium (chromium xxx or Cr6+), Polybrominated biphenyls (PBB), and Polybrominated diphenyl ether (PBDE).

Industry seeks efficient and economical measures to comply with RoHS. Dissolution in acid is commonly used to test and measure compositional qualities of sample material. This method has inherent disadvantages. Laser induced induce breakdown spectroscopy (LIBS) as well as other laser spectrometry methods provide a possible efficient and economical technique in determining or verifying elemental composition of products and other materials.

The LIBS type of spectrometry has been an unreliable and inexact measurement system since there is a large variation in the recorded data. A factor is the inconsistent plasma plume created by the pulse laser. Former LIBS type analysis was unsuccessful in matching known standards achieved with other analysis methods.

Accordingly, it is desirable to have a laser ablation spectrometry apparatus that can achieve valid quantitative and repeatable data.

SUMMARY OF THE INVENTION

In accordance with a first aspect of the present invention, a laser ablation spectroscopy apparatus is provided. A pulse laser is focused on a sample site to generate a plasma plume during a laser ablation process. The plasma plume is detected with a

spectrometer and an intensified charge coupled device. A sample of material is coupled to a stage movable in the x, y and z directions using an array of x-y-z motors. A change in the height of the sample is detected using a sensor. Preferably, the sensor is a triangulation sensor. The apparatus includes a system computer for synchronizing the movement of the stage in the x, y and z direction during the laser ablation process. The height of the sample site can be automatically adjusted following each laser ablation. In one embodiment, the system computer includes a controller, application software and a graphical user interface (GUI).

In accordance with a second aspect of the present invention, a method of laser ablation spectroscopy is provided. The method includes a protocol of generating one or more laser ablations to a sample site. The spectral data of the total number of laser ablations for the sites are averaged together. In one embodiment, the total number of laser ablations for the sample site equals three laser ablations. The protocol includes laser ablating additional sample sites and averaging the spectral data of the total number of sample sites. In one embodiment, the total number of sample sites equals twenty sample sites.

Other features of the present invention will become apparent from consideration of the following description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The novel features of the invention are set forth in the appended claims. However, for purposes of explanation, several embodiments of the invention are set forth in the following figures.

Figure 1 illustrates a schematic diagram of a laser ablation apparatus according to an embodiment of the invention.

Figure 1A illustrates a detail schematic diagram of a laser ablation apparatus according to an embodiment of the invention.

Figure 2 illustrates a detail of a laser ablation graphical user interface according to an embodiment of the present invention.

Figure 3 illustrates a plan view of a testing protocol according to an embodiment of the invention.

Figures 4A and 4B illustrate side views of a topology of a sample according to an embodiment of the invention.

Figure 5 illustrates a plot of spectral information according to an embodiment of the present invention.

Figure 6 illustrates a plot of intensities of known standards according to an

embodiment of the present invention.

Figure 7 illustrates a process flow diagram for a method of ablating according to an embodiment of the present invention.

DETAILED DESCRIPTION

In the following description, numerous details and alternatives are set forth for the purpose of explanation. However, one of ordinary skill in the art will realize that the invention can be practiced without the use of these specific details. In other instances, well-known structures and devices are shown in block diagram form in order not to obscure the description of the invention with unnecessary detail.

Figure 1 shows a schematic overview of a laser ablation apparatus 100 according to the present invention. The apparatus 100 generally includes a pulse laser 102, a stage 106, a position sensor 112, a spectrometer 120 and a system computer 140. The apparatus 100 is configured to generate laser pulses from the pulse laser 102. The laser pulses are focused onto a sample 105 with a lens 104 to produce a plasma plume 114 of the sample 105 at a sample site 110. The position sensor 112 is electrically coupled with the system computer 140 for sending a displacement error signal to automatically correct positioning of the stage 106 during an ablating process as describe further below. The apparatus 100 can include a system frame for housing the various components described herein. The system frame can include an air filter for filtering contaminants produced during the ablating process.

The pulse laser 102 in an exemplary embodiment comprises a neodymium doped yttrium aluminum garnet (Nd:YAG) laser for generating energy in the near infrared region of the electromagnetic spectrum with a wavelength of 1064 nm. The pulse duration can be approximately 4 ns for generating a laser beam with a power density that can exceed one GW/cm^2 at a focal point or ablation impact point. The laser 102 can have a repetition rate of approximately 10 hz or alternately lower than 10 hz in some embodiments. Alternatively, the pulse duration can vary to tens or hundreds of nanoseconds. In another embodiment, the pulse duration can be shortened to ultra short femtoseconds. The lens 104 comprises an objective lens used to focus the laser beam on a surface of the sample site 110. The laser beam can be focused to a spot size of approximately 10-500 micrometers on the sample site 110. In an exemplary embodiment, the laser beam can be focused to a spot size of approximately 150-200 micrometers on the sample site 110.

In an alternative embodiment, a spark generator can be used as the ablation source instead of the pulse laser 102. An electric spark is passed through a sample material until the sample material reaches a temperature where characteristic spectral emissions can be

detected. In an exemplary embodiment, the electric spark can be controlled in an argon atmosphere. A person of ordinary skill in the art can appreciate the construction of such spark generators in spark spectroscopy systems.

A dichroic mirror 107 is used for directing the laser beam toward the sample site 110 and a mirror 109 allows viewing of the sample site 110 using a video camera 116.

The stage 106 includes an attached array of 'x-y-z' motors 108 for providing translation of the stage 106 in a three dimensional space. The x-y-z motors can comprise suitable stepper motors as known by a person of skill in the art. In one embodiment, the stage 106 can have a translation rate of approximately 10 cm/s. The stage 106 can include a sample securing means.

The position sensor 112 preferably comprises a laser triangulation sensor. The position sensor 112 preferably uses the principle of triangulation to determine changes in height of the stage 106 and the associated sample 105. As shown in greater detail in Figure 1A, triangulation occurs when the position sensor 112 emits a triangulation laser 113 that is focused on the sample site and a first reflection 115a is sensed by a photodetector within the position sensor 112. A change in height of the sample 105 causes a displacement in the triangulation laser 113 to produce a second reflection 115b and a displacement signal generated by the position sensor 112 is communicated to a system computer 140. The system computer 140 provides positioning information to maintain an optimum height of the sample. The position sensor 112 can comprise a suitable laser displacement measuring device as known to a person of skill in the art. In one embodiment, the triangulation laser 113 coincides with a spot circle of the laser 102 generated at the sample site. The triangulation laser 113 can also be used as a targeting marker when selecting a specific point on the sample site 110 as seen with the video camera 116 as the triangulation laser 113 can produce a visible spot on the surface of the sample site 110.

