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(71) Applicant *(for all designated States except US)*: **MICROBAR, INC.** [US/US]; 1252 Orleans Drive, Sunnyvale, CA 94089-1137 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **GOLDEN, Josh, H.** [US/US]; 111 Pendegast Avenue, Santa Cruz, CA 95060 (US). **GOTTS, Hugh, E.** [US/US]; 1440 Glenwood Avenue, San Jose, CA 95125 (US). **JUNG, Jay** [US/US]; 1616 Belleville Way, Sunnyvale, CA 94089 (US). **VAN DEN BERG, Marc** [US/US]; 14631 Carnelian Glen Court, Saratoga, CA 95070 (US).

(74) Agents: **SWIATEK, Maria, S.** et al.; DORSEY & WHITNEY LLP, 4 Embarcadero Center, Suite 3400, San Francisco, CA 94111 (US).

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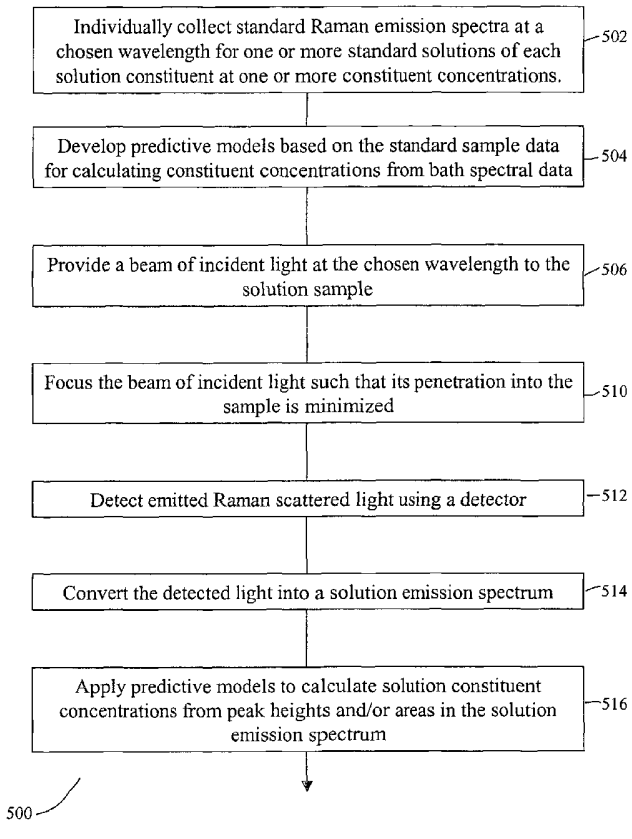

(57) Abstract: A method (500) and system (100) for determining the presence of arsenic and/or other aqueous solution constituents using Raman spectroscopy is described. Solution samples are analyzed by Raman spectroscopy by minimizing the penetration depth of the incident light beam. A chemical auto-dosing system (204) is also described for reducing the concentration of arsenic and/or other solution constituents dynamically in response to real-time concentration measurements.

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METHOD AND SYSTEM FOR THE DETERMINATION AND REMEDIATION OF ARSENIC IN AQUEOUS MEDIA

RELATED APPLICATIONS

This application is a continuation in part of U.S. Patent Application Serial Number 10/196,001 filed on July 15, 2002, the disclosures of which are hereby incorporated by reference in their entireties. This application is related to copending U.S. Patent Application Serial No._____: "Method and System for Analyte Determination in Metal Plating Solutions" (Attorney Docket No. A-70454-1/MSS/MDV), the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates generally to the field of arsenic detection and arsenic bearing wastewater treatment and analysis. More specifically, the present invention is related to a method and system for determining the presence of arsenic in aqueous media using Raman spectroscopy, and using said method to control an arsenic remediation process.

BACKGROUND

Treatment and removal of arsenic in both industrial wastewaters and potable water sources in the U.S. and worldwide has recently gained widespread notice, due to the carcinogenic properties of aqueous arsenic, as well as the ongoing debate regarding establishment of a revised maximum contaminant level (MCL) standard for arsenic that is both reasonably attainable and adequately protective of human health. The MCL currently imposed by the United States Environmental Protection Agency is 10 parts per billion (ppb or mg L^{-1}). Promulgation of a new, more stringent MCL is expected to bring new and more efficient arsenic removal technologies to the forefront, while creating new commercial opportunities in both potable and industrial water applications. In addition to improved treatment methods for arsenic removal from aqueous media, there is also a need for an efficient real time *in situ* method for arsenic determination in aqueous systems and furthermore for automated remediation process control technologies in both potable and industrial applications.

Arsenic occurs in 4 valence states: -3, 0, +3, and +5. In most waters, the +3 and +5 oxidation states are respectively found as the AsO_3^{3-} (arsenite) and AsO_4^{3-} (arsenate) anions. Arsenate is the most common form of soluble arsenic in semiconductor processing waste waters. Compounded solid arsenic in the form of GaAs particles may be obtained from ingot processing and dicing operations. The arsenate anion is negatively charged at low pH values because it is the anion of a strong acid, *o*-arsenic acid (H_3AsO_4, pK_{a1}=2.20). In contrast, arsenite (AsO_3^{3-}) removal by absorption and coagulation is less effective because its main form, arsenious acid (H_3AsO_3), is a weak acid (pK_{a1}=9.23), and is only partially ionized at pH values where removal by absorption occurs most effectively (pH 5-8). To insure that the arsenic is in the +5 oxidation state, the water may be treated with oxidants including chlorine or permanganate. Absorption of arsenate anion and other negatively charged and partially protonated species by aluminum and ferric hydroxide gels between pH 5 and 8 remains the predominant form of treatment. This is typically achieved by direct injection of acidic aluminum or ferric chloride solutions into the wastewater with the appropriate pH adjustment. The arsenate anion (AsO_4^{3-}) remains

negatively charged even at low pH values, and is thus effectively absorbed and removed by the ferric or aluminum hydroxide gels. The pH dependent absorption of arsenate anion by ferric hydroxide is shown in Figure 1. The decrease in arsenate absorption above pH 8 is due to the formation of a negatively charged ferric hydroxide surface which repels negatively charged arsenate.

A variety of new arsenic removal technologies have been proposed and are the subject of intense research. However, coagulation and precipitation by aluminum and ferric salts remains the most widely used method. Arsenic removal technologies are reviewed in greater depth in for example: *Proceedings of the Inorganic Contaminants Workshop*, AWWA, Feb. 27-29, 2000; J. Hering, et al. Arsenic Removal by Ferric Chloride, Jour. AWWA, 1996, 88, pp. 155-167; J. Hering, M. Elimelech, *Arsenic Removal by Enhanced Coagulation and Membrane Processes*, AWWA Research Foundation, Denver, CO, 1996; L. G. Twidwell, et al., "Technologies and Potential Technologies for Removing Arsenic from Process and Mine Wastewater," *Proceedings of the REWAS Global Symposium on Recycling, Waste Treatment, and Clean Technology*, 1999, pp.1715-1726, Minerals, Metals, and Materials Society, Warrendale, PA.

One industrial wastewater application where arsenic detection and removal is extremely important involves effluent obtained from the semiconductor manufacturing. The rapidly increasing use of compound semiconductors derived from the elements found in group 3 and group 5 of the periodic table is driven by the demand for high speed application specific integrated circuits (ASICs), solar cells, light emitting diodes, and lasers diodes. Examples of "3/5" compounds used in these and other applications include GaN, InGaN, InP, GaAlP, InGaAsP, and GaAs. Of particular interest are semiconductor and semiinsulator devices based on gallium arsenide (GaAs) due to several intrinsic GaAs advantages over silicon. For example, GaAs electron mobility is approximately a factor of six greater than that of silicon, which results in faster response to external radiation signals and clock-speeds two to three times greater than that of comparable silicon-based devices. Higher speeds are also indirectly realized from the larger GaAs bandgap (1.424 eV) versus that of Si

(1.1 eV), which results in reduced parasitic capacitance within the device. These properties make GaAs devices ideal candidates for high frequency and high temperature applications in broadband telecom, datacom, optical, and solar cell applications.

GaAs single crystals are typically produced by the Czochralski method in which ingots are pulled from a melt of the elements at elevated temperatures. Arsine (AH_3) gaseous byproduct may be suppressed by a low density barrier layer floating on top of the GaAs melt. Epitaxial growth of extremely pure GaAs is commonly achieved by metal organic chemical vapor deposition (MOCVD), as shown in equation 1:

$$(CH_3)_3Ga + AsH_3 \rightarrow GaAs + 3CH_4 \quad (1)$$

Destruction of arsine gas, phosphine (PH_3) gas, and volatile organogallium and indium compounds from 3/5 semiconductor synthesis and ion implantation processes are achieved by oxidative combustion in a point of use (POU) thermal processing unit (TPU). In a typical TPU, in the presence of oxygen, methane gas serves as the primary fuel to maintain continuous combustion at temperatures ranging from 750 to 1000 °C. The 3/5 compound precursors are fed into the TPU at flow rates as high as 1000 standard cm^3 min^{-1} (sccm) to produce fully oxidized intermediate products such as As_2O_5, P_2O_5, Ga_2O_3, and In_2O_3. These hot and corrosive intermediate products are then exposed to cold water in a POU wet scrubber for conversion to hydrated oxides and/or hydroxides (group 3 oxides) and water soluble acids (group 5 oxides). The following two chemical equations illustrate the conversion of arsine gas to arsenic acid:

$$2AsH_3 + 3O_2 \rightarrow As_2O_5 + H_2O + 4H^+ \quad (2)$$

$$As_2O_5 + 3H_2O \rightarrow 2H_3AsO_4 \quad (3)$$

POU water scrubbers found in a typical fab are generally of the packed tower and sieve tray type, with recirculation flow rates of up to 50 gallons per minute (gpm). Chemical species of particular concern in scrubber aqueous waste streams (with flow

rates of approximately 1-2 L min^{-1}) are phosphoric acid (H_3PO_4) and arsenic acid (H_3AsO_4), and their related pH-dependent anions. Respective average concentrations of these species in scrubber effluent are approximately 1000 to 1700 parts per million (ppm) over 24 hours at a gaseous precursor flow rate of 1000 sccm. In addition to wet scrubbers, arsenic-bearing aqueous effluents from compound semiconductor processing are obtained from slicing, dicing, and etch processes. Generally, the flow rates of these contaminated waters can vary from approximately 1 gpm to 50 gpm or more, again depending on dilution factors and wastewater blending schemes. As mentioned previously, arsenate is typically removed from these wastewaters by absorption onto ferric hydroxide floc, which involves the addition of ferric chloride solution.

A variety of methods have been developed to determine arsenic in wastewaters and potable waters. Sensitivity ranges from parts per billion to many g L^{-1}. These techniques include:

- Absorption spectroscopy
- Ion-selective electrode methods
- Atomic fluorescence spectroscopy
- Neutron activation analysis
- Atomic emission spectroscopy
- Atomic absorption spectroscopy
- Gas chromatography
- High performance liquid chromatography.

All of these methods have their strengths and their limitations. What they do have in common is that none of these methods are real-time or *in situ*. For example, determination of arsenic by ultraviolet-visible absorption spectroscopy typically involves the treatment of a water sample to form a colored complex which is then analyzed in a spectrophotometer. Two methods are well established. One involves a blue chromophore complex based on the hetero-acid related to molybdenum blue (heteropoly blue) and the other involves a red chromophore complex with silver diethyldithiocarbamate (SDDC). These chemical derivatization methods require

several steps, and are most efficiently performed in a laboratory with special apparatus. These methods are time consuming, are not readily adaptable to *in situ* analysis, and do not give quantitative results in real time. Some of these techniques may also require the handling of organic solvents and toxic reagents.

Ion selective electrodes have also been proposed for arsenic detection, but suffer from interferences from similar oxo-anions such as phosphate, and may require a pre-derivatization step such as titration. This method requires significant skill in the art of electrochemistry to interpret the results. Other methods for arsenic detection such as atomic absorption, emission, neutron activation, and chomatography suffer from the need for costly and bulky equipment in a laboratory environment. The techniques also require sample dilution and typically require 20 minutes to one hour to obtain results. Because of these drawbacks, there is a need for a rugged, less costly, real-time, *in situ* quantitative method for arsenic detection in industrial wastewaters and in potable waters. It is also desirable that such a system have a small footprint.

Ideally, an *in situ*, real-time method for arsenic analysis would continuously monitor the concentration of arsenic, and include a feedback loop to a system for arsenic removal via autodosing of appropriate removal chemicals to ensure that the remediation process is stable. Spectroscopic methods are direct, with results obtained in real-time and thus can be used for real-time process control with minimal lag time. A direct *in situ* spectroscopic method is clearly preferable to an indirect method such as titration, atomic absorption, or electrochemical analyses. Typical spectroscopic absorption techniques are of little to no utility for in situ real time analysis of arsenic in water. For example, infrared (IR) spectroscopic techniques have severe limitations in detecting arsenic because aqueous solutions are highly absorbing in the several regions of the IR range. Specifically, water has a very strong -OH vibrational band at about 3500 cm^{-1} that obscures most useful chemical information. As mentioned previously, UV-visible detection of arsenic requires the preparation of an arsenic species that has been chemically derivatized. Moreover, UV-visible detection of derivatized arsenic must be performed under tightly controlled conditions in which

proper pH is maintained and the complex is deemed stable over a particular time period of approximately 15 minutes. Finally, UV-visible detection of analytes typically requires dilution of the analyte so that the absorption maximum is less than or equal to unity, for optimal accuracy of measurement. Raman spectroscopy is a spectroscopic technique that works well in an aqueous environment with little interference from the water solvent. Raman spectroscopy operates on the principle that light of a single wavelength striking a molecule is scattered by the molecule through a molecular vibration state transition. The resultant scattered light has wavelengths different than the incident or excitation light. The wavelengths present in the scattered light are characteristic of the structure of the molecule. The intensity and wavelength or "Raman Shift" of the scattered light is representative of the concentration of the molecules in the sample. Raman spectroscopic analysis interrogates polarizability changes in the molecule to determine the presence or absence of molecular bonding, and by inference, the chemical species. Approximately 1 part in 1 million of the incident light is scattered. When a photon of incident light interacts with a molecule, in most cases, this interaction leads to the molecule assuming a more excited (higher energy) vibrational state with the emission of a photon at a longer (less energetic) wavelength. Because a small fraction of molecules in any sample already exist in an excited vibrational state, some interactions between an incident photon and a molecule may lead to a decrease in the molecule's vibrational energy state with a concomitant emission of a photon at a shorter (more energetic) wavelength. These Raman effects, including resonance Raman spectroscopy (RRS), surface enhanced Raman spectroscopy (SERS) and surface enhanced resonance Raman spectroscopy (SERRS) are generally described in greater detail in Grasselli et al., *Chemical Applications of Raman Spectroscopy*, Wiley-Interscience, John Wiley and Sons, New York, 1981. In addition, a variety of Raman spectroscopy devices have been developed in the industry. For example, a fiber optic type device is described in Angle, S.M., Vess T. M., Myrick, M.L., Simultaneous multipoint fiber optic Raman sampling for chemical process control

using diode lasers and a CCD detector, *SPIE* vol. 1587, p. 219-231, *Chemical, Biochemical, and Environmental Fiber Sensors III*, 1992.

Many important molecular functional groups are inactive or weak in absorption processes, but show significant activity in Raman spectroscopy. These functional groups include, but are not limited to, carbon-carbon bonds; metals and semi-metal oxygen bonds (arsenate or arsenite); and other main group oxyanions such as sulfate, phosphate, and nitrate. A preferred Raman sensitive functionality has the proper symmetry of chemical bonds so that a strong Raman response is obtained. Raman responses are typically characterized as being in the range from weak (lowest sensitivity) to very strong (highest sensitivity). For example, the Raman sensitive functionality may comprise a chemical group, such as for example a nitrile or a quaternerized amine, that has a strong scattering response in a wavelength range where water scattering does not occur. Other Raman sensitive groups may include, among others, carbonyls, ketones, hydrazones, saturated and unsaturated carbon, alcohols, organic acids, azo, cyanates, sulfides, sulfones, and sulfonyls. A great variety of organic and inorganic compounds yield useful Raman signals. A large variety of transition metal oxo-anions and complexes, as well as ions selected from the main-group elements also have a good Raman scattering response. Examples include, but are not limited to, arsenate, tungstate, sulfate, nitrate, phosphate, and borate.

While Raman spectroscopy has been described, in current applications it suffers from many difficulties that limit its usefulness in commercial applications. One significant problem with Raman spectroscopy is the low intensity of the scattered light compared to the incident light. Isolating, amplifying and processing the scattered light signal typically requires elaborate and costly equipment. A further problem is interference with the Raman signal due to fluorescence, or emission of light due to electronic state transitions, from a solution or composition under analysis. Many compounds fluoresce or emit light when exposed to laser light in the visible region. Fluorescence bands are generally broad and featureless, and the Raman signal

can often obscured by the fluorescence. Again, complicated and costly sensors and signal processing equipment are needed to process the signal.

