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Kounaves

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(54) **TOTAL ORGANIC COMPOUND (TOC) ANALYZER**

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This patent is subject to a terminal disclaimer.

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(51) **Int. Cl.**
G01N 27/403 (2006.01)

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(58) **Field of Classification Search** 205/782-783, 205/785.5, 787; 204/424

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,336,127 A 6/1982 Bertletson
4,505,801 A 3/1985 Detwiler et al.

4,725,345 A 2/1988 Sakomoto et al.
4,755,473 A 7/1988 Nishino et al.
4,977,785 A 12/1990 Willoughby et al.
5,209,916 A 5/1993 Gruen
5,328,676 A 7/1994 Gruen
5,370,855 A 12/1994 Gruen
5,462,776 A 10/1995 Gruen
5,571,577 A 11/1996 Zhang et al.
5,620,512 A 4/1997 Gruen
5,645,645 A 7/1997 Zhang et al.
5,772,760 A 6/1998 Gruen et al.
5,808,178 A 9/1998 Rounbehler et al.

(Continued)

FOREIGN PATENT DOCUMENTS

JP 60-220854 A 11/1985

(Continued)

OTHER PUBLICATIONS

Iniesta et al. "Electrochemical oxidation of phenol at boron-doped diamond electrode," *Electrochimica Acta* 46 (2001) 3573-3578.*

(Continued)

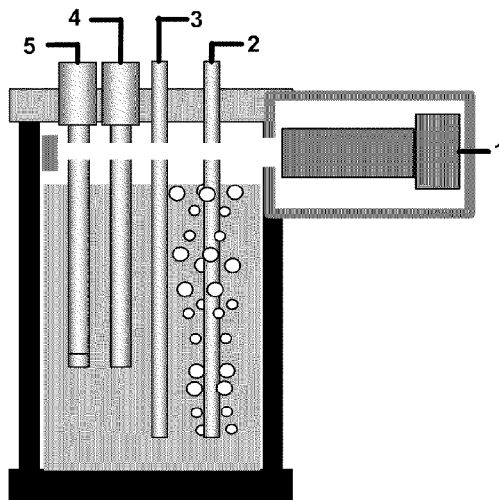
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(57) **ABSTRACT**

The invention disclosed is a total organic carbon (TOC) analyzer comprised of an electrochemical cell comprising a diamond-film electrode doped with boron or other conductivity inducing material. The diamond-film electrode is the working electrode and carries out the oxidation of TOC to produce carbon dioxide. The apparatus further comprises sensors for detecting the carbon dioxide produced. Such sensors include but are not limited to a tunable diode laser and/or ion-selective electrode. The invention also discloses a method for measuring TOC in an aqueous solution using a total organic carbon analyzer.

25 Claims, 1 Drawing Sheet



U.S. PATENT DOCUMENTS

5,849,079 A 12/1998 Gruen et al.
 5,855,760 A 1/1999 Zen et al.
 5,897,924 A 4/1999 Ulczynski et al.
 5,900,127 A 5/1999 Iida et al.
 5,902,640 A 5/1999 Krauss
 5,902,751 A 5/1999 Godec et al.
 5,932,791 A 8/1999 Habitzer et al.
 5,970,804 A 10/1999 Robbat, Jr.
 5,989,511 A 11/1999 Gruen et al.
 6,106,692 A 8/2000 Kunimatsu et al.
 6,267,866 B1 7/2001 Glesener et al.
 6,272,905 B1 8/2001 Drzewiecki
 6,305,212 B1 10/2001 Drzewiecki
 6,541,272 B1 4/2003 Mitra
 6,588,266 B2 7/2003 Tubel et al.
 7,632,393 B2 12/2009 Kounaves
 2003/0170906 A1 9/2003 Swain et al.
 2005/0226774 A1 10/2005 Kounaves
 2007/0183929 A1 8/2007 Erickson

FOREIGN PATENT DOCUMENTS

JP 01-197631 A 8/1989
 WO 03/104765 A3 12/2003
 WO 2007/092665 A2 8/2007

OTHER PUBLICATIONS

LI-6252 CO2 Analyzer specifications Downloaded on Nov. 7, 2011 from <http://www.eol.ucar.edu/isf/facilities/isf/sensors/LiCor/li6251/6252spec.htm>.*

"Shimadzu TOC 5000," Webpage: <http://www.gmi-inc.com/AnyLab/Shimadzu%20TOC%205000.htm>, pp. 1-3.