The spectrometer 120 (Figure 1) collects electromagnetic information from the plasma plume 114. The spectrometer 120 can be a monochromator or a polychomator. The electromagnetic information includes spectral information identifying an elemental composition of the sample site 110. A spectral range for the spectrometer 120 can be chosen to suit different applications. In an exemplary embodiment the spectral range can be approximately 35 nm for observing a portion of the electromagnetic wavelength range. Alternatively, the spectrometer 120 can detect electromagnetic radiation in a range of 200 to 900 nm. Collection optics 122 receive the light and plasma lumina generated from the plasma plume 114 and transmits the light and plasma lumina through a fiber cable 124 to the spectrometer 120. The collection optics 122 can be orientated horizontally as shown in

Figure 1. Alternatively, the collection optics 122 can be orientated at any angle above the sample 105 surface plane. A mirror (not shown) within the spectrometer 120 reflects the plasma lumina to a grating that disperses the plasma lumina.

An intensified charge coupled device (ICCD) or detector 130 is coupled with the spectrometer 120 for detecting the dispersed plasma lumina. The detector 130 provides the detected plasma lumina to the system computer 142. The system computer 140 generates spectral information from the plasma lumina of the laser plume 114. The spectral information includes intensity data representing elemental information and composition of the sample site 110. The spectral information can be produced on a display 142.

The detector 130 provides increased resolution and greater selectivity of the spectral information. The detector 130 includes a microchannel image intensifier plate. The intensifier plate is preferably gated during period of time when the plasma plume 114 emits characteristic atomic emission lines of the elements. This period coincides with an optimum plume luminance period. This period follows emission of continuum radiation. Continuum radiation lacks useful specific species or elemental information. In one embodiment, a delay generator (not shown) can be included to provided gating of the detector 130 to allow temporal resolution of the detector 130 response time. Alternative embodiments of the detector 130 can include a detector other than an ICCD, for example a suitable charge coupled device (CCD) or suitable photomultiplier. Accuracy of the spectrometer 120 and detector 130 in one embodiment can generate compositional data in the range of 20 ppm or less. Alternatively, the accuracy can be in the range of a few %. In another embodiment, the accuracy can be in the range of 1%, which is approximately 10,000 ppm.

The system computer 140 can include application software and a controller in the system computer 140 for providing synchronization of the laser 102, spectrometer 120, detector 130, position sensor 112 and the x-y-z motors 108 positioning of the stage 106. The system computer 140 is electrically coupled with the laser 102, spectrometer 120, detector 130, position sensor 112, the x-y-z motors 108 and the camera 116. The system computer 140 includes a display 142 for displaying spectral information. The system computer 140 can present the spectral data generated on the display 142. Alternatively, a separate personal computer can also be coupled with the system computer 140 for separately analyzing the spectral information. The system computer 140 can include a power controller to regulate power to all the apparatus 100 components.

The application software decodes the spectral information from the detector 130 and facilitates analysis of the spectral information and generates composition information of the sample 105. In one embodiment, the intensity data of an elemental peak is subtracted from

background data of the elemental peak to calculate a change in intensity (delta I). The application software allows setting of certain parameters for performing the laser ablations of the sample site 110. A spot circle can be set as a parameter and can be consistently and precisely maintained through the laser ablation process described in further detail below. Alternatively, a z value for the sample site 110 can be set as a parameter and can be consistently and precisely maintained through the laser ablation process. The spot circle increases or decreases depending on the change in height of the sample site 110. Keeping the laser 102 spot circle precisely adjusted insures that the sample site 110 produces the plasma plume 114 with consistent optimum plume luminance. Height changes in the sample site can be detected by the position sensor 112 and a correction to the height of the sample site 110 is generated by the controller within the system computer 140. The application software and the controller generate correction signals to reposition the height of the stage 105 after each laser ablation of the sample site.

Figure 2 shows a representative graphical user interface (GUI) 200 according to an embodiment of the present invention. The GUI 200 includes a first data window 218 and a second data window 220. The first data window 218 provides real-time video of a sample site 110. A spot circle 118 can be observed on the sample site 110 during and following an ablation. The second data window 220 provides spectral information generated from the system computer 140. In an exemplary embodiment, the spectral information includes a waveform 222 representing intensity and wavelength data of a sample site ablation.

Figure 3 shows a top view 300 of a protocol for ablating a sample 305 according to an embodiment of the present invention. The protocol includes ablating multiple sample sites 312. In an exemplary embodiment, the sample sites can be uniformly and evenly distributed throughout a surface of the sample 305. Alternatively, the sample sites 312 can be randomly distributed through the surface of the sample site. The number of sample sites 312 ablated can vary depending on a particular sample or a particular application. In one embodiment, the number of sample sites comprises twenty. Alternatively, the number of sample sites can be ten or fewer. In another embodiment, the number of sample sites can be thirty or more.

The protocol 300 can include a specific number of pulse laser ablations per sample site 312. Heterogeneous material can include elements having varying thermal properties. A single shot laser ablation can vaporize disproportionately more volatile elements than the less volatile elements. Spectral information from a single ablation may not be a reliable indication of the composition of the sample 305. In an exemplary embodiment, the number of laser ablations per site comprises three laser ablations. Alternatively, the number of laser ablations per site comprises two. In another embodiment, the number of laser ablations per

site comprises a single laser ablation. In still another embodiment, the number of laser ablations per site comprises four or more laser ablations.

Figures 4A and 4B show side views of a first sample 405A and a second sample 405B according to an embodiment of the present invention. The first sample 405A comprises a material having sample sites 410A with substantially uniform topology. The height of the sample sites 410A are substantially the same. The second sample 405B, however, comprises a material having sample sites 410B with erratic or varying topology. The height of the sample sites 410B can be different. The apparatus 100 is configured to provide consistent spectral data for either the uniform sample sites 410A or sample sites 410B with varying heights. The system computer 140 adjusts the height of the stage 106 to achieve the optimal plasma lumina.

Figure 5 shows a plot 500 of spectral data according to an embodiment of the present invention. The plot 500 includes a waveform plotted along a wavelength (nm) versus an intensity (a.u.). An elemental peak 'A' can represent the spectral information for the element Lead (Pb). The elemental peak 'B' can represent spectral information of a different element.