Additional problems with Raman spectroscopy include overlapping peaks of multiple compounds in a sample being analyzed and solution self-absorption. When a variety of compounds are present in a sample to be analyzed, all of the compounds contribute to the Raman signal. Determining and quantifying chemical analytes in solutions on a real time basis in an industrial setting requires a method and system capable of identifying the analytes despite spectral interference from one or more other compounds present in the aqueous solution. In solutions with strong absorbance at or near the wavelength of the incident light, the strength of the resultant Raman signal is decreased due to absorption of both the incident light and Raman scattered light by the solvent and solution components. Attenuation of the incident light degrades the intensity of the Raman interactions of irradiated molecules by decreasing the incident photon flux while absorption of the scattered light increases the difficulty of extracting useful species identification and quantification information from the background spectral noise. Thus, further developments in Raman spectroscopy systems and methods are needed.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method and system for identifying the presence of arsenic in aqueous solutions. More specifically, the present invention provides a method and system for determining the presence and/or concentration of arsenic in aqueous solutions using Raman spectroscopy. The present invention also provides a system and method of controlling via a feedback loop the automatic autodosing of chemical reagents into the wastewater as needed to remove arsenic and maintain optimal wastewater remediation process parameters.

In one embodiment of the present invention, a Raman spectroscopy system for quantifying concentrations of arsenic is provided. The system includes a monochromatic light source that provides incident monochromatic light at a

wavelength chosen to fall within a region of low light absorbance on the ultraviolet-visible light absorbance spectrum for the aqueous solution. A detector for detecting an emission spectrum of Raman scattered light from the aqueous solution is also provided. Incident monochromatic light is conducted to the sample via a probe assembly that comprises an immersible head. The immersible head includes a probe window that is transparent to the chosen incident monochromatic wavelength as well as to wavelengths at which Raman emissions are expected. In operation, the immersible head is immersed in a subvolume of the solution such that the probe window is completely submerged to exclude ambient light. A first fiber optic cable transmits the incident monochromatic light from the source to the immersible head from which it is directed into the sample subvolume through the probe window to produce an emission spectrum of Raman scattered light with peaks at one or more scattered wavelengths. A second fiber optic cable transmits Raman scattered light that passes into the immersible head through the probe window from the immersible head to the detector. Each of the arsenic emission spectrum peaks has an associated area and a height. These areas and/or peak heights are input into a spectrum processor that calculates the concentration of the arsenic using a linear algebra-based method to deconvolute the peaks in the solution emission spectrum of Raman scattered light based on pre-calculated ratios of the areas under a plurality of peaks in a standard emission spectrum for the aqueous solution contaminants.

In a further embodiment of the present invention, a method is provided for quantifying the concentration of arsenic in an aqueous solution. A standard emission spectrum is collected for aqueous arsenic. Based on these standard spectra, a ratio of peak areas or heights between each of the resultant peaks in each spectrum is calculated. Incident monochromatic light at a chosen wavelength is transmitted from a monochromatic light source to a sample of the aqueous solution. The wavelength of the monochromatic light is selected to fall within a region of low light absorbance on an ultraviolet-visible light spectrum collected for the aqueous solution. The incident monochromatic light from the source is conducted via a first fiber optic cable to an immersible probe submerged in the aqueous solution sample. The focal point of

the incident laser light is adjusted such that its penetration depth into the sample is in the range of approximately 0.1 mm to 1 cm. Light emitted by Raman scattering in the sample subvolume is received by the immersible head and transmitted to a light detector via a second fiber optic cable which detects the emitted light and converts it into an aqueous solution emission spectrum. The resultant aqueous solution emission spectrum is analyzed to quantify the concentrations of aqueous solution chemical species in the subvolume by creating a series of coupled linear equations in which the concentrations of the aqueous species are unknowns and the pre-calculated peak area or height ratios are knowns. The set of linear equations is solved using linear algebra or other applicable methods of analysis.

In a new embodiment of the present invention, a Raman spectroscopy system is provided for dynamically quantifying concentrations of one or more constituents in an aqueous solution. A beam of incident monochromatic light from a light source is directed to induce emission of a Raman scattered light spectrum containing one or more peaks from the solution. A detector is provided for rapidly quantifying one or more of the area under the peaks and/or the height of the peaks as a function of peak wavelength or wavenumber. The beam passes through a lens that focuses it at a focal point that is disposed less than approximately 1 cm within the bulk of the solution. A spectrum processor is configured to determine concentrations of each of the constituents based on the peak heights and/or areas at short time intervals using one or more predictive models for Raman peak response as a function of wavelength. The predictive models are determined by analyzing one or more standard solutions of the constituents, preferably at different concentrations.

In an alternative new embodiment of the present invention, a method is provided for quantifying concentrations of one or more constituents of an aqueous solution in approximately real time. Standard Raman emission spectra are individually collected in response to monochromatic light at a chosen wavelength for each of one or more constituents in the solution at varying concentrations of the constituents. Based on these spectra, the resulting peak area and/or height data are fitted to one or more predictive models relating constituent concentration to observe

peak height and/or area. A beam of incident monochromatic light at the chosen wavelength from a monochromatic light source is directed toward the solution. The beam is focused such that the focal point penetrates less than approximately 1 cm into the bulk of the solution. Raman scattered light emitted from the solution is detected on a light detector and converted into a solution emission spectrum. The solution spectrum is analyzed to quantify the concentrations of the constituents based on the predictive models.

In a further new embodiment,

BRIEF DESCRIPTION OF THE DRAWINGS

Other objects and advantages of the present invention will become apparent upon reading the detailed description of the invention and the appended claims provided below, and upon reference to the drawings, in which:

Figure 1 is a chart showing arsenic removal by absorption with ferric hydroxide as a function of pH.

Figure 2 is a chart showing a Raman spectrum of an aqueous solution containing arsenic.

Figure 3 is a schematic diagram illustrating the Raman device of according to one embodiment of the present invention.

Figure 4 is a schematic diagram showing a more detailed view of a sampling probe according to one embodiment of the present invention.

Figure 5 is a schematic diagram showing a more detailed view of a flow cell according to one embodiment of the present invention.

Figure 6 is a schematic diagram showing a detail of a probe head with a ball lens according to one embodiment of the present invention.

Figure 7 is a schematic diagram showing a detail of a probe head with an adjustable focal length lens according to one embodiment of the present invention.

Figure 8 is a graph showing an prototypical example of a Raman calibration curve of peak area vs. concentration for an arsenic aqueous solution.

Figure 9 is a flow chart showing the steps by which a spectrum of overlapping peaks is deconvoluted to calculate concentrations of multiple analytes.

Figure 10 is a schematic diagram showing an integrated aqueous arsenic analyzer system according to one embodiment of the present invention.

Figure 11 is a spectrum showing the detection of arsenic in accordance with one embodiment of the method and system of the present invention. The arsenic signals are observed at ca. 765 and 930 cm^{-1}.

Figure 12 is a schematic diagram illustrating the Raman device of a new embodiment of the present invention.

Figure 13 is a flow chart showing the steps of the method of the present invention according to a new embodiment for determining the concentrations of one or more analytes in an aqueous solution in real time.

Figure 14 is a schematic diagram illustrating a wastewater treatment system with real-time Raman influent analysis of a new embodiment of the present invention.

Figure 15 is a flow chart showing the steps of the method of the present invention according to a new embodiment for controlling the dosing of reagent chemicals to a wastewater treatment process according to real time influent concentration measurements with a Raman analysis system.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method and system for identifying chemical analytes in solutions. More specifically, the present invention provides a method and system for determining the presence and/or concentration of arsenic in solutions using Raman spectroscopy.

The present invention provides a rapid and real-time method and system of quantifying organic and inorganic species in aqueous solutions and, in a further embodiment, of automatically replenishing the concentrations of additives used to precipitate or remove arsenic from solution in response to the measurements. Concentrations of these species may be in the ppm (part per million) range or in the grams per liter range. More specifically, the present invention provides a

methodology and system for the quantification of aqueous arsenic in wastewaters and potable waters over a broad concentration range. The present invention provides a method for detection and quantification that employs Raman spectroscopy in conjunction with inventive techniques that diminish or eliminate photon absorbance characteristics of the aqueous system that can interfere with accurate detection of analytes of interest. The Raman spectroscopy system and method of the present invention provides rapid and quantitative measurement of relatively dilute organic and inorganic species which are extremely difficult to quantify in real time using prior art methods.

First discovered by C. V. Raman in 1928 (Nature (London), v. 121, p. 501 (1928)), Raman spectroscopy has great potential as a novel and efficient method for real-time quantitative analysis of chemicals as solids, slurries, or in solution. In general, Raman spectroscopy involves the scattering of incident light by molecules. While most of the incident radiation is scattered elastically, a small fraction of photons return with higher or lower energy, usually 1 in 1 million or so. A net loss of photon energy (increase in wavelength) results from the photon's induction of a molecular vibration in a molecule it encounters. In contrast, a gain in energy (decrease in wavelength) by the photon is a result of the absorption of a molecular vibration by the photon interacting with a previously excited molecule that drops to a less energetic vibrational state as a result of the interaction. Formally, the photon interactions are a result of a change of molecular bond polarizability (P) due to the interaction with a photon's electric field (E), as expressed in equation 1:

$$P = \alpha E \tag{4}$$

The Raman effect increases in strength at shorter incident light wavelengths Observed Raman peaks are typically shifted to lower energies than the incident radiation (Stokes shift). This is due to the higher probability of a change in polarizability, or vibrational transition at room temperature, because most of the molecules are at a lower energy vibrational state. However, the photon can interact with a small fraction of high energy vibrational states that are also populated,

resulting in emission of a higher energy photon (anti-Stokes shifted). Raman response is also dependent on laser wavelength. Signal intensity I, is dependent on wavelength (λ), as expressed in equation 2:

$$I \approx \lambda^{-4} \quad (5)$$

According to equation 2, a 532 nm laser yields approximately 5 times greater Raman response intensity than a 785 nm laser. Therefore the inventors have discovered that it is advantageous to choose a higher energy laser to promote greater signal to noise ratio and shorter spectrum acquisition times. However, the higher energy of shorter wavelength photons can also induce fluorescence emissions which may mask the Raman response in some samples. According to the present invention, a further consideration in Raman spectroscopy is taught that, though the intensity of Raman signal is linearly dependent on the power of the incident light and it may in some cases be advantageous to employ a higher powered light source, sheer brute force application of additional incident radiation power may not be advantageous due to the potential for inducing undesirable physical and chemical changes in the sampled solution under high power density conditions.

Raman spectroscopy has significant advantages over absorption techniques such as UV-visible, near infrared and mid infrared, especially in aqueous solution analysis. Water is a weak Raman scatterer in the range of approximately 300 to 800 nm. However, non-Raman spectroscopic techniques may be overwhelmed by absorption of incident photons by dissolved ions or water itself due to its presence in overwhelming excess. An effective normalized range for Raman signals in wavenumbers is typically from 200 cm^{-1} to 3000 cm^{-1}, which allows for the detection of a large variety of inorganic and organic species in aqueous media.

Identifying the window of relatively high transmission in the absorption spectrum of an aqueous solution allows a choice of incident laser light, preferably a diode laser source, that transmits light with a wavelength in the range of approximately 300 to 785 nm. If a laser is chosen that transmits radiation at or near the absorption maxima of the solution, the Raman effect is greatly diminished as

photons that would otherwise be available to stimulate Raman emissions from the molecules of interest are attenuated by absorbance within the bulk fluid. Moreover, substantial solution absorption at the laser wavelength results in an exponential relationship between intensity and concentration, which is a significant source of error in quantitative detection of the analyte or analytes of interest. Therefore, it is important to choose the correct laser incident wavelength. In this embodiment of the present invention, an 84 mW green Nd:YAG laser source that transmits at 532 nm is used. The power of the laser is not limited, however, a range of 5 to 200 mW is preferred for best signal generation. A 532 nm diode laser source is preferred for the analysis of solutions because it emits within the window of solution light transmission and is compact and efficient. Those skilled in the art can select the correct wavelength of incident monochromatic light for other applications based on the teaching of the present invention.

In this embodiment of the present invention, a method and system for sensing analytes in solutions is provided wherein a Raman spectroscopy sensor is utilized. The Raman sensor generally includes a monochromatic light source to probe an aqueous solution containing one or more analytes. Generally, the solution is passed through a fluid path which intersects the light source. The monochromatic light source may be a diode laser, gas laser, filtered high intensity light source and the like. As the monochromatic light source probes the solution, light is scattered. Individual wavelengths of the scattered light are separated using a compact monochromator in either a static or scanning mode, with detection provided by a detector such as a high sensitivity CCD or diode array detector. Additionally, source photons may be carried to the solution utilizing a series of bundled fibers which return the light to the detector for subsequent evaluation.

A Raman spectroscopy sensor 100, particularly suitable for detection of analytes in solutions, in accordance with this embodiment of the present invention is illustrated in Figure 3. The sensor 100 generally includes a monochromatic light source 102, a spectrograph 104, a probe 120 that is coupled to the light source and spectrograph through an excitation fiber 130 and a collection fiber 132 respectively,

for delivering incident light to and collecting scattered light from a sample 124, a fiber input 106 and CCD array 110 coupled to the spectrograph 104, and a personal computer data processor with interface electronics 112 for controlling the system and processing the output from the spectrograph 104.

In the exemplary embodiment shown in Figure 3, the monochromatic light source 102 is preferably comprised of a frequency doubled YAG diode laser, operating at 20 mW, 0.1 nM stability with 1.5 mrad beam divergence. The diode laser is powered by a power supply (not shown) which preferably is 120 V temperature stabilized. In one embodiment, the excitation light from the diode laser is focused onto a fiber end of the excitation fiber 130 which conducts the incident light to the probe 120 for focusing into a sample subvolume 124. Preferably both the excitation fiber 130 and the collection fiber 132 are comprised of a poly-micro fiber optic cladded light guide.

A solution sample 124 to be analyzed enters the sample subvolume either through normal operating circulation of the bulk aqueous solution or via one or more pumps (not shown). The aqueous solution interacts with the excitation light delivered by the excitation fiber 130 to the probe 120 to yield Raman scattered light. Light scattered from the solution – the Raman radiation or signal – is collected by the probe 120 and delivered to the fiber input 106 via the collection fiber 132. From the fiber input 106, collected scattered light passes into the spectrograph 104 wherein it is analyzed to yield a spectrum which is quantified in real time via a CCD array 110.

The Raman signal preferably passes through a filter 133 which is preferably a reject filter chosen to filter out light at the incident wavelength to prevent swamping of the CCD detector, and is coupled via a SMA connection to fiber optic borosilicate glass, prior to analysis in the spectrograph. Borosilicate fiber has a Raman shift of a well defined wavelength notch for baseline frequency calibration. Various spectrographs 104 may be used. In one embodiment, the spectrograph is a CS400 Micropac with Hamamatsu 256Q cooled array. A serial interface 114 may be provided for coupling the processed signal to a computer system and interface electronics 112 for display and/or analysis.

The spectrometer is optical and mechanical in nature. The Raman scattered light delivered via the collection fiber 132 from the sample is projected onto the CCD array 110. A charge-coupled device (CCD) is a light sensitive integrated circuit that quantifies the intensity of the light by converting the light into an electrical charge. The CCD data or spectrum is then analyzed to calculate the concentration levels of additives and byproducts. The computer system 112 preferably consists of a computer, a CCD controller card that plugs into the computer mother board, communication PC cards such as a modem and an Ethernet card among others, and digital and analog input/output ports.

Figures 4 and 5 are schematic diagrams providing additional detail of an exemplary system according to one embodiment of the current invention. An immersible probe 120 that transmits the incident light 122 from a diode laser light source 102 to the analyte solution sample 124 and also receives the scattered signal 126 is used in this embodiment. Incident light 122 is transmitted from the monochromatic light source 102 to the probe via an excitation fiber optic cable 130. Scattered light is collected by the probe and transmitted to a fiber input 106 to a spectrograph 104 by a collection fiber optic cable 132. The focal point, or working distance 134 of the laser light 122 is adjusted so that its penetration depth into the solution sample 124 is preferably in the range of approximately 0.1 mm to 1 cm, with a range of approximately 0.1 to 5 mm most preferred. The working distance 134 is adjusted according to the turbidity of the solution as well as its self-absorption characteristics. The probe 120 is constructed of materials that resist the effects of an acidic or caustic aqueous environment such as, for example Monel alloy, Teflon, or other inert materials. A probe window or more preferably a lens 136 is provided through which incident and scattered light pass out of and into, respectively, the probe. This window or lens 136 is preferably constructed of either sapphire or quartz. The probe 120 is immersed into the aqueous solution or some other subvolume containing a sample such that ambient light is excluded. It is preferred that the probe 120 is immersed in a subvolume or region of the aqueous solution or test solution in which circulation past the probe is sufficient for continuous monitoring of a dynamic

chemical environment that is representative of the aqueous solution as a whole. The probe 120 may be preferably placed in a pipe or some other custom built chamber with appropriate pumps to circulate the solution past the probe and prevent interference from ambient light.