03734494.2 Supplemental European Search Report, EPO, Jul. 24, 2007.

Hagans P L; Natishan P M; Stoner B R; O'Grady W E: "Electrochemical oxidation of phenol using borondoped diamond electrodes", Journal of the Electrochemical Society, vol. 148, No. 7, Jul. 2001, pp. E298-E301, XP7909722, ISSN: 0013-4651.

Hattori S; Doi M; Takahashi E; Kurosu T; Nara M; Nakamatsu S; Nishiki Y; Furuta T; Iida M: "Electrolytic decomposition of amaranth dyestuff using diamond electrodes", Journal of Applied Electrochemistry, vol. 33, No. 1, Jan. 2003, pp. 85-91, XP2377272, ISSN: 0021-891X.

PCT/US2003/18164 International Search Report, US, Jun. 8, 2004.
 Qian et al. "Automated High-Performance, High-temperature Combustion Total Organic Carbon Analyzer," Anal. Chem. 1996, 68, 3090-3097.

Hutte, R. S., Godec, R.D., O'Neill, K.J., Sievers Instrukments Inc., "An Improved Oxidation Reactor for Total Organic Carbon Measurements," SAE Technical Paper Series, vol. 941393, Jun. 20-23, 1994.
 Japan Industrial Standards, Organic Carbon (TOC) Automatic Measuring Instrument, Continuous Total Organic Carbon Analyzer K 0805-1988.

PCT International Search Report and Written Opinion for International Application No. PCT/US07/60791 dated Oct. 1, 2007.

PCT International Preliminary Report on Patentability for Application No. PCT/US07/60791 dated Aug. 12, 2008.

PCT International Preliminary Examination Report for Application No. PCT/US03/18164 dated Aug. 6, 2004.

May 27, 2010 Office Action in CA. Serial No. 2,642,150.

Dec. 17, 2008 Office Action in U.S. Appl. No. 11/350,420.

Feb. 10, 2009 Office Action in U.S. Appl. No. 11/350,420.

Dec. 24, 2009 Office Action in U.S. Appl. No. 11/350,420.

Aug. 3, 2009 Notice of Allowance/Allowability in U.S. Appl. No. 10/517,584 (Kounaves).

May 15, 2009 Office Action in U.S. Appl. No. 10/517,584 (Kounaves).

Oct. 29, 2008 Office Action in U.S. Appl. No. 10/517,584 (Kounaves).

Jun. 9, 2009 Final Rejection in JP 2004-511789 (Kounaves) (JP and Eng Tr).

Jan. 6, 2009 First Rejection in JP 2004-511789 (Kounaves) (JP and Eng Tr).

Jan. 29, 2010 Second Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Sep. 11, 2009 First Examination Report in EP 03 734494.2 (Kounaves) (EP).

Jan. 16, 2009 Response to Dec. 17, 2008 Office Action in U.S. Appl. No. 11/350,420.

Jun. 10, 2009 Response to Feb. 10, 2009 Office Action in U.S. Appl. No. 11/350,420.

Jan. 27, 2009 Response to Oct. 29, 2008 Office Action in U.S. Appl. No. 10/517,584 (Kounaves).

Mar. 31, 2009 Response to Jan. 6, 2009 First Rejection in JP 2004-511789 (Kounaves) (JP and Eng Tr).

Jan. 19, 2010 Response to Sep. 11, 2009 First Examination Report in EP 03 734494.2 (Kounaves) (EP).

Jul. 30, 2010 Response to Jan. 29, 2010 Second Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Nov. 12, 2010 Office Action in U.S. Appl. No. 12/762,218 (Erickson).

Aug. 10, 2010 Third Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Dec. 20, 2010 Response to Aug. 10, 2010 Third Examination Report in EP 03 734494.2 (Kounaves) (EP).