Figure 6 shows a plot 600 of compositional data 600 according to an embodiment of the present invention. The plot 600 includes a waveform plotted along a composition (nm) versus an intensity (a.u.). The plot 600 is generated by performing laser ablation according to the method described herein on a known standard sample. The known standard produces intensities I1, I2 and I3 for associated elements at the respective compositions 34 ppm, 146 ppm and 406 ppm. Quantitative analysis of different elements of a particular sample is performed by comparing spectral data of the particular sample with the compositional data 600. For example, spectral information obtained from analysis with the apparatus 100 can include intensity I4. The quantity of the element can be approximated to 90 ppm.

Figure 7 shows a process flow diagram for a method 700 of laser spectroscopy according to an embodiment of the present invention. The laser ablation apparatus 100 (Figure 1) is used as an example. The method 700 begins at the step 710. In one embodiment, the method 700 can be fully automated using application software included in the system computer 140. A specific protocol can be entered into the application software instructing the application software of desired parameters or settings for the apparatus 100. Alternatively, the method 700 can be manually performed. At the step 720, a laser pulse is generated to ablate the sample site 110. A real-time video image of the sample site 110 is

generated on a first window 218 of the GUI 200. The real-time video is received from the video camera 116. The plasma plume 114 is analyzed by the spectrometer 120 and the detector 130. The plasma lumina and the electromagnetic radiation generated by the plasma plume is optically communicated to the spectrometer 120 and detected by the detector 130. The position sensor 112 provides a displacement signal to the system computer 140 indicating any change in the height of the sample site 110. The system computer receives spectral information from the spectrometer 120 and the detector 130.

At the step 730, the system computer 140 generates spectral and wavelength information for presentation on the display 142. In one embodiment, intensity and wavelength data are represented as waveforms on the GUI 200. The waveform is presented in a second window 220 of the GUI 200 and includes the intensity and wavelength data. In another embodiment, a second waveform is superimposed on the first waveform 222 in the second window 220. The second waveform can include additional spectral information. For example, particle imaging information, tracking information or scaled or gated representations of the first waveform 222.

At the step 740, the steps 720 and 730 are repeated for each sample site on the sample. The spectral data for a total number of laser ablations for the sample site 110 can be averaged together. In an exemplary embodiment, the total number of laser ablations for the sample site 110 equals three laser ablations. The spectral data of the three laser ablations are averaged together to generate a 'site sum'. The site sum is a reliable and accurate representation of the elemental composition of the sample 105 at the sample site 110. Alternatively, the site sum comprises spectral data from two laser ablations. In another embodiment, the site sum comprises spectral data from one laser ablation. In still another embodiment, the site sum comprises spectral data from four or more laser ablations.

At the step 750, the site sum can be compared with spectral information generated from performing the method described herein on a known standard material. The known standard material comprises specific known elements at a known composition. Laser spectroscopy performed on the known elements generates known spectral data including known intensity values. An elemental composition for the sample site 110 can be approximated by comparing the site sum with the known standard spectral data.

At the step 760, the steps 720 through 750 can be repeated for one or more additional sample sites to generate additional site sums. The spectral data for the total number of site

sums can then be averaged together. In an exemplary embodiment, the total number of site sums equals twenty. The spectral data of the twenty site sums can be averaged together to generate a 'sample sum'. The sample sum is a reliable and accurate representation of the elemental composition of the sample 105 as a whole. Alternatively, the total number of sites sums can be ten or fewer. In another embodiment, the number of sites sums can be thirty or more.

The apparatus 100 can perform laser ablation or laser induced breakdown spectroscopy (LIBS) on a variety of materials. The materials can be heterogeneous or homogeneous solids or semi-solids. Alternatively, the materials can comprise a liquid or even a gas. In another embodiment, the apparatus 100 can be used for LIBS on biological materials. Analysis of biological material can include building a library of known spectral signatures including elemental and compositional data for specific biological material. The spectrometer 120 can collect and detect with the detector 130 spectral information on a broad range from 200 to 900 nm. An unknown biological sample can be compared with the library to determine the biological substance. The method ends at the step 780.

In an alternative embodiment, the method 700 can be used in a remote configuration. The sample material is positioned in a location that is remote from the ablation source or laser. A telescopic device can be integrated with the apparatus 100 to provide optical coupling of plasma lumina. The generation and analysis of spectral data can proceed similarly as described herein. Other forms of laser ablation can be used within the scope of the present invention. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be used as an alternative to the LIBS technique described herein.

While the invention has been described with reference to numerous specific details, one of ordinary skill in the art will recognize that the invention can be embodied in other specific forms without departing from the spirit of the invention. Thus, one of ordinary skill in the art will understand that the invention is not to be limited by the foregoing illustrative details, but rather is to be defined by the appended claims.

CLAIMS

What is claimed is:

1. Method of ablation spectroscopy, comprising:

ablating a location of a material coupled to a stage movable in any of an x-y-z direction;

generating spectral data associated with the ablated material;

averaging spectral data of two or more ablations of the location to generate a 'site sum', automatically adjusting a height of the material; and

ablating one or more additional locations to generate additional site sums and averaging the spectral data of the total number of site sums to generate a 'sample sum', automatically adjusting the height of the material.

2. The method of claim 1, further comprising completing the method of claim 1 on a known standard material to generate a calibrated spectral data before completing the method of claim 1 on the 'material', and using the calibrated spectral data to generate the 'spectral data'.

3. The method of claim 2, wherein the calibrated spectral data comprises spectral intensity values, wavelength values and composition values, wherein the spectral data comprises spectral intensity values and wavelength values.

4. The method of claim 3, wherein the spectral data is generated by comparing the spectral intensity values of the 'spectral data' with the spectral intensity values of calibrated spectral data and approximating composition values for the spectral data.

5. The method of claim 1, wherein ablation spectroscopy comprises laser induced breakdown spectroscopy.

6. The method of claim 1, wherein the stage is movable using an array of stepper motors coupled thereto, the array of stepper motors controlled by a system computer.

7. The method of claim 1, wherein the generated spectral data is presented on a

graphical user interface.

8. The method of claim 1, wherein a sensor generates a displacement signal proportional to a change in the height of the material.

9. The method of claim 8, wherein the sensor comprises a laser triangulation sensor.

10. The method of claim 8, wherein a computer coupled with the sensor is used in automatically adjusting the height.

11. The apparatus of claim 8, wherein the sensor comprises a laser triangulation sensor, the triangulation sensor generating a visible spot on a surface of the material, the visible spot being coincident with an ablation impact point of the ablation source.

12. An apparatus for ablation spectroscopy, comprising:

an ablation source configured to ablate a material on a stage movable in any of an x-y-z direction;

a sensor generating a displacement signal proportional to a change in height of the movable stage;

a spectrometer and detector configured for detecting spectral data and generating intensity values, wavelength values and composition values of one or more elements of the material; and

a system computer coupled with the sensor and the movable stage automatically adjusting the height of the material.