Figure 4 also shows additional details regarding a preferred embodiment of the probe. In a preferred embodiment of the present invention, an 84 mW green Nd:YAG laser source is provided that transmits at 532 nm in conjunction with a short path length quartz flow cell to reduce the absorbing characteristics of the solution. The sample 124 is housed in a pipe or chamber (not shown) that interfaces with the probe 120. In this embodiment, light conducted to the probe by the first or excitation fiber optic fiber 130 enters the chamber and passes through a collimating lens 140 which collimates the light. The collimated light beam 142 then passes through a bandpass filter 144 and a dichroic filter 146 before exiting the probe via a focusing lens 136 that focuses the light beam 142 on the sample 124 at the desired working distance 134. Light scattered from the sample 120 passes back through the focusing lens 136 into the probe 120 where the dichroic filter 146 diverts light that differs from the incident beam wavelength at a 90° angle to a mirror 150 angled at 45° to redirect the scattered light beam 152 parallel to the incident collimated beam 142. The scattered light passes through a second focusing lens 154 that focuses it into the second, collection fiber optic fiber 132 for transmittal to the detector.

Because absorbency is proportional to path length, the path length is chosen to minimize absorbance of the incident laser by the solution under analysis. A path-length that is too long may result in the capture of both incident laser light and the emitted Raman signal by the inherent absorbancy of the sample. A flow cell with a fixed path length as shown in Figure 5 may preferably be used for continuous monitoring of the dynamic aqueous solution environment. Sample solution 161 is circulated through the flow cell 160 via pressure or aspiration by mechanical and/or micromechanical pumps 162. The flow cell path length may preferably be in the range of approximately 0.1 to 10 mm. More preferably, the flow cell path length through which incident light from the probe passes is in the range of approximately

0.1 to 1 mm. The cell preferably interfaces with a fiber optic probe of the same general design as shown in Figure 4.

In another embodiment of the present invention, an immersible probe as shown in Figure 4 is provided that includes a ball lens. Use of a ball lens provides the following advantages: the focal distance is always tangent to the ball lens surface and thus constant thereby providing a constant sample volume, the probe is always properly aligned when it is in contact with a sample, and there are no moving parts. A general schematic of an exemplary ball probe according to this embodiment is shown in Figure 6 which includes a ball lens 170 having a focal point 172 on its surface 174. The ball lens 170 is mounted in a probe head 120 that includes appropriate optics (not shown) to convey an excitation beam of monochromatic light 122 to the ball lens 170 and a beam of scattered light 126 away from the ball lens and to an appropriate detector or detectors. In general, the ball lens 170 is housed in a barrel-shaped probe that is preferably constructed of materials such as for instance Monel alloy, Teflon, or other inert, acid or caustic resistant materials. The ball lens is preferably constructed of sapphire or quartz or other materials that are both acid and caustic resistant and transparent to the incident and scattered light wavelengths. Because the ball lens probe has its focus at the surface of the sphere, constant sampling precision and repeatability is enhanced. It is preferable to position the probe in contact with the aqueous solution such that ambient light is excluded and where circulation of the aqueous solution past the probe is sufficient to allow for continuous monitoring of the dynamic chemical environment within the bulk of the aqueous solution. The probe is thus preferably placed in a pipe or chamber or other customized subvolume equipped with appropriate pumps to circulate a sample of the aqueous solution past the ball lens and exclude ambient light.

In a preferred embodiment of the present invention, an immersible probe 180 as illustrated in Figure 7 is provided. The probe 180 includes an adjustable focal point 182 for incident light 122 provided by an excitation fiber 130 from a monochromatic light source 102 as shown in Figure 3. The focal point 182 of the incident laser light is adjusted by moving an adjustable lens 184 within the probe

body 186. The focal point 182 is adjusted such that it is within the sample subvolume immediately outside of a sealed probe window 190 through which the focused beam is projected. The close proximity of the beam focal point to the window – it is preferably in the range of approximately 0.1 to 5 mm from the outer surface of the window 190 – mitigates potentially confounding effects of solution absorption and light scattering by particles on the collected Raman spectrum and subsequent analytical steps.

Spectral data collected via the aforementioned embodiments are preferably analyzed for features that can be ascribed to certain chemical species. The Raman shift of individual chemical species is preferably identified prior to analysis by separate measurement of individual components. Quantification of the individual components in a aqueous solution mixture is preferably achieved by determination of the peak area and/or height of the chemical species of interest, followed by comparison of these data to a straight-line calibration curve. The linear calibration curve is preferably generated by plotting peak area and/or height versus concentration of samples in which the concentration of the analyte of interest is known. Standard methods of statistical analysis including, but not limited to, linear regression may be applied to obtain a best fit straight line calibration curve. Figure 8 shows an exemplary calibration curve generated by Raman analysis of known samples of a solution containing arsenic. Peak height and or area are collected for a series of standard solutions with varying concentrations. The data from these analyses are analyzed by linear regression to generate the calibration curve shown.

Commercially available software packages for spectral analysis may be used in conjunction with the above described system and method. These include Unscrambler by CAMO Technologies, Woodbridge, NJ which is used to create calibration curves and goodness of fit metrics and to perform integration of peak areas and quantification of peak height. In addition, the software includes routines that eliminate extraneous effects that could have a negative impact on the area or peak height measurement, such as, for instance, fluorescence. Spectral software package for qualitative and quantitative analysis that include quantification of peak area and

height are Unscrambler by CAMO and the GRAMS/AI package provided by Thermo Galactic, Salem, NH. PLSplus/IQ, also provided by Thermo Galactic is used to perform partial least squares analyses on spectral data as is Unscrambler. Another useful software, MATLAB, is offered by Mathworks of Natick, Massachusetts. Eigenvector Research, Inc., of Manson, WA also provides a useful software program for data analysis called PLS Toolbox.

In a preferred embodiment of the present invention, a method is provided for calculating concentrations of individual additives and other analytes in a aqueous solution based on a single Raman spectrum captured as described above in the previous embodiments. The sample spectrum contains a plurality of peaks, some of which are attributable to Raman scattering by analytes of interest such as one or more aqueous solution additives. In general a spectrum of a solution containing multiple analytes has regions of the spectrum where peaks attributable to more than one analyte overlap. This embodiment of the present invention provides a method for deconvoluting a spectrum comprised of peaks from numerous analytes. Prior to analysis of a sample spectrum, standard spectra are prepared for each analyte expected to be found in the sample. A primary and one or more secondary peaks are identified for each standard. In general, the peak heights and/or areas of each of the primary and one or more secondary peaks vary linearly with the concentration of the analyte. As such, the ratios of the area and/or height of an individual secondary peak to the primary peak as well as to other secondary peaks in the spectrum of a single analyte are approximately constant and independent of the concentration of the analyte. This property is used in conjunction with standard spectra and peak ratios from the expected analytes to differentiate the concentrations of multiple overlapping analytes in a sample spectrum as follows. A region of the sample spectrum containing only a single primary or secondary peak from a first analyte is identified. The concentration of that analyte is determined based on a calibration curve like the one shown in Figure 8 based on the area and/or height of that peak in the standard spectrum. If, for example, a secondary peak from the first analyte occurs in the same region of the sample spectrum as the primary peak of a second analyte, the total area

and/or height observed on the sample spectrum in the wavelength region of the primary peak of the second analyte is reduced by the expected height and/or area under the first analyte's secondary peak based on the concentration of the first analyte known from the primary peak height and/or area of the first analyte, the calibration curve, and the known ratio of the height and/or area of the primary and secondary peaks of the first analyte. This process is repeated as necessary to quantify all of the analytes of interest in a sample spectrum. Overlapping of multiple peaks from multiple analytes in a single wavelength region of a sample spectrum requires construction of a matrix of linear algebraic equations. The resulting matrix can be readily solved top identify the concentrations of each of the analytes by one of skill in the art provided that at least one peak of one analyte occurs alone in a discrete region of the spectrum.

Bilinear projection methods, like PCA (Principal Components Analysis), PCR (Principal Components Regression), PLS (Partial Least Squares regression, or Projection to Latent Structures regression) extract systematic information from the combination of many measurement variables. They also offer great interpretation features, to visualize sample patterns and variable relationships in easily interpretable graphical pictures. The multivariate models can then be used for indirect measuring, data reduction, exploration, prediction or classification/identification. These methods are easy to use and handle most multivariate problems despite intercorrelations, noise, errors, missing data, or extreme data table dimensions. Sub-routines and algorithms may also be used to streamline the data analysis process or for conversion of peak height or areas directly to additive concentrations.

In a further embodiment of the present invention, the Raman analysis and aqueous solution additive concentration system and method are integrated with a commercially available chemical auto-dosing system to maintain the concentration of arsenic species and/or other chemical compounds of interest in a treated solution, such as for instance a waste water or potable water stream, below a maximum contaminant level or some similar upper limit. In this embodiment, the contaminant concentrations as well as those of one or more treatment additives such as for instance ferric

hydroxide are maintained within acceptable ranges during an ongoing, dynamic process. In this embodiment, shown schematically in Figure 9, an integrated aqueous solution analyzer system 200 maintains the proper concentrations of treatment additives in an aqueous solution by providing a feedback signal from a Raman spectroscopy system to an autodosing system to control the rates at which selected additives are added to the aqueous solution. In this embodiment, an analyzer subsystem 202 interfaces with a process subsystem 204 to provide chemical concentration data as well as control capability.

In general, an aqueous solution reactor 206 contains a solution comprising one or more contaminants including arsenic discharged from an industrial process and/or provided as influent to a water treatment process. The contaminant concentrations in the solution flow input to the system of the present invention are non-constant. However, outflows from the system of the present invention are maintained at contaminant concentrations below preset, programmed limits. Maintaining the concentration level of the contaminants in the solution, is essential in controlling the process. Typically, the aqueous solution reactor 206 and the additive metering hardware are a part of the process subsystem. However, it is not a requirement.

The analyzer subsystem 202 includes a spectrograph 104 including a fiber input and CCD array (not shown in Figure 9) as described above. The spectrograph is preferably connected to a personal computer based control system 112 with control electronics for processing the signals received and quantified by the spectrograph and CCD array. The computer system 112 preferably consists of a computer, a CCD controller card that plugs into the computer mother board, communication PC cards such as a modem and an Ethernet card among others, and digital and analog input/output ports.

One or more additives supplied from one or more additive reservoirs 210 are metered into the aqueous solution reactor 206 via metering pumps 212 to maintain the required concentration levels of the additives and the one or more contaminants. In this embodiment, the concentrations of contaminants and additives are monitored via

Raman spectroscopy as outlined in the preceding embodiments. These data are used to safe guard against discharge of the aqueous solution with contaminant concentrations that exceed the prescribed limits. Additives are supplied to the aqueous solution reactor 206 via supply lines 214 from the additive reservoirs at rates metered by the metering pumps 212 based on feedback received from the analyzer subsystem 202. In this closed-loop control scheme, the concentrations of key components of the aqueous solution are tightly controlled without dependence on empirical relationships or historical data regarding contaminant concentrations in the input aqueous solution. As a treatment additive is added into the aqueous solution via any control and metering process, the concentration of that additive is at its peak and similarly the removal rate of the contaminant to be treated by the additive is at its highest. The additive concentration gradually decreases over time during processing. The amplitude of the additive concentration variability can theoretically be minimized by supplying a continuous, uniform addition of additives to the aqueous solution reactor 206. However, because real process conditions and the influent concentration of the contaminants whose removal depletes the additive concentrations are never ideal or constant, constant corrections of the addition rate are necessary. Analyzer subsystem 202 provides continuous feedback to a process subsystem controller 216 that in turn controls the metering pumps 212 to adjust the delivery rate of the additives from the reservoirs 210 to the aqueous solution reactor 206. The process subsystem controller 216 has built in algorithms and hardware inputs and outputs to directly control the additive metering pumps 212.

The system and method provided by this embodiment is capable of directly controlling the metering pumps 212 or transmitting data on the concentrations of additives and byproducts.

The aforementioned embodiments of the system and method of the present invention are directed to analysis of aqueous solution additives in industrial and potable waters. In an alternative embodiment, the system and method of the present invention are applied to analysis of arsenic in aqueous solutions.

EXPERIMENTAL

A number of experiments were conducted according the method and system of the present invention. These experiments are intended for illustration purposes only, and are not intended to limit the scope of the present invention in any way.

Example 1

In one example, standard samples containing aqueous arsenic were tested. The concentration range was 100 ppm to 10,000 ppm. Figure 10 shows the linear calibration curve generated for the standard samples. This plot shows that peak area/height is a linear function of concentration. Raman spectra of aqueous arsenic are shown is shown in figures 2 and 11 .. The arsenic signals are identified at approximately 930 and 765 wavenumbers. The signals at approximately 1040 and 718 wavenumbers are from the nitrate anion.

Example 2

In another experimental example, a sample of wastewater containing an unknown amount of arsenic was measured. It was found that the solution contained 10,000 ppm of arsenic. The system used to analyze the aqueous solution is as described above and depicted schematically in Figure 3. A 532 nm, 84 mW green Nd:YAG laser was used in conjunction with a fixed probe head as described above. The system integrates an internal laser calibration system based on an internal neon discharge. This enables greater measurement precision and a discrete non-varying laser output. The result is greater repeatability and more consistent peak areas. A thermoelectrically cooled CCD detector of the dimensions 1024 x 128 was used. The spectral resolution is 4 cm^{-1}. The bandwidth of analysis was 400 to 3000 cm^{-1}. A personal computer running commercially available spectral analysis software packages (Unscrambler by CAMO Technologies and GRAMS/AI and PLSplus/IQ by Thermo Galactic) were used for data analysis and peak height and area determination. A 3 mL sample was withdrawn from the aqueous solution and a placed in a borosilicate glass vial. Acquisition times varied from approximately 1 to 10 minutes.

Based on comparison of the aqueous solution emission spectrum to known controls and a standard calibration curve, it was determined that the data thus obtained was consistent with the arsenic concentration measured by atomic emission spectroscopy.

Example 3

In a further experimental example of the present invention, an aqueous solution containing arsenic was analyzed using a 785 nm Raman system. To compensate for the approximately fourfold reduction in sensitivity at this wavelength versus 532 nm as predicted by equation 5, the incident laser power was boosted to 150 mW. As noted above, Raman signal sensitivity is a linear function of power.

An aqueous solution containing arsenate ion was analyzed using a quartz cell with a Renishaw Ramascope Raman System 1000 coupled to an Leica DMLM microscope. The system is equipped with diode laser excitation (785 nm., 150 mW of power), a entrance slit of 50 microns, an 1800 groves/mm high efficiency aluminized grating, and a high sensitivity thermoelectrically cooled CCD detector. The Raman spectra for reference areas were collected on adjacent clear field areas. Raman spectra are collected at 4 cm^{-1} resolution from 200 to 3600 cm^{-1}, on liquid samples ranging from 300 microliter to 1 liter volumes. Under these conditions, an acquisition time of one minute was sufficient to generate spectral data for calibration and unknown analysis with less than 1 % error.

NEW EMBODIMENTS

One of the primary hindrances to the use of Raman spectroscopy to quantify the concentrations of constituents of an aqueous solution, such as for example a waste water stream containing one or more toxic compounds including arsenic, is the high absorbance of the solution for the incident laser light. The previously described embodiments disclosed a method and system in which a wavelength for the incident beam of excitation light for generating a Raman spectrum is chosen to avoid overlap with peaks in the solution absorbance spectrum. In this new embodiment, a method and system are described for obtaining reproducible measurements of concentrations

in an aqueous solution without tuning the incident Raman excitation light to a wavelength at which the solution absorbance is minimized. This approach provides the advantage of permitting high sensitivity spectral measurements of the solution over a broader range of wavelengths. In a dynamic, real-time monitoring system based on the method of the present invention, changes in the background spectral properties of the solution over time do not require a change in the incident light wavelength. Additionally, by permitting a broader choice of incident light wavelength, it is possible to choose a shorter wavelength light source with the accompanying increase in photon energy and Raman signal intensity as shown in equation 5.