Jan. 13, 2011 Fourth Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Mar. 23, 2011 Response to Jan. 13, 2011 Fourth Examination Report in EP 03 734494.2 (Kounaves) (EP).

Mar. 29, 2011 Fifth Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Jun. 1, 2011 Response to Mar. 29, 2011 Fifth Examination Report in EP 03 734494.2 (Kounaves) (EP).

Jun. 10, 2011 Sixth Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Dec. 20, 2011 Response to Jun. 10, 2011 Sixth Examination Report in EP 03 734494.2 (Kounaves) (EP).

Jan. 16, 2012 Seventh Examination Report Action in EP 03 734494.2 (Kounaves) (EP).

Aug. 12, 2011 Office Action in CA. Serial No. 2,527,498.

Jan. 24, 2012 Response to Office Action dated Aug. 12, 2011 in CA. Serial No. 2,527,498.

Nov. 12, 2010 Office Action in U.S. Appl. No. 12/762,218.

Mar. 14, 2011 Response to Nov. 12, 2010 Office Action in U.S. Appl. No. 12/762,218.

Apr. 1, 2011 Final Office Action in U.S. Appl. No. 12/762,218.

Jul. 15, 2011 Response to Apr. 1, 2011 Office Action in U.S. Appl. No. 12/762,218.

Nov. 7, 2011 Extended European search report in EP 07 710235.8.

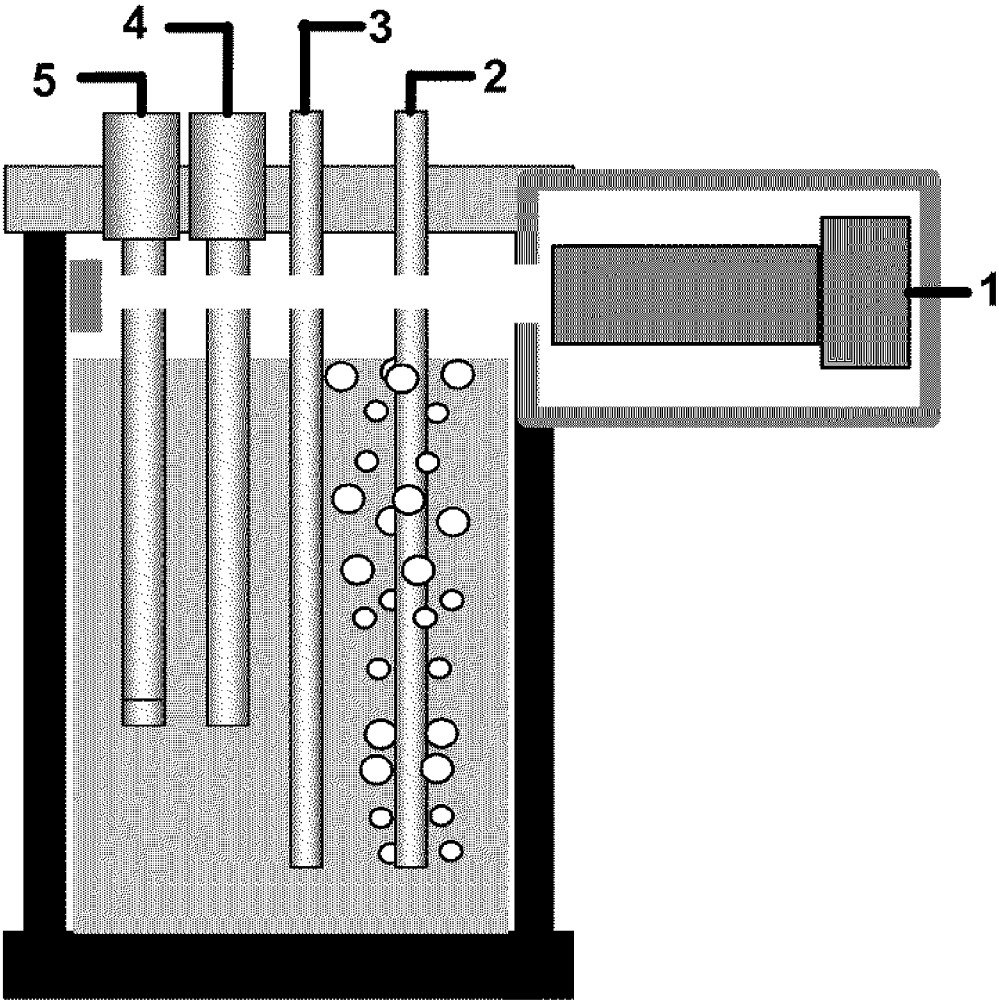
Nov. 25, 2010 Response to May 27, 2010 Office Action in CA. Serial No. 2,642,150.