13. The apparatus of claim 12, wherein ablation spectroscopy comprises laser induced breakdown spectroscopy.

14. The apparatus of claim 12, wherein the ablation source comprises a laser.

15. The apparatus of claim 12, wherein the stage comprises an array of stepper motors coupled thereto, the array of stepper motors being controlled by the system computer.

16. The apparatus of claim 12, wherein the sensor comprises a laser triangulation sensor, the triangulation sensor generating a visible spot on a surface of the material, the visible spot being coincident with an ablation impact point of the ablation source.

17. The apparatus of claim 12, wherein the generated spectral data is presented on a graphical user interface.

18. The apparatus of claim 12, wherein the spectrometer comprises a monochromator or a polychromator.

19. The apparatus of claim 12, wherein the detector comprises a photomultiplier or a charge couple device (CCD).

20. The apparatus of claim 12, wherein the detector comprises an 'intensified' CCD or ICCD.

21. The apparatus of claim 12, wherein the system computer includes a controller configured to synchronize the ablation source, the movable stage, the sensor, the spectrometer, and the detector.

22. The apparatus of claim 21, further comprising a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) apparatus.

23. Method of ablation spectroscopy, comprising:
ablating a location of a material;
generating spectral data associated with the ablated material to generate a 'site sum';
and
ablating one or more additional locations to generate additional site sums and averaging the spectral data of the total number of site sums to generate a 'sample sum',

automatically adjusting the height of the material.

24. The method of claim 23, wherein the ablating the location comprises averaging spectral data of two or more ablations of the location, automatically adjusting a height of the material.

25. The method of claim 23, wherein the ablating the location comprises a single ablation of the location, automatically adjusting a height of the material.

26. The method of claim 23, further comprising completing the method of claim 23 on a known standard material to generate a calibrated spectral data before completing the method of claim 23 on the 'material', and using the calibrated spectral data to generate the 'spectral data'.

27. The method of claim 26, wherein the calibrated spectral data comprises spectral intensity values, wavelength values and composition values, wherein the spectral data comprises spectral intensity values and wavelength values.

28. The method of claim 27, wherein the spectral data is generated by comparing the spectral intensity values of the 'spectral data' with the spectral intensity values of calibrated spectral data and approximating composition values for the spectral data.

29. The method of claim 23, wherein the location of the material is coupled to a stage movable in any of an x-y-z direction.

30. The method of claim 29, wherein the stage is movable using an array of stepper motors coupled thereto, the array of stepper motors controlled by a system computer.

31. The method of claim 23, wherein ablation spectroscopy comprises laser induced breakdown spectroscopy.

32. The method of claim 23, wherein the generated spectral data is presented on a

graphical user interface.

33. The method of claim 23, wherein a sensor generates a displacement signal proportional to a change in the height of the material.

34. The method of claim 33, wherein the sensor comprises a laser triangulation sensor.

35. The method of claim 33, wherein a computer coupled with the sensor is used in automatically adjusting the height.

36. The apparatus of claim 33, wherein the sensor comprises a laser triangulation sensor, the triangulation sensor generating a visible spot on a surface of the material, the visible spot being coincident with an ablation impact point of the ablation source.

37. Method of ablation spectroscopy using an ablation apparatus having an adjustable ablation impact point, comprising:
ablating a location of a material;
generating spectral data associated with the ablated material;
averaging spectral data of two or more ablations of the location to generate a 'site sum', automatically adjusting the ablation impact point to optimize a plasma lumina; and
ablating one or more additional locations to generate additional site sums and averaging the spectral data of the total number of site sums to generate a 'sample sum', automatically adjusting the ablation impact point to optimize the plasma lumina.

38. The method of claim 37, further comprising completing the method of claim 37 on a known standard material to generate a calibrated spectral data before completing the method of claim 37 on the 'material', and using the calibrated spectral data to generate the 'spectral data'.

39. The method of claim 38, wherein the calibrated spectral data comprises spectral intensity values, wavelength values and composition values, wherein the spectral data comprises spectral intensity values and wavelength values.

40. The method of claim 39, wherein the spectral data is generated by comparing the spectral intensity values of the 'spectral data' with the spectral intensity values of calibrated spectral data and approximating composition values for the spectral data.

41. The method of claim 37, wherein the location of the material is coupled to a stage movable in any of an x-y-z direction.

42. The method of claim 41, wherein the stage is movable using an array of stepper motors coupled thereto, the array of stepper motors controlled by a system computer.

43. The method of claim 37, wherein ablation spectroscopy comprises laser induced breakdown spectroscopy.

44. The method of claim 37, wherein the generated spectral data is presented on a graphical user interface.

45. The method of claim 37, wherein a sensor generates a displacement signal proportional to a change in the height of the material.

46. The method of claim 45, wherein the sensor comprises a laser triangulation sensor.

47. The method of claim 45, wherein a computer coupled with the sensor is used in automatically adjusting the height.

48. The apparatus of claim 45, wherein the sensor comprises a laser triangulation sensor, the triangulation sensor generating a visible spot on a surface of the material, the visible spot being coincident with the ablation impact point of the ablation source.