In the new embodiment, the incident light beam is focused such that penetration into the sampled volume of the solution is minimized, and advantageously it is not necessary to minimize the solution absorbance. In this manner, the incident light beam passes through only a short thickness of the solution prior to reaching the focal point, and the emitted light returned to the detector travels a similarly short distance through the solution. In general, the Raman spectroscopy system 400 of this new embodiment, as shown in Figure 16, includes a monochromatic light source 410, a detector 412, a lens 414, and a spectrum processor 416.

More specifically, with reference to Figure 12, a sample of the solution 420 is illuminated by a light beam 422 from the monochromatic light source 410. The light source 410 may be a diode or gas laser, a filtered high intensity light source, or other source providing a collimated, monochromatic beam of light. The beam 422 passes through a lens 414 which focuses the beam 422 at a focal point 424 very close to the periphery or surface or interface 426 of the plating bath sample 420. In a preferred embodiment, the monochromatic beam 422 penetrates less than 2 cm into the sample 420 before reaching the focal point 424. More preferably, the beam 422 penetrates less than 1 mm into the bulk of the sample 422 before reaching the focal point 424. Even more preferably, the focal point 424 lies less than 50 μm inside the sample 422. At the focal point 424, the light beam 422 interacts with the sample 420 to produce an emission of Raman scattered light 430. This scattered light is emitted in all directions

from the focal point 424. The light beam 422 may travel from the light source 410 to the lens 414 directly, as shown in Figure 16, or alternatively it may be conveyed via one or more fiber optic cables (not shown). Similarly, scattered light 430 may be transmitted directly from the sample 420 to the detector 412. Alternatively, the scattered light 430 may be focused onto one end of one or more fiber optic cables (not shown) such that it is conveyed to the detector 412. In another alternative embodiment, one or more mirrors and/or beam splitters (not shown) may be employed to route the incident light beam 422 and/or the scattered light 430 between the light source 410 and the lens 414 and between the focal point 424 and the detector 412, respectively. It is preferred that extraneous light is excluded from the sample to avoid interference with detection of scattered light from the sample 420.

The detector 412 quantifies the intensity of the scattered light 430 as a function of wavelength and outputs this information to the spectrum processor 416. It is preferred to use a compact monochromator in either static or scanning mode to separate the scattered light 430 into one or more spectral wavelengths prior to quantification on the detector. It is also preferred to pass the scattered light through a filter 434 to remove back-scattered or reflected light at the wavelength of the incident light beam 422. The filter 434 is preferably a reject filter at the wavelength of the incident light beam 422. In this manner, the scattered light intensity is not swamped by the several orders of magnitude more intense incident light. In one embodiment, the detector 412 is one or more CCD arrays. Alternatively, the detector 412 is one or more diode array detectors. The detector 412 quantifies the scattered light using the peak height and/or peak area of each wavelength peak in the spectrum and outputs this information to the spectrum processor 416.

The spectrum processor 416 comprises one or more computer systems and interface electronics for coupling the computer system to the detector 412 and converting the output signals from the detector 412 into data that is readable by the computer system. Output data from the detector 412 is analyzed by the computer system using data from one or more calibration experiments to convert the peak heights and/or areas of the emitted light spectrum to a concentration value for one or

more analytes in the plating bath sample 420. In general, a series of standard solutions of varying concentration, each containing one of the analytes in a plating bath, is analyzed to determine the peak height and/or area of one or more peaks in the standard spectrum for each analyte as a function of wavelength. Based on these predictive models, which may be linear calibration curves, or possibly more complex mathematical relationships between one or more peak metrics and the analyte concentration, the spectrum processor 416 converts measured peak data from the bath sample to concentration data for each of the plurality of analytes in the plating bath. For more complicated bath spectra in which more than one analyte peak overlap in the same region of the bath spectrum, an algorithm that is capable of deconvoluting a complicated spectrum of one or more overlapping peaks from one or more analytes in a sample may be run on the computer system to obtain concentration data for the one or more analytes in the plating bath. One algorithm by which this analysis may be performed is described above in the description of the previous embodiments.

The sample 420 may be contained in a transparent spectroscopy vial. Alternatively, the sample 420 may be contained within a subvolume of the solution as a whole or the incident light beam may be supplied directly into the solution as a whole. In this embodiment, a window that is transparent to the incident light and Raman scattered light is provided through which the light beam 422 passes into the sample 420 and through which the scattered light 430 passes out of the sample to the detector 412. In a preferred embodiment, the lens is in direct contact with the sample. In one embodiment, the lens may be a ball lens as described above. If the lens is in direct contact with the sample, its focal length is preferably such that the focal point 424 is as close as possible to the lens surface in contact with the sample 420. As noted above, the focal point 424 preferably lies less than approximately 2 cm inside the sample 420, more preferably less than 1 mm, and most preferably less than 50 μm inside the sample 420. If the system includes a transmission window between the lens and the sample 420, the focal length of the lens is chosen such that it is slightly longer than the distance between the lens and the inside wall of the window or the vial such that the penetration distance into the sample is minimized as described above.

Because the sample volume is typically substantially smaller than that of the solution volume as a whole and because the volume that is actually irradiated at the focal point by the focused incident light beam 422 is generally even smaller, it is preferred to include one or more pumps or other mechanisms for circulating the solution such that the sampled portion is in equilibrium with the remainder of the solution. The use of such a circulation mechanism or comparable system is preferred when the system of the present invention is used to calculate real time changes in the concentrations of one or more analytes in a solution such as a waste water stream. Alternatively, for use in a waste water stream an immersible probe as described above may be inserted within the moving stream of waste water so that movement of the waste water past the probe and the resultant fluid turbulence causes the sampled solution to be representative of the real time changes in concentrations in the stream as a whole. Waste waters may be extremely caustic and/or acidic. As such, it is preferable for the lens and/or transparent window as well as any other components of the Raman spectroscopy system that are in contact with the analyzed solution to be constructed of one or more materials that are resistant to acidic, caustic, or other chemical attack.

In an additional embodiment, the system of the present invention may be used in conjunction with an adjustable focal length ball lens probe assembly as described above and shown in Figure 5. In this embodiment, the ball lens probe is operated such that the focal point 424 of the beam 422 is at the surface of the lens, which is also the lens-sample interface such that the incident light has an effectively negligible path length through the sample 420. Incident light is transmitted to the lens via one or more optical fibers and scattered light is conveyed back to a detector via one or more other optical fibers. Alternatively a system of lens and/or mirrors may be used to direct light from the incident light source and back to the detector.

In another embodiment of the present invention, the Raman spectroscopy analysis system described above is incorporated into a chemical autodosing system such that feedback from the analysis subsystem to a process control subsystem is used to determine real time or nearly real time concentrations of one or more contaminants

in the solution and therefrom calculate and execute appropriate dosings of one or more chemicals to the solution for the purpose of reducing the concentrations of the contaminants. In this embodiment, one or more chemical additive reservoirs are provided. Each reservoir contains a supply of one or more chemical additives, such as, for example acidic aluminum, ferric chloride, ferric hydroxide or other chemicals that react with the contaminants, either in solution, or in some other meterable form. A pump or other comparable supply metering device such as a metering valve or the like is coupled to each reservoir for supplying each additive to the plating bath at a controllable rate. The process control subsystem may be a computer or other programmable device executing one or more algorithms. These algorithms take as inputs the outputted contaminant concentration data from the analyzer subsystem. Based on the concentration data, the process control subsystem provides commands to the metering devices to supply additives to the solution as needed to reduce the contaminant concentrations below the desired effluent concentration of the waste water. In this embodiment, it is preferred that the analyzer subsystem operates on a continuous basis. As such, a ball lens probe positioned within the flowing solution stream or within the bulk of the solution in a batch system is a preferred embodiment of the analyzer system. Alternatively, one or more sampling pumps may be used to mix the solution and to circulate a sample of the solution past a window through which the incident excitation light beam is focused as described above. Alternatively, a flow cell comprising a transparent vial into which the beam is focused may be used.

In a further embodiment of the present invention, a method is provided for determining concentrations of one or more components of an aqueous solution. As summarized in Figure 13, the method 500 includes the following steps. Individual standard Raman emission spectra are collected for each of the solution components of interest, as well as for other solution components that are expected to be present that might interfere with the observed peaks of other components 502. These emission spectra are collected at the chosen wavelength of the incident light to be used in analysis of the solution. A standard spectrum is collected for each component at one or more concentrations. Based on the standards, one or more predictive models are

developed 504. The simplest predictive model is a linear calibration curve. However, mathematical relationships of any complexity relating one or more peak metrics such as height and/or area to the concentration of a given component may be applied. A beam of incident light at the chosen wavelength is used to excite a Raman emission spectrum from a sample of the solution 506. The beam is focused such that its penetration into the sample is minimized 510. It is preferred that the penetration depth of the focused beam is less than approximately 2 cm. More preferably, the focal point of the beam is less than approximately 1 mm and most preferably less than approximately 50 μm inside the bulk of the sample. Alternatively, the penetration depth may be manually or automatically varied from approximately the depth of the surface monolayer (50 μm) to approximately 1 or 2 cm. In this alternative embodiment, the penetration depth or focal point may be adjusted by observing its effect on the signal intensity. The focal point is then fixed at the penetration depth at which the signal has the greatest magnitude.

Raman scattered light emitted from the sample is detected using a detector which may be a CCD array or other diode array detector 512. This detected light is converted into a solution emission spectrum 514 which is then analyzed using one or more of the predictive models discussed above to convert the observed peak heights and/or areas into solution component concentration values 516. For more complicated solution spectra in which more than one analyte peak overlap in the same region of the bath spectrum, an algorithm that is capable of deconvoluting a complicated spectrum of one or more overlapping peaks from one or more solution constituents in a sample may be run on the computer system to obtain concentration data for the one or more constituents in the plating bath. One algorithm by which this analysis may be performed using the ratios of peak heights and/or areas obtained from standard spectra of individual constituents is described above in the description of the previous embodiments.

The method and system of the new embodiments described herein are preferably operated such that real time or near real time solution constituent concentration data may be obtained. The detector and spectrum processor are

preferably set to collect and process spectral data into concentration data at a frequency of greater than one analysis per five minutes. More preferably, more than approximately one sample cycle occurs per minute. More frequently collected data, such as at the rate of multiple sampling cycles or more per minute is also envisioned and included as an equivalent embodiment of the present invention.

In further embodiments of the present invention, a system and method are provided for removal of arsenic and/or other dissolved wastewater contaminants by precipitating and incorporating these compounds into suspended solids which are then removed from the wastewater by one or more solids separation systems. In general, dissolved metal ion removal may be accomplished by adding a metal chelating small molecule or metal chelating polymer or, which forms a particle or floc, or easily filterable precipitate, upon contact with dissolved metal ions, such as cadmium, chromium, copper, lead, mercury, nickel, silver, etc., and other potential constituents of industrial and municipal wastewaters. Arsenic is typically removed by adsorption onto ferric hydroxide as described above. Coagulation and flocculation of suspended particles, followed by a solids separation system or method, completes the removal process.

An exemplary system 600 representative of this embodiment is shown in Figure 14. While one possible configuration of the system is shown, the present invention may be employed with other types of waste water treatment systems. In general, the system 600 comprises an influent wastewater stream 602 containing one or more dissolved or suspended contaminants. The influent stream 602 is analyzed for the concentration of the contaminant or contaminants of interest using one or more of the Raman analytical systems as described above 604. The rates of addition of one or more reagent chemicals, whose purpose is to promote precipitation of the contaminant(s) and cause them to form readily removed suspended solid particles, is controlled by a controller subsystem 606 that controls one or more reagent metering means 610 in response to the measured influent concentration or concentrations and the influent wastewater flow rate. Reagents are mixed with the influent stream in one or more reaction tanks 612 before suspended solids are removed via one or more

particle concentration and/or separation systems 614. The system shown in Figure 14 indicates arsenic as the target contaminant in the influent stream. However, the present invention is intended to encompass dynamic feedback water treatment systems designed for a variety of dissolved aqueous contaminants.

More specifically, with reference to Figure 14, the arsenic bearing wastewater influent 602 is sampled by a Raman analysis system 602. The analysis system, which is described in greater detail above in reference to other preferred embodiments of the invention comprises a probe or other previously described means for contacting an incident monochromatic light beam with a sample of the influent. The analysis system 604 also includes a detector and spectrum processor configured to determine approximately real-time arsenic concentrations in the influent stream 602 based on predictive models for converting one or more Raman emission spectra peak metrics into concentrations. The Raman analysis system 604 is connected via a feedback loop to a controller subsystem 606 which dynamically controls one or more reagent metering systems 610 for controlling the rate at which one or more reagents are added to the influent stream 602 in one or more reaction tanks 612. The Raman analysis system 604 and the process controller may be integrated into a single microprocessor-based control system or may be separated into multiple microprocessor-based control systems that function as a whole through hardware and/or software interfacing. In the example shown in Figure 14, these subsystems are schematically represented as separate, though this is not necessary. Chemical metering, as described above in regards to the autodosing system of the present invention, may be employed to control the reaction environment (pH level) and to promote the kinetics of the process chemistry by autodosing chemicals at a controlled rate based on the arsenic concentration in the influent waste water stream as determined by the Raman sensor and the influent flow rate. Mixers may be employed to aid in pH control and in the flocculation process. In the exemplary system shown in Figure 14, a first and a second reaction tank 614 are provided for this purpose.

In the reaction tanks 612, reagents are added to change the solubility of the dissolved contaminants. For arsenic removal, these reagents may include pH

adjusters and/or hydrogen peroxide to force the aqueous arsenic into the +5 oxidation state. When the pH of this mixture is adjusted into the approximate range of 5 to 8 coupled with the addition of ferric ion in the form of a ferric salt, arsenic adsorbs onto ferric hydroxide floc. Further addition of one or more chemical flocculants and or polymer coagulants may be used to enhance the formation of readily removable solid particles. In the exemplary embodiment shown in Figure 14, an additional auxiliary tank 616 is provided for additional mixing of the waste water solution to promote flocculation or to add other chemical reagents as needed. From the reaction and flocculation tanks, the waste water is passed to one or more solids separation tanks 614. In the example shown in Figure 14, these tanks contain microfiltration membranes and are further coupled to additional flow systems to remove filter solids 620 to a solids holding tank 622 and ultimately to a filter press 624 for dewatering as well as return plumbing loops for returning filter backflush flow 626 and filter press filtrate liquids 630 back into the waste water treatment system for additional treatment.

The control subsystem 606 may preferably be configured and/or programmed to accomplish a variety of tasks, including monitoring and recording arsenic levels, pH levels, fluid levels, fluid flows, and vessel pressures throughout the system; controlling the kinetics of the process chemistry by autodosing chemicals at a controlled rate; controlling the reaction environment (pH level); controlling the bulk distribution of process and pH adjustment chemistries into the system; controlling the flow rate into the filter tanks to create the appropriate environment (pressure) within the filter tanks for the solids separation system 614; automatically backflushing the solids separation system (in this example the filteation units) 614 as needed to effect the removal of accumulated solids from the filter membranes; automatically routing the fluid flow through the system as needed to best ensure continuous operation; and providing a stopped mode of system operation that ensures effluent is not released if it contains unacceptable levels of arsenic.

Autodosing of chemicals in response to commands from the control subsytem 606 may preferably be accomplished via the use of chemical metering pumps and or

metering valves 610, which are controlled based on an algorithm using the influent and effluent arsenic concentrations, as determined by the Raman detection system and/or an additional Raman-based analytical subsystem (not shown) positioned to sample the treatment system effluent 632, and the waste water influent flow rate. Treatment system environmental control may be accomplished via the use of chemical metering pumps and mixers or stirrers or other similar systems in the first and second reaction tanks 614 as well as in the auxiliary tank 616. The bulk distribution of process and pH adjustment chemistries into the system may preferably be controlled via the use of air-operated pumps and valves. The flow rate into the solid separation system 614 may preferably be controlled to create the appropriate process conditions (such as for instance, pressure) within the solids separation system 614 via the use of transfer pumps and automated valves. Backflushing of the filter tanks 614 in the example in Figure 14 may be accomplished via one or more diaphragm pumps and/or automated valves (not shown). The fluid flow is preferably automatically routed through the system 600 as needed to best ensure continuous operation via the use of automated valves. The control subsystem 606 preferably has a graphical user interface for setting the configurable parameters for the above functions.

Waste water treatment such as is described for the system of the preceding embodiment may preferably be implemented using a method such as described below. A method flow chart 700 that is illustrative of this embodiment, is shown in Figure 15. The basic steps of the method include analyzing a wastewater stream using Raman spectroscopy as described in the preceding embodiments to determine the influent concentration of one or more aqueous contaminants 702. Based on the measured influent concentration and the influent flow rate, one or more chemical reagents are added to the wastewater 704 to reduce the solubility of the contaminant or contaminants and to promote the formation of removable solids particles. These particles are removed by a solids separation system such as a microfiltration or some other membrane-based system, a gravitational settling system, or a porous media filtration system 706. By measuring the influent concentration of the contaminants in

approximately real-time, the addition rates of the chemical reagents may be controlled dynamically both to prevent over-dosing during low influent concentrations and the resulting waste and to appropriately increase the reagent dosing during higher influent concentrations to prevent elevated effluent concentrations from the treatment method.