Apr. 8, 2011 Office Action in CA. Serial No. 2,642,150.

Oct. 7, 2011 Response to Apr. 8, 2011 Office Action in CA. Serial No. 2,642,150.

Jan. 31, 2012 Supplementary Amendment in CA. Serial No. 2,527,498.

* cited by examiner



TOTAL ORGANIC COMPOUND (TOC) ANALYZER

GOVERNMENT SUPPORT

This invention was made with government support under NAG5-11806 awarded by the National Aeronautics and Space Administration. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

The measurement of total organic carbon (TOC) is frequently performed in environmental, clinical, and industrial settings. Current techniques require hazardous reagents, such as strong acid and oxidizing agents, ultraviolet light, or high temperature ovens, to carry out the oxidation reactions. The development of a safe and cost-effective electrochemical device capable of oxidizing organic carbon and determining TOC in aqueous solution would represent a significant advance in the art.

The concept of electrochemically oxidizing organics was demonstrated in the early 1990's as a technology for incineration of toxic organic industrial wastes. Unfortunately, this technology has thus far proven inefficient and of limited use. Over the years, a variety of working electrodes for electrochemically oxidizing organic carbon have been developed. The properties of a working electrode in an electrochemical cell is critically important since the working electrode is directly involved in the oxidation of the organic molecule. The most common working electrode material has typically been carbon-based or made from metals such as platinum, silver, gold, mercury, or nickel. Such electrodes, however, poorly oxidize because of their limited anodic range. These electrodes eventually themselves become oxidized, and therefore are inefficient for any practical use. To overcome these limitations, recent attention has focused on the potential use of diamond-film electrodes. Such electrodes are composed of a substrate material, such as silicon or titanium, coated with diamond. Such electrodes are made conductive by doping the diamond film with a conductivity inducing material which promotes p-type semiconductivity to almost metallic levels (e.g., boron).

The unique properties of highly boron-doped diamond (BDD) films include: i) low and stable voltammetric and amperometric background currents, ii) wide working potential window in electrolyte solutions, iii) reversible to quasi-reversible electron transfer kinetics for redox species, iv) morphological and microstructural stability at extreme anodic and cathodic potentials, v) low adsorption of polar molecules, and vi) long-term response stability. Recently it has been reported that BDD films have been coated on several substrates and used to replace earlier electrodes (e.g., gold or platinum) for substrates for electrochemical oxidation of organic wastes. In these uses, the BDD-film electrodes have been reported to be highly robust, capable of withstanding high anodic potentials, and resistant to self-oxidation. An example is the use of a BDD-film electrode for the electrochemical oxidation of phenol. Cyclic voltammetry showed that phenol, one of the most difficult organic molecules to oxidize electrochemically, was oxidized by a BDD-film electrode with no visible oxidation of the electrode itself, even after multiple cycles.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagrammatic representation of the total organic carbon analyzer apparatus.

SUMMARY OF THE INVENTION

The present invention relates to a total organic carbon analyzer apparatus for measuring total organic carbon (TOC) in an aqueous solution. The apparatus comprises an electrochemical cell having a diamond-film electrode, a reference electrode, and a counter electrode. The diamond-film electrode, where the diamond is doped with boron or other suitable atoms which will raise the conductive band of the diamond, is the working electrode and carries out the oxidation of the organic material to produce carbon dioxide. The apparatus further comprises a sensor or sensors for detecting the carbon dioxide produced by the diamond-film electrode. A suitable sensor is one that can detect carbon dioxide at the levels generated by the BDD electrode. Examples of sensors exhibiting this degree of sensitivity include a tunable diode laser spectrometer (TDL) and an ion-selective electrode (ISE).