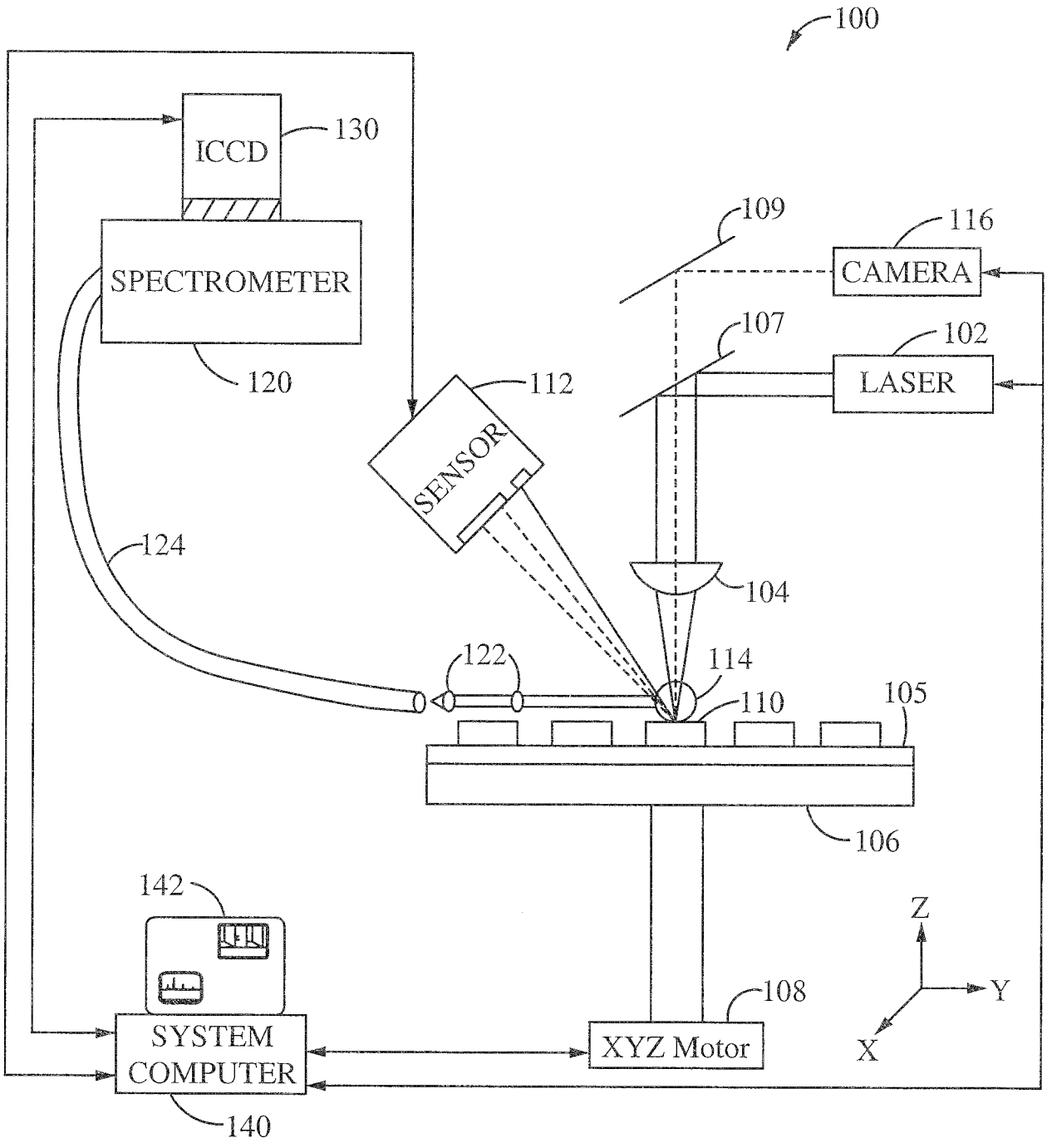
100
ICCD
130
SPECTROMETER
120
109
116
CAMERA
107
102
LASER
112
SENSOR
124
104
122
114
110
105
106
142
Z
Y
X
108
SYSTEM
COMPUTER
XYZ Motor
140

Fig. 1

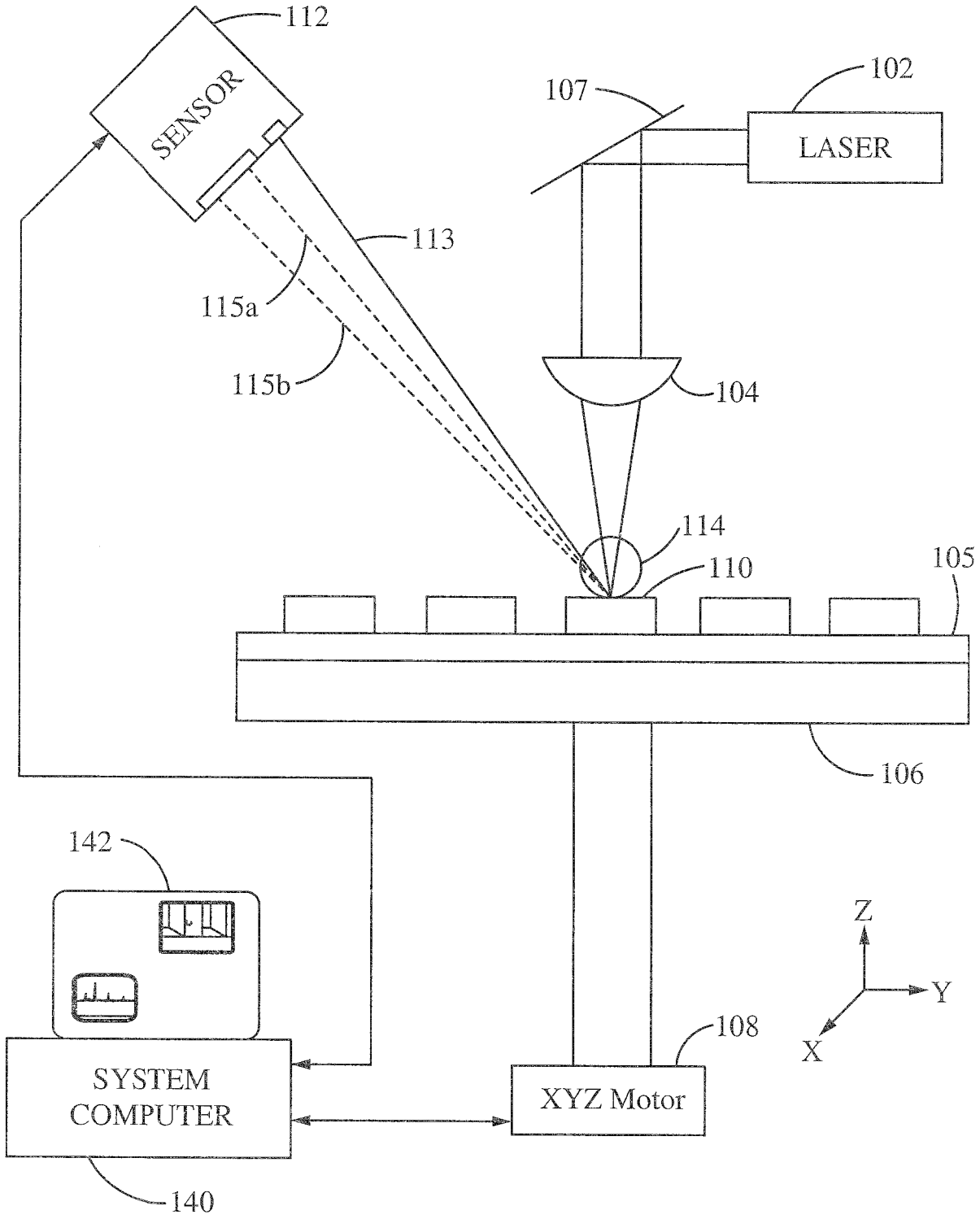
112
SENSOR
107
102
LASER
113
115a
115b
104
114
110
105
106
142
SYSTEM
COMPUTER
140
XYZ Motor
108
Z
Y
X