Experimental Example 4

An arsenic bearing wastewater stream was analyzed using a 532 nm Chromex Sentinel Raman System (Chromex, Inc., Albuquerque, NM). The system features self-calibration to a neon discharge and an Andor CCD detector. The 80 mW diode laser system utilized a submersible probe with adjustable focal point as supplied by Infotonics, Inc. (Norwood, MA).

The water was then analyzed for arsenate concentration and a linear calibration curve was produced from a series of samples. A personal computer running commercially available spectral analysis software packages (Unscrambler by CAMO Technologies and GRAMS/AI and PLSplus/IQ by Thermo Galactic) were used for data analysis and peak height and area determination.

Experimental Example 5

An arsenic bearing wastewater stream was analyzed using a 532 nm Chromex Sentinel Raman System (Chromex, Inc., Albuquerque, NM). The system features self-calibration to a neon discharge and an Andor CCD detector. The 80 mW diode laser system utilized an external sample holder with integrated probe. Borosilicate glass vials were used to contain the bath samples. The external sample holder was adjusted so that the incident beam focal point was located just within the wall of the glass vial, at the solution interface. In this fashion, solution absorption effects are minimized and signal intensity is maximized. The water was analyzed for arsenic concentration and linear calibration curve was produced from a series of standard samples. The arsenic concentration of a series of unknown samples was predicted using a personal computer running commercially available spectral analysis software

packages (Unscrambler by CAMO Technologies and GRAMS/AI Thermo Galactic). The prediction error was less than 5 %.

New Experimental Example 6

An arsenic bearing wastewater stream was analyzed using a 532 nm Chromex Sentinel Raman System (Chromex, Inc., Albuquerque, NM). The system features self-calibration to a neon discharge and an Andor CCD detector. The 80 mW diode laser system utilized a submersible probe with adjustable focal point as supplied by Infotonics, Inc. (Norwood, MA).

The water was analyzed for arsenic concentration and compared to a linear calibration curve produced from a series of standard samples. The arsenic concentration of the series of unknown samples was predicted using a personal computer running commercially available spectral analysis software packages (Unscrambler by CAMO Technologies and GRAMS/AI Thermo Galactic). The prediction error was less than 5 %. From these data, and other data collected over time, a chemical dosing system for arsenic removal was adjusted so that the ferric chloride solution usage to obtain the required effluent concentration from the system was decreased by approximately 50 % relative to that required in a conventional system without a feedback-controlled autodosing system. The volume of recovered sludge bearing absorbed arsenic was reduced by 75 % in the autodosing system relative to the standard system.

Prospective Example 7

The following prospective example is provided for illustration purposes only and is not intended to limit the invention in any way.

In one prospective example, to carry out the method of the present invention for a facetious GaAs solar cell manufacturing company, Kai Solar and Optics, a 100 gallon per minute (gpm) microfiltration system is preferably installed at the backend of the fab's arsine gas scrubber system. The scrubber effluent contains water bearing arsenic at a concentration of about 1000 ppm, 99 % of which is in the +5 oxidation state, As (V). A microfiltration system, as shown in Figure 14 is employed used due

to its high efficiency. However, any particle separation system with a high particle removal efficiency such as for example sand filtration, gravitational settling, or other membrane processes, may be used. Coupled to the high flow microfiltration system is one or more reaction tanks with pH adjustment means, as well as auto-dosing equipment for ferric ion introduction and coagulant/flocculant addition. The chemical pumps receive signals from a feedback loop to and from the Raman detection system to control the reagent dosages based on arsenic concentration and flow rate.

Specifically, the process is carried out as follows: arsenic bearing wastewater, gravity fed from the arsine gas scrubbers at a flow rate between between approximately 1 and 100 gpm, is are exposed to an appropriate amount of ferric ion at a pH between approximately 5 and 8 in the first reaction tank. Ferric ions are typically introduced at a 10 % mole excess to ensure complete adsorption of arsenic. The size of the reaction tank should be such that the residence time of the water is approximately 1 minute or greater, with greater than approximately 5 minutes being preferred. The reaction mixture is gently stirred, preferably at a rate of at least 10 RPM. The mixture from the first reaction tank is then fed into a second reaction tank where the pH is adjusted to the range of about 5 to 8, with approximately pH 6 being preferred. The size of the second reaction tank should be such that the residence time of the water is approximately 3 minutes or greater, with approximately 10 minutes or greater being preferred. In the pH range of 5 to 8, ferric hydroxide is formed, which absorbs the arsenic (V) created in the previous step. Optionally, an additional polymer coagulant may be injected inline after the first reaction tank, or alternatively into the second reaction tank, to create larger particles for the following filtration step. The concentration of the polymer coagulant in the water is in the range of about 5 to 100 ppm, with 5 ppm being preferred. The polymer coagulant used may be cationic or anionic in nature, with the preferred embodiment being cationic with a molecular weight that ranges from approximately 5,000 to 500,000. Polymer coagulants meeting this criteria include, but are not limited to EPI-DMA, DADMAC and copolymers of poly(acrylamide) and DADMAC.

After the final pH is adjusted in the second reaction tank, with or without polymer addition, the ferric hydroxide particles containing the arsenic are fed by pump or by gravity into a microfiltration system containing the filter arrays. The filtration system can operate automatically for 24 hrs, 7 days a week, with minimal input from the operator. A feedback control system, such as is described above in the embodiments describing the autodosing system and shown in Figure 14, is preferably employed to monitor the arsenic concentration in the waste water treatment system effluent and/or the influent stream entering the treatment system. The arsenic level in the effluent is preferably 50 ppb or less. The autodosing system may be configured as described above to control the rate at which ferric ion and polymers are added. Because the Raman spectroscopy system described above provides near-real time measurement of the arsenic concentration, the rate at which the arsenic-removing reagents are added may be controlled dynamically in response to changing influent and effluent conditions. If the arsenic analysis systems detects a spike in the influent or effluent arsenic concentration, additional reagent addition is ordered to enhance the removal efficiency of the treatment system. Likewise, if a drop in the influent and/or effluent concentration is detected, the system reduces the rate at which the reagents are added to minimize sludge (removable solids) production and reduce costs by controlling unnecessary reagent usage.

The foregoing description of specific embodiments and examples of the invention have been presented for the purpose of illustration and description, and although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby. They are not intended to be exhaustive or to limit the invention to the precise forms disclosed, and obviously many modifications, embodiments, and variations are possible in light of the above teaching. It is intended that the scope of the invention encompass the generic area as herein disclosed, and by the claims appended hereto and their equivalents.

CLAIMS

1. A Raman spectroscopy system for dynamically quantifying concentrations of one or more constituents in an aqueous solution comprising:

a light source providing a beam of incident monochromatic light to induce emission of a Raman scattered light spectrum containing one or more peaks from said solution;

a detector for rapidly quantifying one or more of the area under said peaks or the height of said peaks as a function of peak wavelength;

a lens, said beam passing through said lens and being focused at a focal point, said focal point being disposed less than approximately 2 cm within the bulk of said solution; and

a spectrum processor configured to determine concentrations of each of said constituents from said peak heights and/or areas at short time intervals using one or more predictive models for Raman peak response as a function of wavelength, said predictive models being determined by analyzing one or more standard solutions of said constituents.

2. The Raman spectroscopy system of claim 1 wherein said focal point is disposed less than approximately 1 mm within the bulk of said solution.

3. The Raman spectroscopy system of claim 1 wherein said focal point is disposed less than approximately 50 μm within the bulk of said solution.

4. The Raman spectroscopy system of claim 1 further comprising:

at least a first fiber optic cable for transmitting said incident monochromatic light from said source to said lens; and

at least a second fiber optic cable for transmitting said Raman scattered light passing out of said solution to said detector.

5. The system of claim 1 wherein said detector further comprises

a CCD receiver and a processor housed together and spaced apart from said laser source, said CCD receiver including a plurality of diode cells formed in a linear array, for receiving said Raman scattered light and wherein each of said diode cells exhibit output signals corresponding to the amount of received scattered light; and

said processor for receiving said output signals and generating a measurement signal corresponding to said output signals of said plurality of diode cells.

6. The Raman spectroscopy system of claim 1 further comprising:

a transparent barrier, said transparent barrier having a side that contacts said solution, said transparent barrier being disposed between said lens and said solution.

7. The Raman spectroscopy system of claim 6 wherein said lens and said transparent barrier are housed in an immersible probe.

8. The Raman spectroscopy system of claim 7 wherein said probe is constructed of one or more materials that are resistant to chemical attack.

9. The Raman spectroscopy system of claim 1 wherein said lens is in direct contact with said solution, said lens being constructed of a material that is resistant to chemical attack, said lens having a focal point that is positioned at approximately the interface between said lens and said solution.

10. The Raman spectroscopy system of claim 1 further comprising one or more pumps, said pumps continuously circulating said solution such that a representative sample of said solution is impinged by the incident light beam.

11. The Raman spectroscopy system of claim 1 in which said source of incident monochromatic light is a diode laser.

12. The Raman spectroscopy system of claim 11 wherein said diode laser provides incident light at a wavelength in the range of approximately 340 to 550 nm.

13. The Raman spectroscopy system of claim 11 wherein said diode laser provides incident light at a wavelength of approximately 532 nm.

14. A method for quantifying concentrations of one or more constituents of an aqueous solution in approximately real time, comprising the steps of:

individually collecting standard Raman emission spectra in response to monochromatic light at a chosen wavelength for each of one or more constituents in said solution at varying concentrations of said constituents;

fitting the resulting spectral peak area and/or height data to one or more predictive models;

providing a beam of incident monochromatic light at said chosen wavelength from a monochromatic light source to said solution containing one or more constituents, said beam being focused such that the focal point penetrates less than approximately 2 cm into the bulk of said solution;

detecting light emitted by Raman scattering from said solution on a light detector;

converting said detected emitted light into a solution emission spectrum; and

analyzing said solution spectrum to quantify the concentrations of said one or more constituents based on said one or more predictive models.

15. The method of claim 14 further comprising the step of:

adjusting the focal point of said beam of incident monochromatic light such that the focal point penetrates less than 1 mm into said solution.

16. The method of claim 14 further comprising the step of:

adjusting the focal point of said beam of incident monochromatic light such that the focal point penetrates less than 50 μm into said solution.

17. A method for determining concentrations of a plurality of constituents from a spectrum collected for a solution containing said constituents comprising the steps of:

collecting a spectrum of said solution as in claim 14;

modifying said predictive models to include ratios between the peak heights and/or areas of peaks in the standard spectra of each individual constituent;

identifying and quantifying a first of said plurality of constituents in a region of said solution spectrum wherein analyte peaks do not overlap;

estimating the peak height and/or area attributable to each of one or more of said plurality of constituents with one or more peaks that occur in a region of said solution spectrum wherein two or more constituents peaks overlap;

creating a system of coupled linear algebraic equations based on said estimated peak heights and/or areas; and

solving said system of coupled linear algebraic equations using linear algebraic techniques to determine the concentrations of said plurality of constituents in said solution.

18. A chemical auto-dosing system for controlling the concentration of one or more constituents in an aqueous solution in approximately real time, comprising:

a Raman spectroscopy analyzer subsystem as in claim 1 for quantifying and analyzing a Raman spectrum emitted from said solution to determine real time concentrations of said constituents in said solution;

one or more additive reservoirs, each of said reservoirs containing one or more chemical reagents for reducing the solubility of one or more of said constituents or for promoting the formation of readily removable suspended solids in a solution;

one or more metering pumps that control the flow of said reagents from said reservoirs to said solution; and

a processing subsystem controller that receives and processes concentration data from said analyzer subsystem to provide control outputs to said metering pumps.

19. A treatment system for removing aqueous contaminants from wastewater comprising:

a Raman spectroscopy analysis system as in claim 1, said analysis subsystem providing one or more data outputs regarding the real-time concentrations of one or more contaminants in an influent wastewater;

one or more reagent delivery systems for adding one or more reagents to said influent wastewater to reduce the solubility of said one or more contaminants;

a controller subsystem operatively coupled to said one or more concentration data outputs from said analysis system; said controller subsystem controlling the rate at which said one or more reagent delivery systems add said one or more reagents to said influent wastewater based on said real-time concentration data and the flowrate of said wastewater;

one or more reaction tanks wherein said one or more reagents are mixed with said influent wastewater to promote conversion of dissolved contaminants into suspended solids;

a solids separation system, said solids separation system removing suspended solids from said influent wastewater prior it being discharged.

20. The system of claim 19 wherein said solids separation system is selected from the group consisting of one or more gravitational settling tanks, a porous media filtration system, and a membrane filtration system.

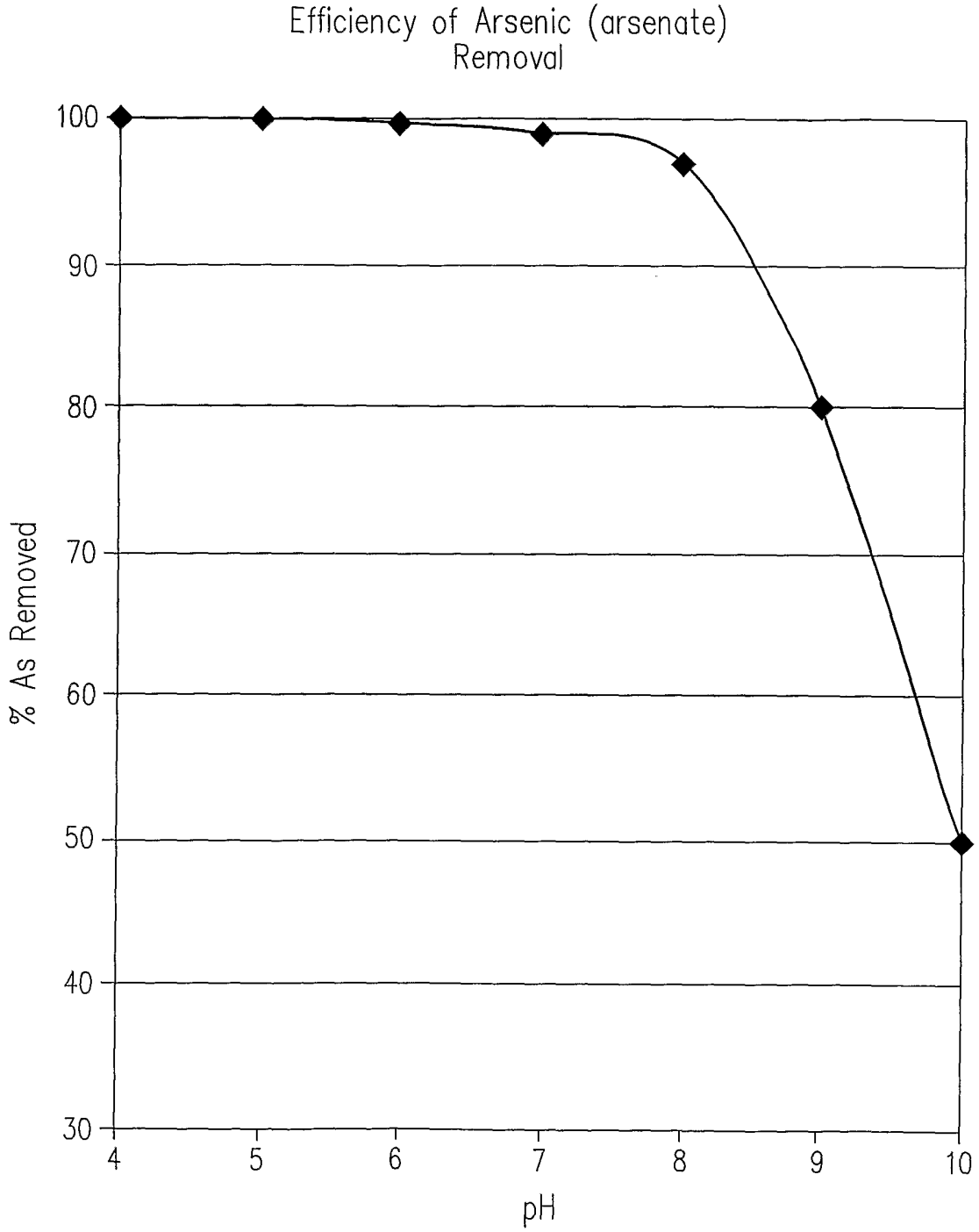
Efficiency of Arsenic (arsenate) Removal
% As Removed
100
90
80
70
60
50
40
30
4
5
6
7
8
9
10
pH