The instant invention also relates to a method for measuring TOC in an aqueous solution using a total organic carbon analyzer apparatus having a diamond-film electrode. The method provides for immersion of the diamond-film electrode of the electrochemical cell into an aqueous solution to be analyzed for TOC. A positive potential, in the range of about 2-2.5 volts, is applied to the diamond-film electrode to oxidize the organics in the solution and produce carbon dioxide. As previously mentioned, the amount of carbon dioxide produced is detected and measured using a carbon dioxide sensor. The amount of carbon dioxide measured is proportional to the amount of carbon oxidized and is used to calculate the amount of total organics in the solution.

DETAILED DESCRIPTION OF THE INVENTION

Accurate detection and measurement of organics in an aqueous solution has historically required the use of costly methods involving large equipment and the use of hazardous reagents. The use of electrochemical oxidation of carbon with detection of the resultant carbon dioxide gas, promises a versatile, easy to use, and cost-effective alternative for accurately determining TOC levels in a solution. While a variety of electrodes made of different materials are readily available, they are limited in their capacity to effectively oxidize organics.

The present invention relates to the use of an electrochemical cell for carrying out the efficient oxidation of organic carbon to water and carbon dioxide. The working electrode is composed of a substrate material, such as silicon, niobium, or titanium, coated with diamond. The electrode is made conductive by doping the diamond film with boron. The carbon dioxide produced at the electrode surface is detected using an appropriate carbon dioxide sensor.

One aspect of the present invention relates to an apparatus for measuring total organic carbon in an aqueous solution. Such an apparatus includes two principle components contained within a suitable sealed housing to create a closed system so that carbon dioxide generated through the oxidation process can not escape from the system prior to detection. The selection of housing and sealing elements are matters of design choice. The first principle component, an electrochemical cell, is comprised of a working electrode, a reference electrode, and a counter electrode. The working electrode is a diamond-film electrode that is suitable for oxidation of organics in an aqueous sample to produce carbon dioxide. As previously mentioned, the diamond-film is doped with a conductivity inducing material, such as boron.

The second principle component, a carbon dioxide sensor, is used to detect the carbon dioxide produced when the electrochemical cell oxidizes the organics in the sample solution. Carbon dioxide sensors having an appropriate degree of sensitivity for use in connection with the present invention are available in either a gas-phase or aqueous-phase format. An example of a suitable gas phase carbon dioxide sensor is a tunable diode laser (TDL) spectrometer, and an example of a suitable aqueous-phase carbon dioxide sensor is an ion-selective electrode (ISE). Both the TDL and ISE sensors are known in the art. The device of the present invention may include one or more carbon dioxide sensors. In preferred embodiments, where only one sensor is provided, that one sensor is a gas-phase carbon dioxide sensor. The gas phase sensor is used to detect carbon dioxide gas bubbled from the aqueous solution containing the organic being oxidized. To quantitate levels of organic in the aqueous solution using a single gas phase sensor, it is necessary to convert substantially all of the organic material in the sample to carbon dioxide and water, and to allow sufficient time for dissolved carbon dioxide to bubble from solution. Alternatively, a combination of a gas-phase sensor and an aqueous-phase sensor may be used to quantitate organics in solution. When a combination of sensors is employed, it is not necessary to allow all dissolved carbon dioxide to bubble into the head space of the closed system (see FIG. 1, for example) wherein it can be measured using a gas-phase sensor. Rather, a liquid-phase sensor (e.g., an ISE) is useful for measuring levels of dissolved carbon dioxide in the aqueous-phase, and the gas-phase sensor (e.g., a TDL) measures the gas phase carbon dioxide in the head space. Assuming that the conversion from organic to carbon dioxide and water is substantially complete, the sum of the gas-phase and aqueous-phase carbon dioxide levels can be used to calculate concentrations of the organic originally present in the aqueous sample.