Fig. 1A

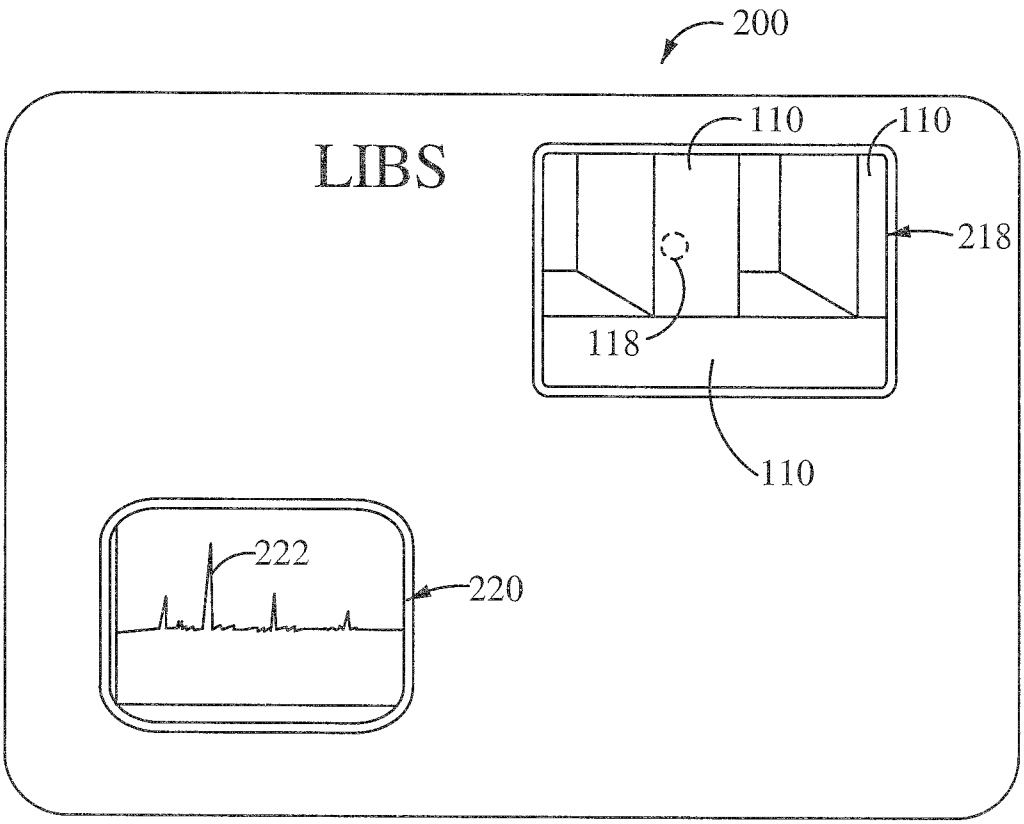

Fig. 2

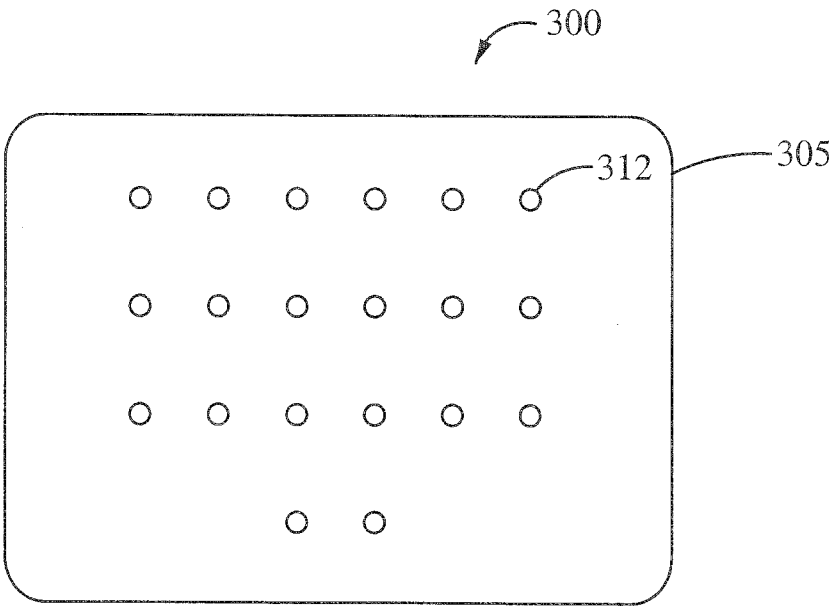

Fig. 3

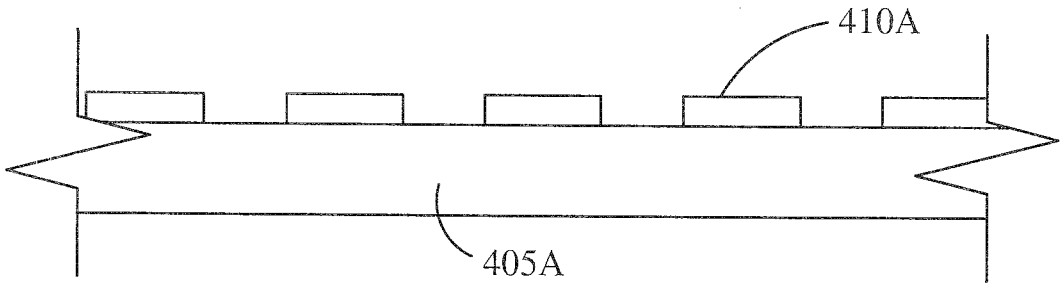

Fig. 4A

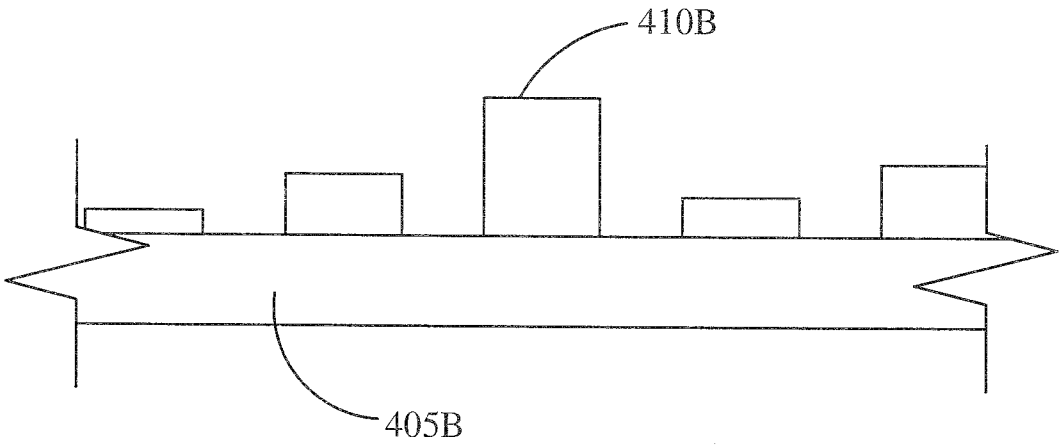