FIG. 1

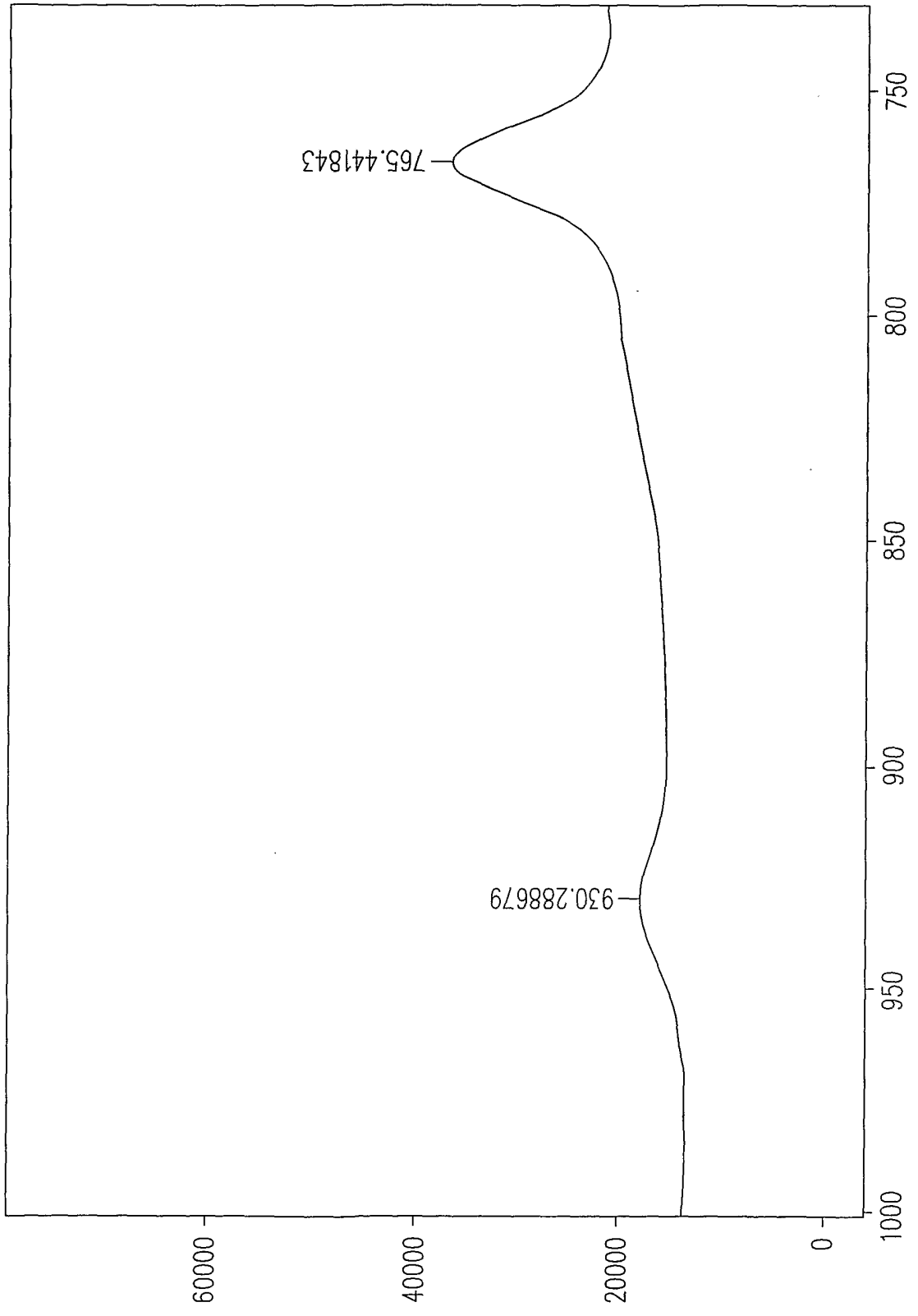
765.441843
930.288679
60000
40000
20000
0
1000
950
900
850
800
750

FIG. 2

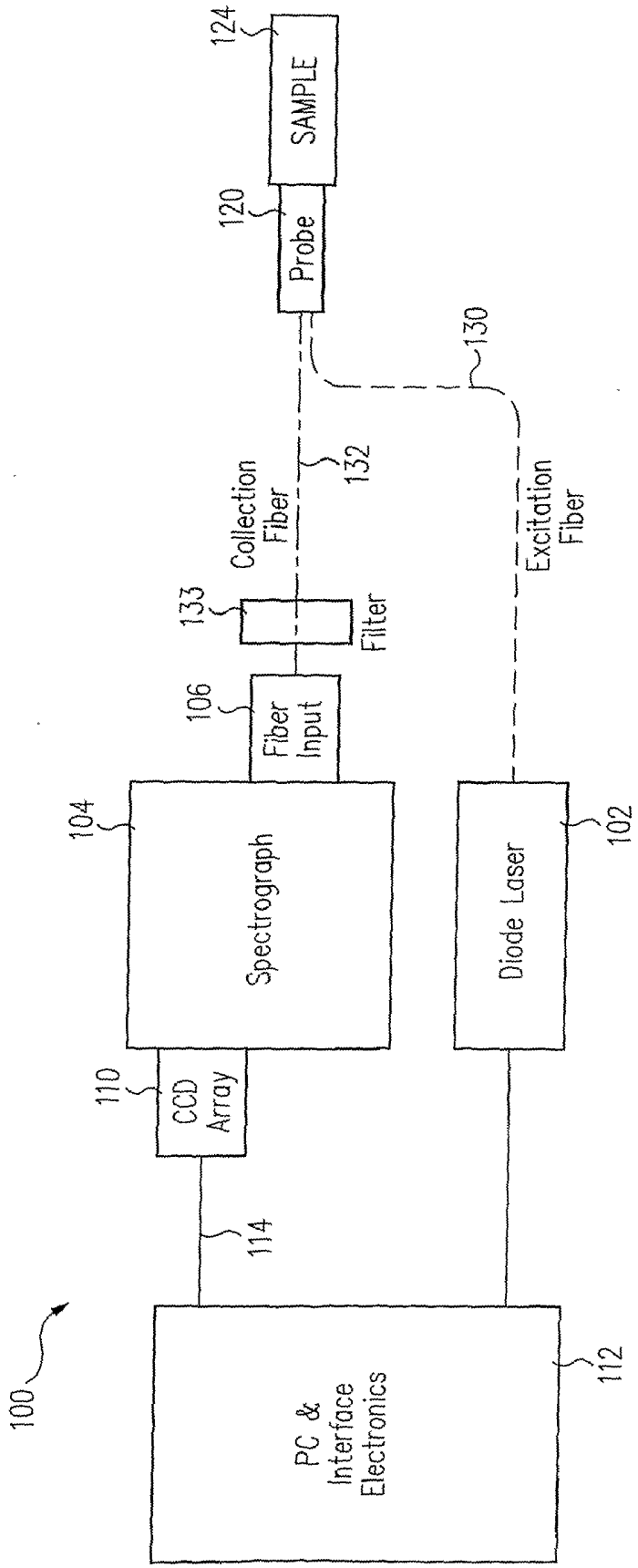
100
PC & Interface Electronics
112
114
CCD Array
110
Spectrograph
104
Diode Laser
102
Fiber Input
106
Filter
133
Collection Fiber
132
Excitation Fiber
130
Probe
120
SAMPLE
124

FIG. 3

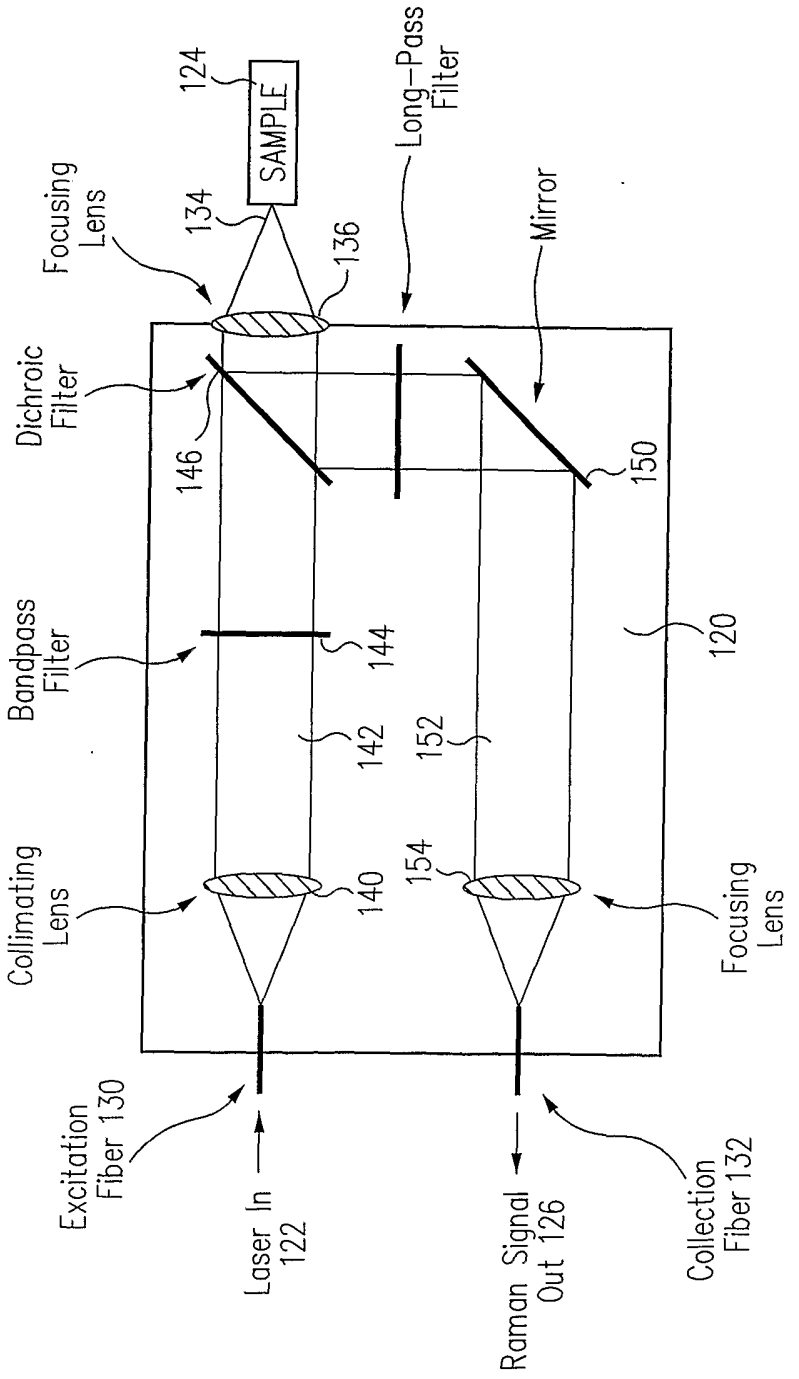
124
SAMPLE
Long-Pass Filter
Focusing Lens
134
136
Mirror
Dichroic Filter
146
150
Bandpass Filter
144
120
142
152
Collimating Lens
140
154
Focusing Lens
Excitation Fiber 130
Laser In 122
Raman Signal Out 126
Collection Fiber 132

FIG. 4

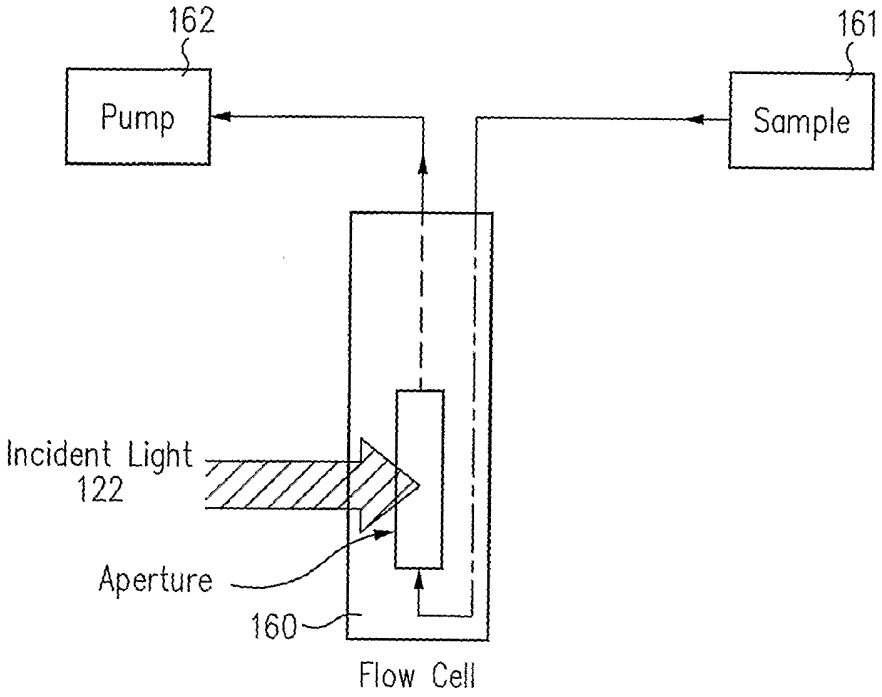
162
Pump
161
Sample
Incident Light
122
Aperture
160
Flow Cell

FIG. 5

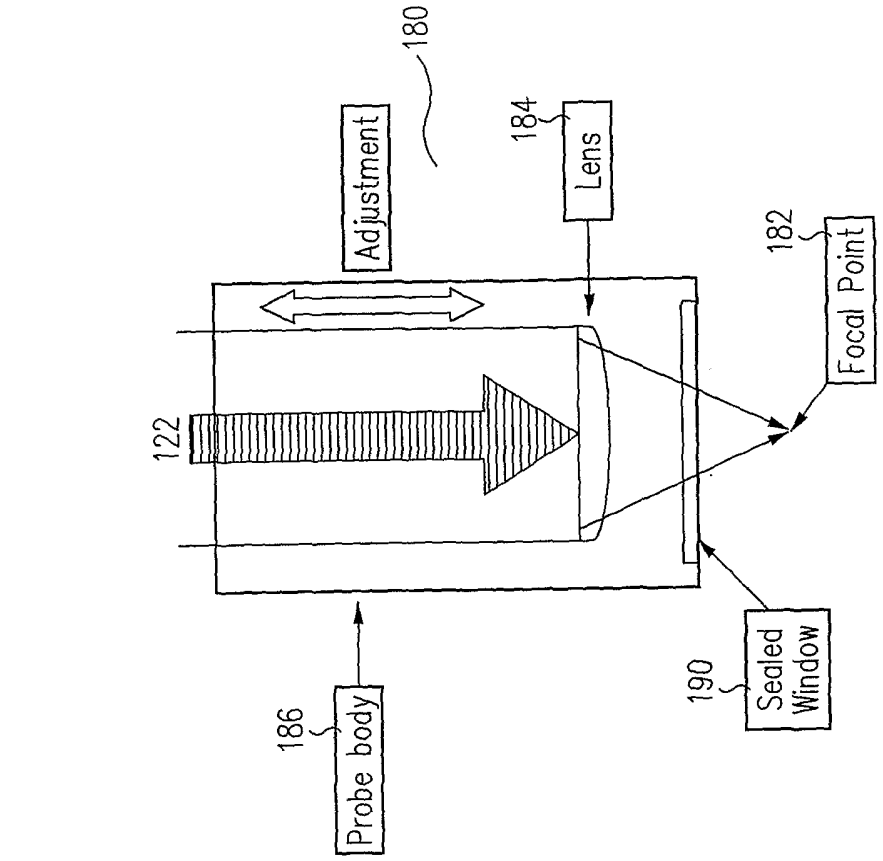
180
Adjustment
184
Lens
182
Focal Point
122
186
Probe body
190
Sealed Window