Such an apparatus, comprising an electrochemical cell having a working electrode made of boron-doped diamond and a TDL carbon dioxide spectrometer or ISE, may be manufactured to be compact and of relatively small size as compared to existing devices intended for similar application. Given the relatively compact formats achievable based on present disclosure, the device of the present invention is particularly well-suited for portable field use.

Another aspect of the present invention relates to a method for measuring total organic carbon in an aqueous solution. First, the diamond-film electrode is brought into contact with a volume of a sample to be tested for its level of total organics. The sample is an aqueous solution, such as water from a municipality, or a solution containing a dissolved specimen.

The electrode may be immersed into the sample solution or a flow-cell may be used, where the sample is circulated through the cell and in contact with the diamond-film electrode. To achieve optimal oxidation of organics in the sample, a positive potential in the range of about 2-2.5 volts is applied to the diamond-film electrode. In preferred embodiments, the positive potential is provided by an external battery. This current will cause oxidation of organics to occur, producing carbon dioxide at the surface of the diamond-film electrode. The carbon dioxide may bubble into a collector chamber (e.g., the headspace above the aqueous solution in FIG. 1) in communication with the carbon dioxide sensor where it is measured spectroscopically and recorded in absorption units (AU). The carbon dioxide may also be dissolved in the aqueous solution where it can be measured by an ISE selective for carbon dioxide and recorded as an electric potential in volts (V).

The TDL may be a small laser diode that produces a very narrow and specific wavelength of light tuned to the harmonic frequency of the carbon dioxide gas molecule in the near infrared band. To specifically measure carbon dioxide with a TDL, the TDL is preferably tuned to the harmonic frequency of carbon dioxide molecules in the near-infrared band. After being adjusted to the carbon dioxide frequency, the tunable laser diode may be tuned to different wavelengths on either side of the carbon dioxide wavelength. The light energy being absorbed by the carbon dioxide is then compared to calibrated values at the surrounding frequencies to obtain a precise quantitative measurement of the amount of carbon dioxide produced. The amount of carbon dioxide measured will be directly proportional to the amount of organics that were present in the aqueous sample. Using aqueous samples containing known quantities of dissolved organics, a standard curve may be generated to allow for the determination of precise concentration of organics within the test solution.

An Ion Selective Electrode (ISE) is a membrane electrode that responds selectively to certain ions in the presence of other ions. The ISE is particularly useful in the present invention for the detection of dissolved carbon dioxide generated by the breakdown of organic compounds at the working electrode. Such dissolved carbon dioxide may be measured by the ISE prior to its buildup in the headspace above the sample solution, where the TDL is useful. To specifically measure carbon dioxide with an ISE, the membrane of the ISE is selected such that carbon dioxide molecules selectively cross the membrane—such ISEs selective for carbon dioxide are well known in the art. The ISE is brought into contact with the sample solution and the potential at the ISE is then compared to that of the reference electrode. The magnitude of the potential at the ISE vs. the reference electrode is directly proportional to the concentration of carbon dioxide dissolved in the aqueous sample. The amount of carbon dioxide measured will be directly proportional to the amount of organics that were present in the aqueous sample. Using aqueous samples containing known quantities of dissolved organics, a standard curve may be generated to allow for the determination of precise concentration of organics within the test solution.

FIG. 1 is a diagrammatic representation of an embodiment of the present invention. The apparatus comprises an electrochemical cell having a diamond-film electrode 2, a reference electrode 4, and a counter electrode 3. The diamond-film electrode 2 is the working electrode and carries out the oxidation of the organic material to produce carbon dioxide. The apparatus further comprises a carbon dioxide sensor for detecting the carbon dioxide produced by the diamond-film electrode. Examples of suitable sensors include a tunable diode laser spectrometer (TDL) 1 and an ion-selective electrode (ISE) 5.