Fig. 4B

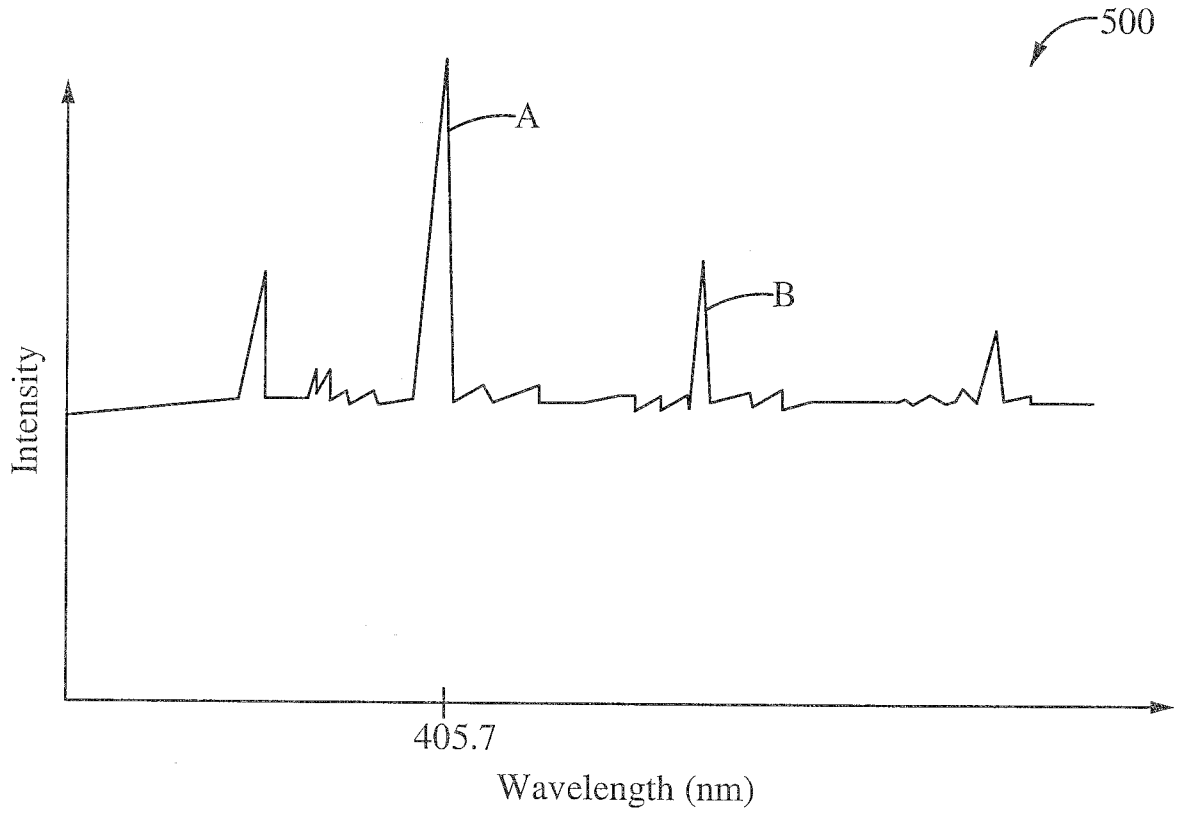
500
A
B
Intensity
405.7
Wavelength (nm)

Fig. 5

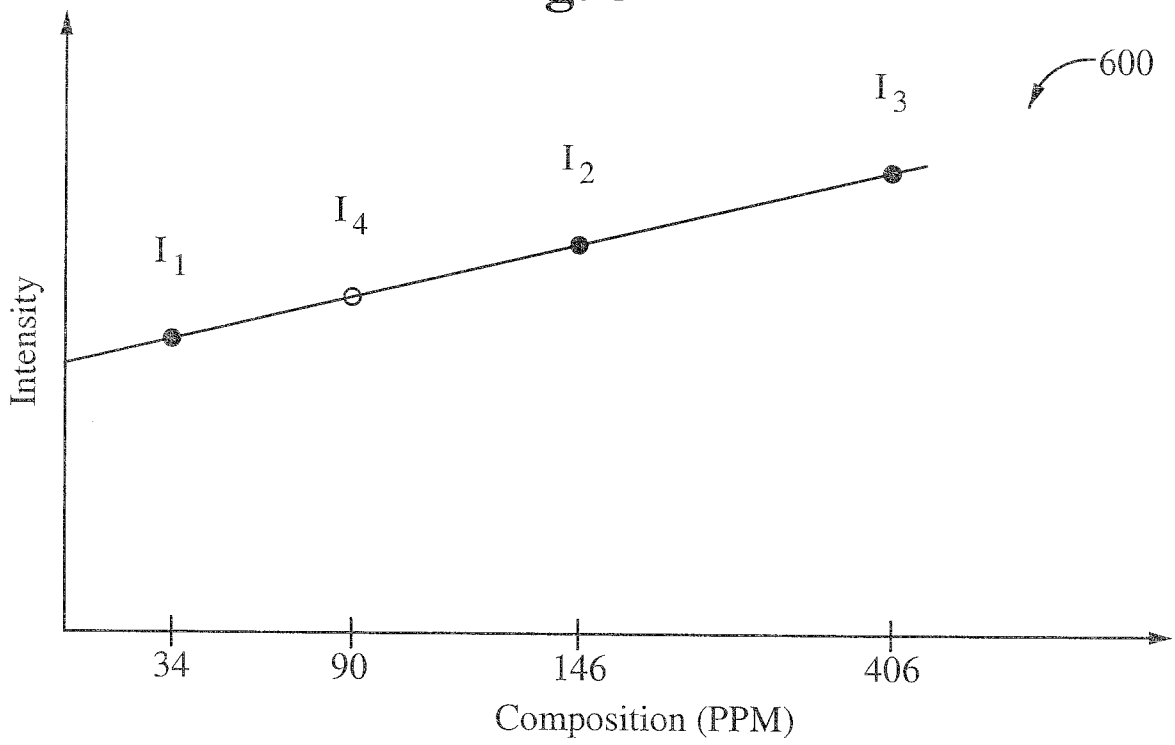
600
I3
I2
I4
I1
Intensity
34
90
146
406
Composition (PPM)