FIG. 7

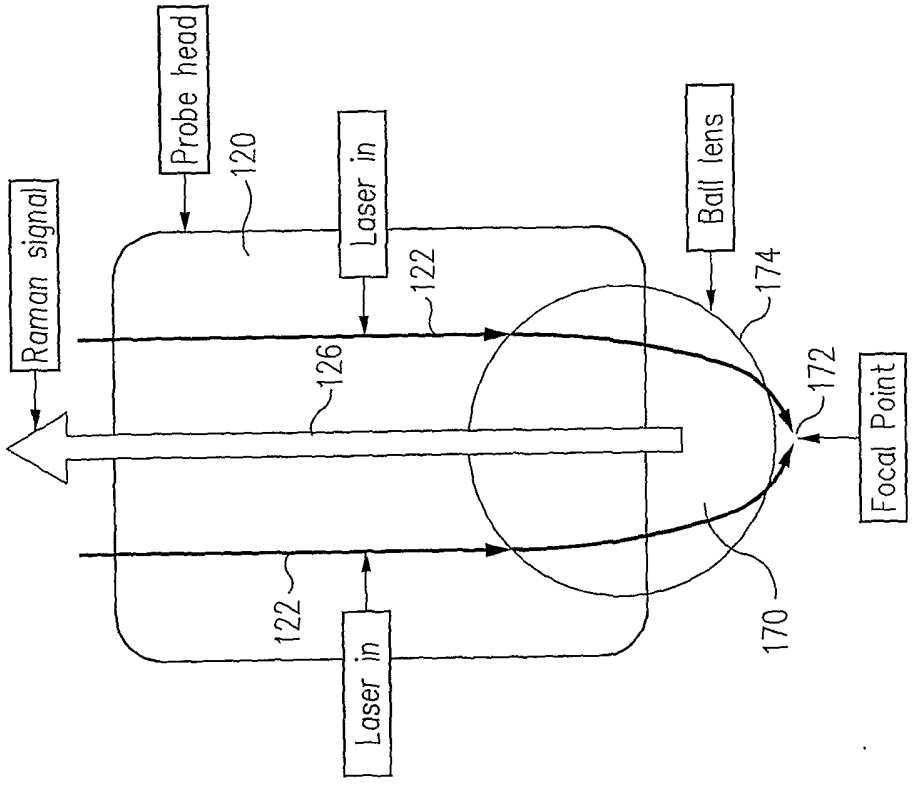
Probe head
120
Laser in
Ball lens
Raman signal
122
174
126
172
Focal Point
122
170
Laser in

FIG. 6

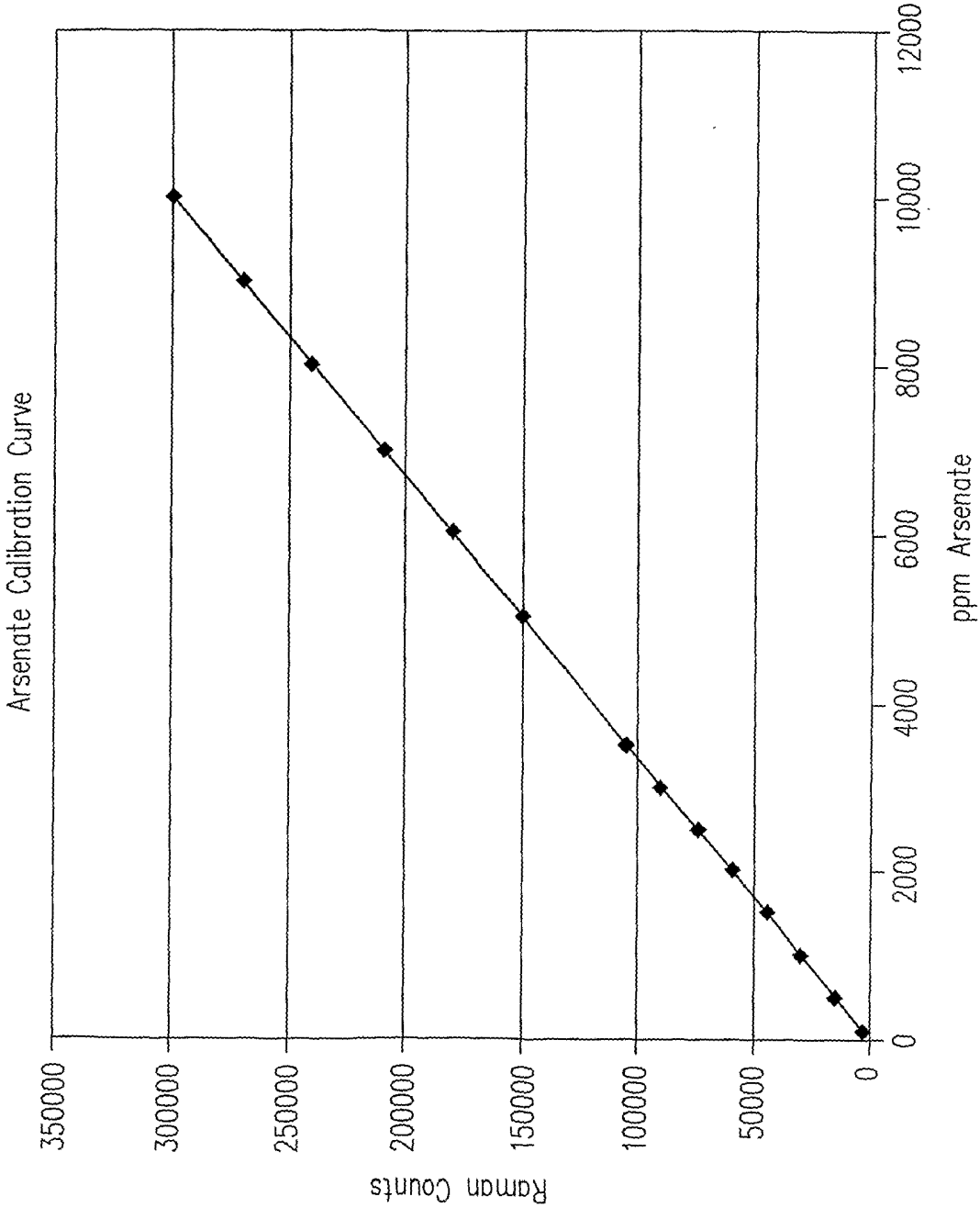
Arsenate Calibration Curve
Raman Counts
350000
300000
250000
200000
150000
100000
50000
0
0
2000
4000
6000
8000
10000
12000
ppm Arsenate

FIG. 8

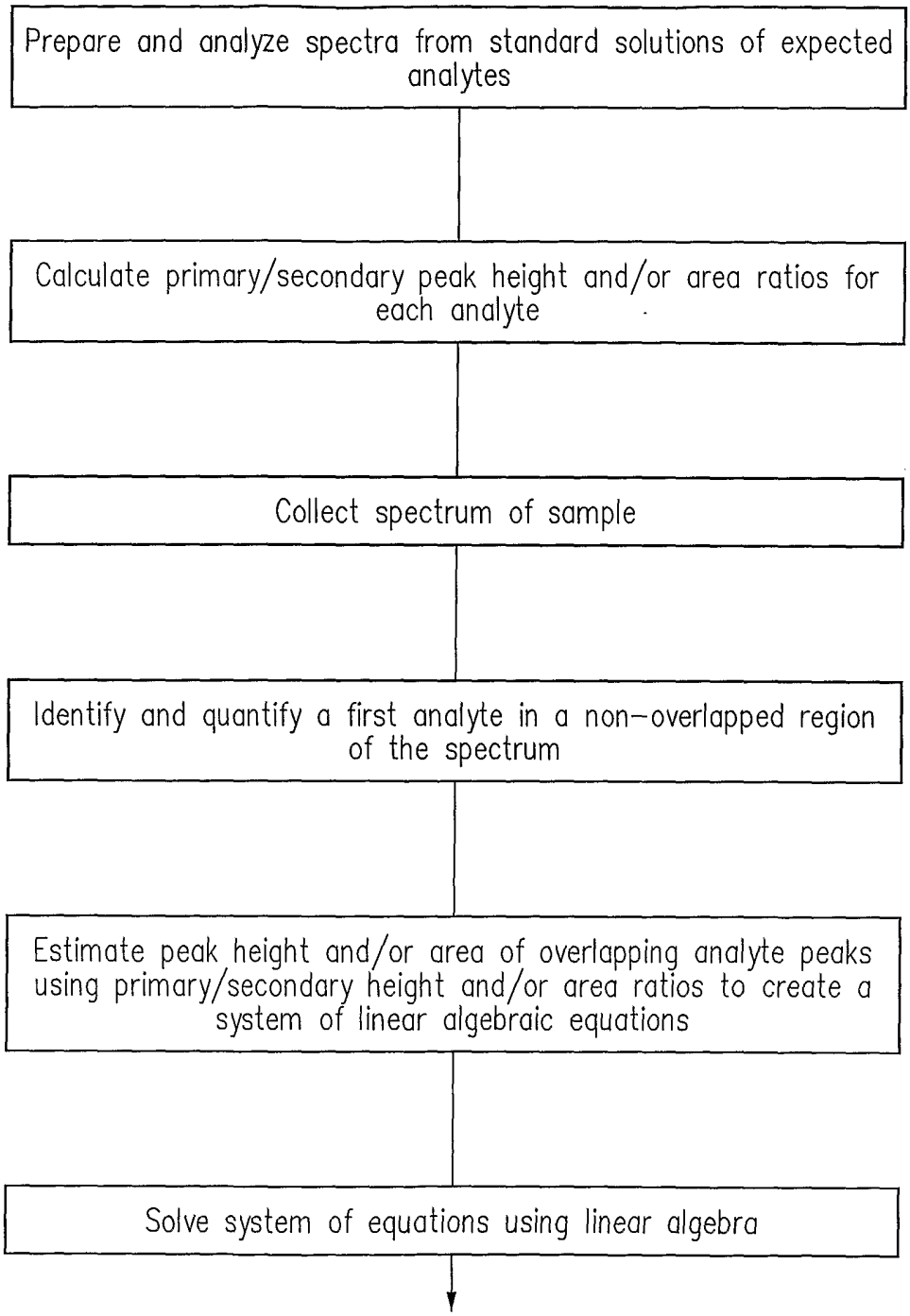
Prepare and analyze spectra from standard solutions of expected analytes
Calculate primary/secondary peak height and/or area ratios for each analyte
Collect spectrum of sample
Identify and quantify a first analyte in a non-overlapped region of the spectrum
Estimate peak height and/or area of overlapping analyte peaks using primary/secondary height and/or area ratios to create a system of linear algebraic equations
Solve system of equations using linear algebra

FIG. 9

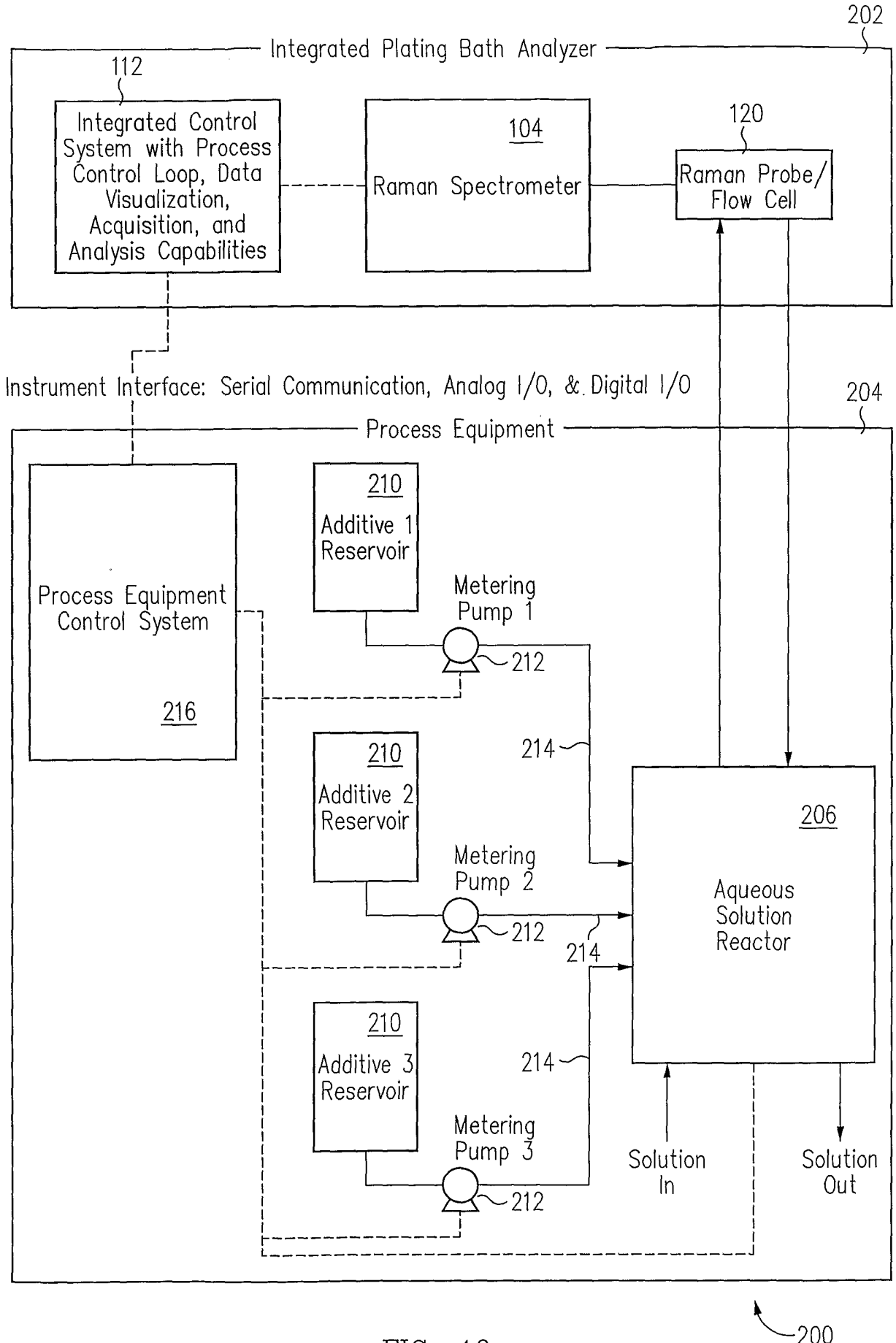
202
Integrated Plating Bath Analyzer
112
Integrated Control System with Process Control Loop, Data Visualization, Acquisition, and Analysis Capabilities
104
Raman Spectrometer
120
Raman Probe/ Flow Cell
Instrument Interface: Serial Communication, Analog I/O, & Digital I/O
204
Process Equipment
Process Equipment Control System
216
210
Additive 1 Reservoir
Metering Pump 1
212
214
210
Additive 2 Reservoir
Metering Pump 2
212
214
210
Additive 3 Reservoir
Metering Pump 3
212
206
Aqueous Solution Reactor
Solution In
Solution Out
200