The invention claimed is:

1. A method for oxidizing organic carbon in aqueous solution, said method comprising:
 - a. providing, i) a diamond-film electrode, said electrode doped with a composition with the ability to raise the conductive band of the diamond-film of the electrode and ii) a sample comprising organic carbon in aqueous solution;
 - b. applying a positive potential to said electrode, the positive potential being sufficient to oxidize organics in the solution thereby producing water and carbon dioxide;
 - c. providing a housing, said housing comprising a head space and a reaction chamber, said reaction chamber comprising the sample comprising organic carbon in aqueous solution; and

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- d. detecting carbon dioxide produced by the oxidation reaction of step b) in the head space.
2. The method of claim 1, wherein said composition with the ability to raise the conductive band of the diamond-film electrode is boron.
3. The method of claim 1, wherein said positive potential is from about 2.0-2.5 volts.
4. The method of claim 1, wherein said carbon dioxide produced by the oxidation reaction of step b) is measured with one or more ion-selective electrodes.
5. The method of claim 1, wherein said carbon dioxide produced by the oxidation reaction of step b) is measured with one or more tunable diode laser spectrometers.
6. The method of claim 4 or 5, wherein said measurement of carbon dioxide is standardized to a reference electrode.
7. The method of claim 1, further comprising detecting carbon dioxide produced by the oxidation reaction of step b) in the solution while the solution is aqueous.
8. The method of claim 1, further comprising detecting carbon dioxide produced by the oxidation reaction of step b) in the solution without combusting any part of the sample.
9. The method of claim 1, further comprising detecting carbon dioxide which has bubbled into the head space.
10. The method of claim 1, further comprising detecting carbon dioxide with an aqueous-phase detector.
11. The method of claim 1, further comprising providing a counter electrode.
12. A total organic carbon analyzer, comprising:
 a housing comprising a head space and a reaction chamber, said reaction chamber being configured to contain a sample solution;
 a diamond-coated electrode operative to electrochemically oxidize organic material in the sample solution; and
 a carbon dioxide detector configured to detect gas-phase carbon dioxide in the head space, wherein the gas-phase carbon dioxide has been electrochemically-oxidized by the diamond-coated electrode.
13. The total organic carbon analyzer of claim 12, wherein the housing is sealed.
14. The total organic carbon analyzer of claim 12, wherein the carbon-dioxide detector is disposed within the housing.

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15. The total organic carbon analyzer of claim 12, wherein the gas-phase carbon dioxide has bubbled into the head space.
16. The total organic carbon analyzer of claim 12, further comprising an aqueous-phase carbon detector.
17. The total organic carbon analyzer of claim 12, wherein the diamond-coated electron has been doped with a composition with the ability to raise the conductive band of the diamond-film of the electrode.
18. The total organic carbon analyzer of claim 17, wherein the compound comprises boron.
19. The total organic carbon analyzer of claim 12, further comprising a reference electrode.
20. The total organic carbon analyzer of claim 19, further comprising a counter electrode.
21. The total organic carbon analyzer of claim 12, further comprising a counter electrode.
22. A total organic carbon analyzer, comprising:
 a reaction chamber, said reaction chamber being configured to contain a sample solution;
 a diamond-coated electrode operative to electrochemically oxidize organic material in the sample solution; and
 a gas-phase carbon dioxide detector, wherein said gas-phase carbon dioxide detector is configured to detect carbon dioxide that has bubbled from the sample solution.
23. The total organic carbon analyzer of claim 22, further comprising a counter electrode.
24. A total organic carbon analyzer, comprising:
 a reaction chamber, said reaction chamber being configured to contain a sample solution;
 a diamond-coated electrode in contact with the sample solution; and
 a carbon dioxide detector, said carbon-dioxide detector configured to detect aqueous-phase carbon dioxide that has been electrochemically-oxidized by the diamond-coated electrode.
25. The total organic carbon analyzer of claim 24, further comprising a counter electrode.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 8,216,447 B2
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INVENTOR(S) : Samuel P. Kounaves

Page 1 of 1

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

Title page, item [73], delete "O.I. Corporation, College Station, TX (US)"; and insert --Trustees Of
Tufts College, Medford, MA (US)--

Signed and Sealed this
Eighth Day of October, 2013



Teresa Stanek Rea
Deputy Director of the United States Patent and Trademark Office