Fig. 6

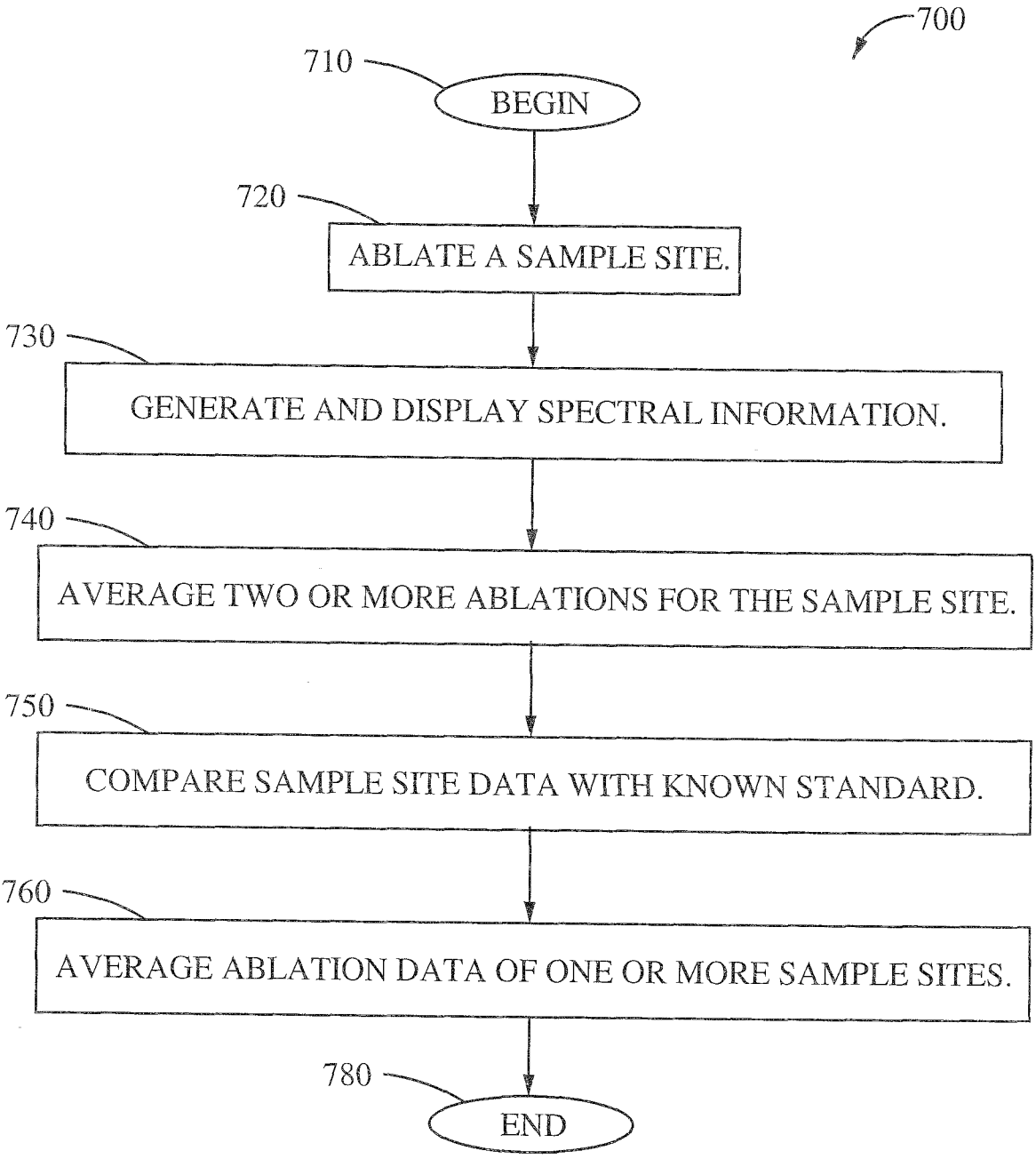
700
710
BEGIN
720
ABLATE A SAMPLE SITE.
730
GENERATE AND DISPLAY SPECTRAL INFORMATION.
740
AVERAGE TWO OR MORE ABLATIONS FOR THE SAMPLE SITE.
750
COMPARE SAMPLE SITE DATA WITH KNOWN STANDARD.
760
AVERAGE ABLATION DATA OF ONE OR MORE SAMPLE SITES.
780
END

Fig. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/42862

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - G01J 3/00 (2009.01)
USPC - 356/326
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 356/326

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 356/300, 72, 316, 311; 702/155, 127, 85 (see also text search below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Electronic Databases Searched: pubWEST, USPTO, Google, Answers.com, Google PatentSearch Terms Used: ablation, spectroscopy, spectral, data, laser, averaging, generate, sample, site, sum, automatic, adjust, height, array, stepper, motor, CCD, intensity, wavelength, composition, triangulation, sensor, detector, change, d

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007/0296966 A1 (BENICEWICZ et al.) 27 December 2007 (27.12.2007) para [0010], [0018], [0020]-[0021], [0024], [0027]-[0028], [0030]-[0031], [0034], [0042], [0044]-[0047], [0053] and [0055]	1-48
Y	US 2006/0164657 A1 (CHALMERS et al.) 27 July 2006 (27.07.2006) para [0019], [0076]-[0077], [0085], [0173]-[0177], [0180], [0187], [0203], [0230], [0240], [0265] and [0277]-[0278]	1-11, 21, 23- 48
Y	US 2008/0037005 A1 (BAREKET et al.) 14 February 2008 (14.02.2008) para [0022], [0024] and [0027]	1-22, 29-30 and 41-42
Y	US 2006/0180581 A1 (SWARINGEN et al.) 17 August 2006 (17.08.2006) para [0011]-[0012], [0014], [0026] and [0028]-[0030]	8-22, 33-36 and 45-48
Y	US 2007/0046934 A1 (ROY) 01 March 2007 (01.03.2007) para [0009], [0020] and [0045]	5, 13, 22, 31 and 43
Y	US 2006/0023218 A1 (JUNG et al.) 02 February 2006 (02.02.2006) para [0315] and [0356]-[0359]	6, 15, 18, 30 and 42

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 June 2009 (23.06.2009)	06 JUL 2009
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774