FIG. 10

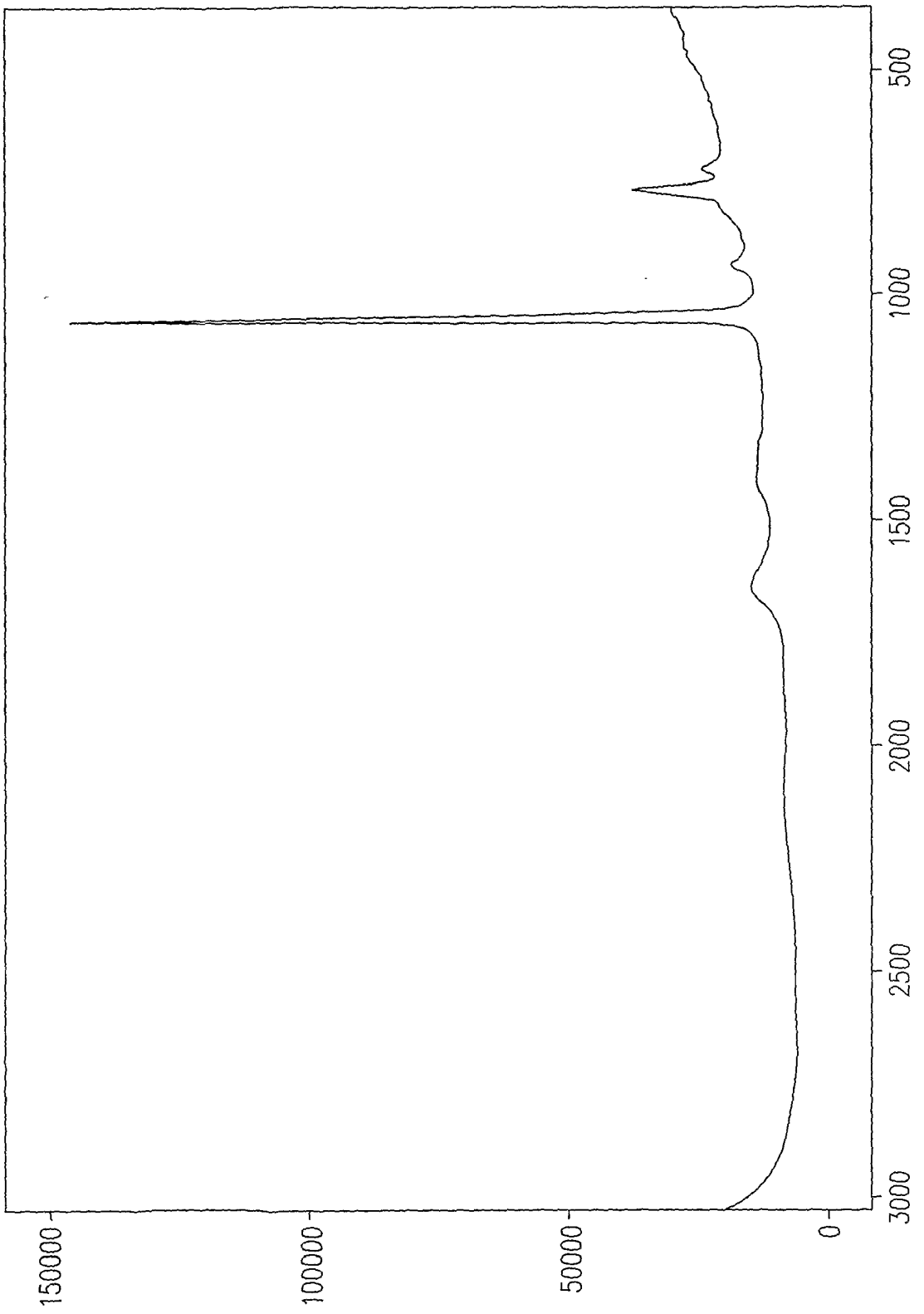

FIG. 11

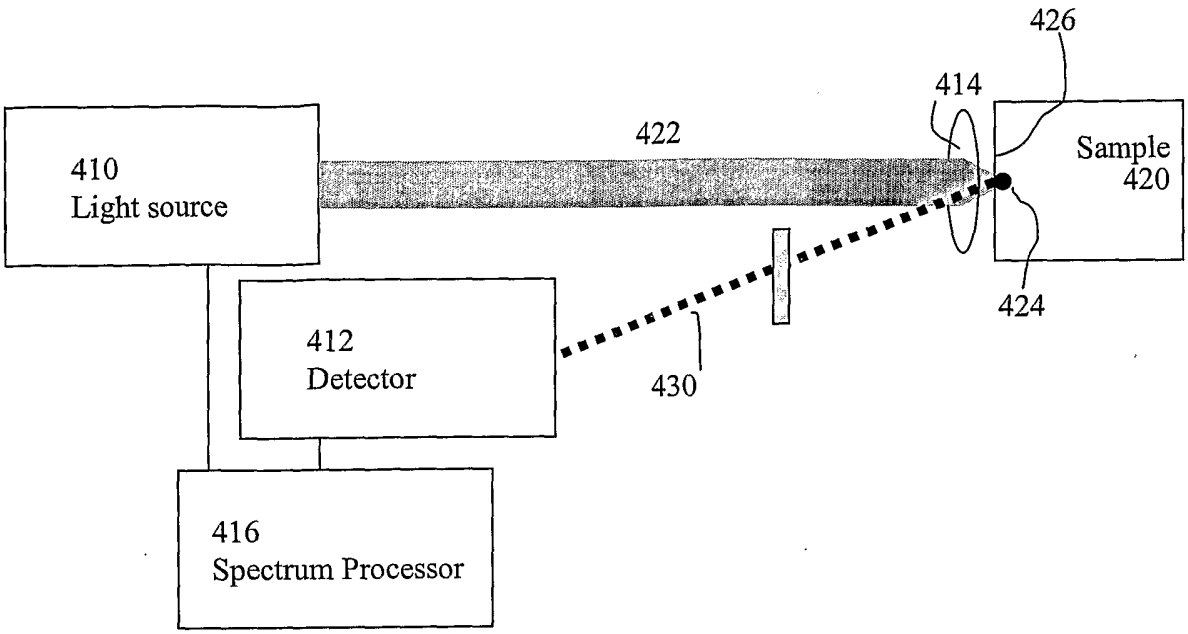
426
414
422
Sample
420
410
Light source
424
412
Detector
430
416
Spectrum Processor

Figure 12

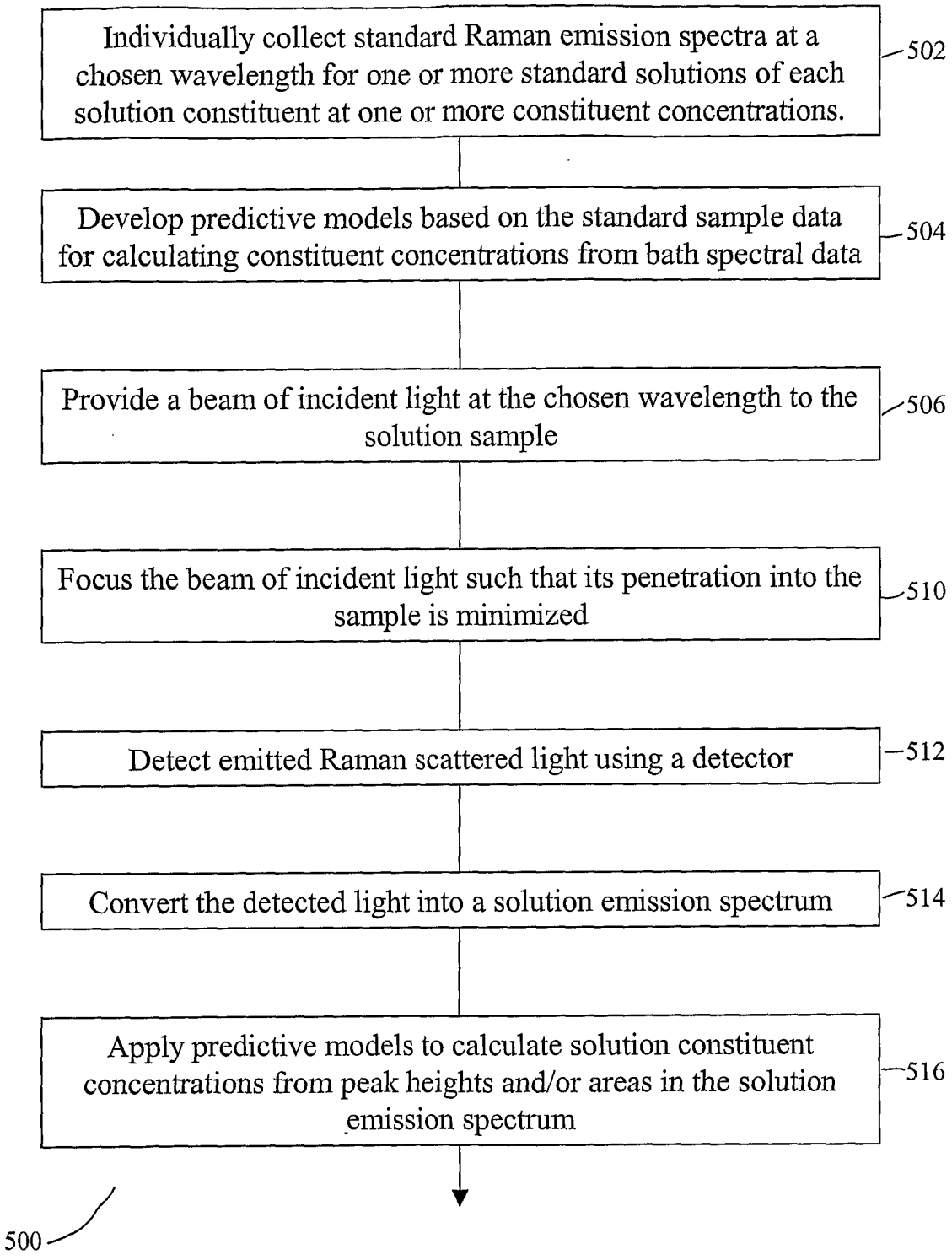
Individually collect standard Raman emission spectra at a chosen wavelength for one or more standard solutions of each solution constituent at one or more constituent concentrations.
502
Develop predictive models based on the standard sample data for calculating constituent concentrations from bath spectral data
504
Provide a beam of incident light at the chosen wavelength to the solution sample
506
Focus the beam of incident light such that its penetration into the sample is minimized
510
Detect emitted Raman scattered light using a detector
512
Convert the detected light into a solution emission spectrum
514
Apply predictive models to calculate solution constituent concentrations from peak heights and/or areas in the solution emission spectrum
516
500

Figure 13

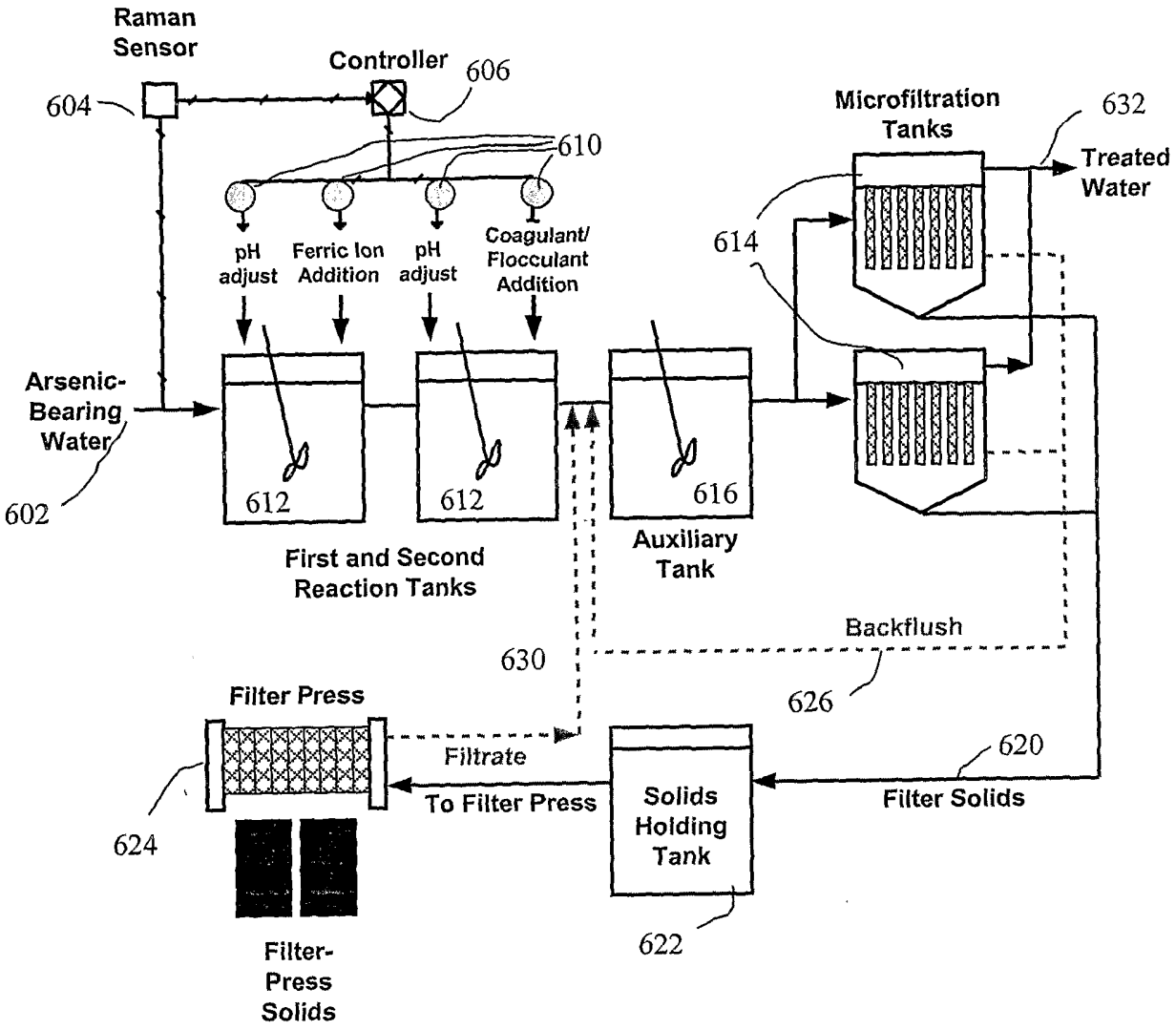
Raman Sensor
604
Controller
606
610
pH adjust
Ferric Ion Addition
pH adjust
Coagulant/ Flocculant Addition
Microfiltration Tanks
632
Treated Water
614
Arsenic-Bearing Water
602
612
612
616
First and Second Reaction Tanks
Auxiliary Tank
Backflush
630
626
Filter Press
Filtrate
To Filter Press
620
Filter Solids
Solids Holding Tank
622
624
Filter-Press Solids
600

Figure 14

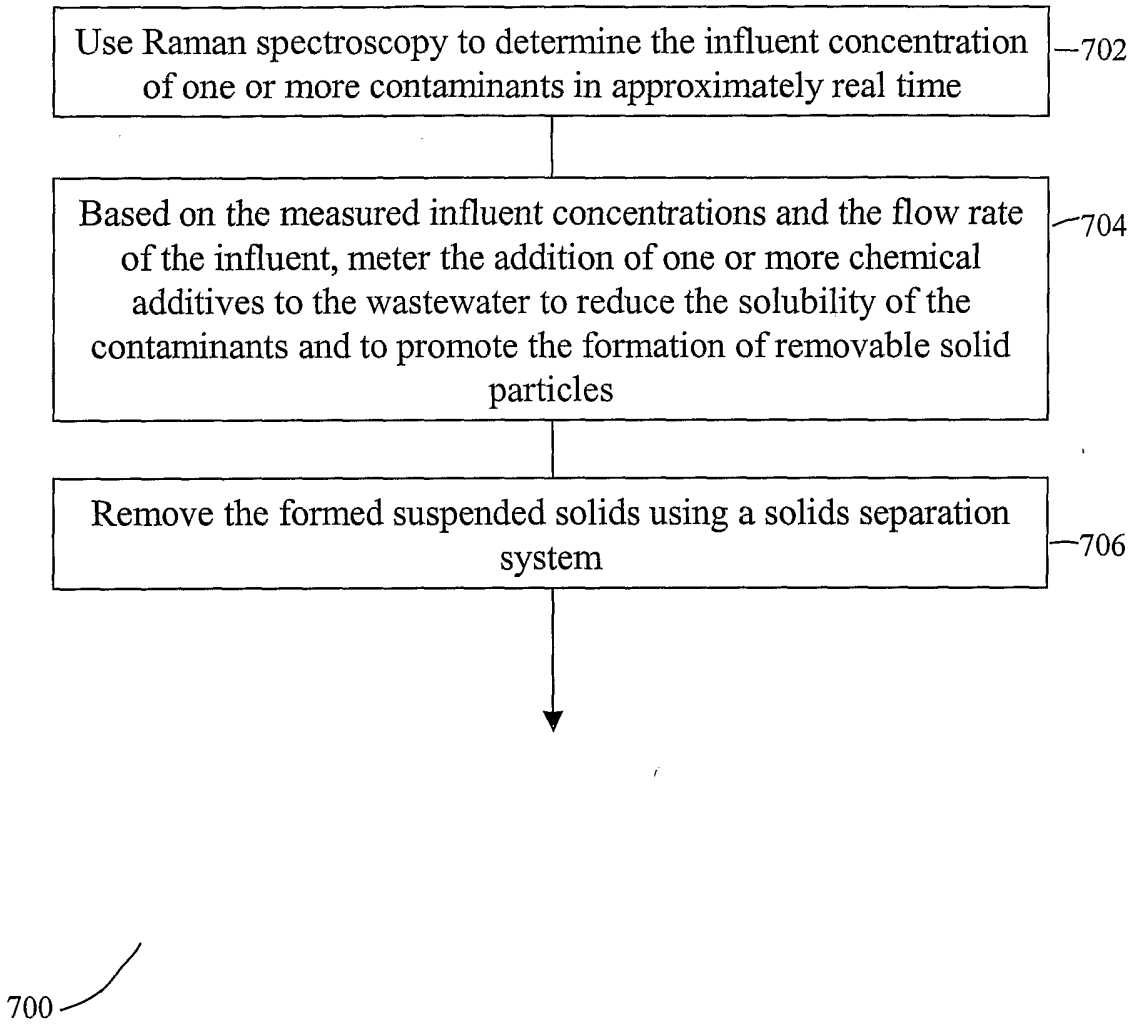
Use Raman spectroscopy to determine the influent concentration of one or more contaminants in approximately real time
702
Based on the measured influent concentrations and the flow rate of the influent, meter the addition of one or more chemical additives to the wastewater to reduce the solubility of the contaminants and to promote the formation of removable solid particles
704
Remove the formed suspended solids using a solids separation system
706
700

Figure 15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/01536

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01J 3/44; G01N 21/65
US CL : 356/301

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)
U.S. : 356/301

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,008,894 B1 (SCHMUCKER et al) 28 December 1999 (28.12.1999), see column 1, lines 35-37 and column 3, lines 36-51.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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 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
09 May 2003 (09.05.2003)

Date of mailing of the international search report
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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. (703)305-3230

Authorized officer
F. L. Evans

Telephone No. (703) 308-0956

Deborah P. Vega
Paralegal Specialist

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