EUROPEAN PATENT SPECIFICATION

(54) Regulating water treatment agent dosage based on operational system stresses
Regulierung der Wasserbehandlungsmittel dosierung, auf Basis von Betriebssystemspannungen
Régulation du dosage d’un agent de traitement de l’eau basée sur des tensions du système d’exploitation

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EP-A- 0 504 520
US-A- 4 783 314

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The present invention is in the technical field of regulating the in-system concentration of water treatment agents particularly the in-system concentration of water treatment agents in industrial water systems, such as cooling water systems, boiler water systems, water reclamation/purification systems, water systems of manufacturing processes and the like, by analysis of target specie(s) in the system, particularly scaling ions and contaminants, so as to increase the efficiency of the water treatment agents in which they are used.

The in-system concentration of water treatment agents in industrial water systems is conventionally controlled based on intermittent measurements of the concentration of the target specie(s) and/or the concentration of the water treatment agent(s) in the water of the system or unselective measurements (e.g., conductivity). The control goal of most water-treatment programs is to maintain a predetermined or optimum ratio of water treatment agent(s) to target specie(s) and/or system consumption for the water treatment agent(s) is regulated to attain or maintain this ratio or the target specie concentration is adjusted to meet specified values. For instance, if the concentration of hardness ions entering a boiler system increases, an increase in the in-system concentration of the water treatment agent(s) may be needed to maintain the water treatment agent(s) to target specie(s) ratio goal. The measurements of the concentration of the target specie(s) and/or the concentration of the water treatment agent(s) in the water of the system, and the responsive in-system concentration adjustments, are commonly based only on occasional grab samples, taken for instance once or twice per shift (a shift commonly encompassing about 8 to 12 hours of system operating time) or once every several days. Concentration determinations for water treatment agents and/or target species in industrial water systems have heretofore generally been based on classical (wet chemistry) analysis techniques, conductivity and/or hydraulic meter readings, for instance water flowmeter readings.

Classical analysis techniques for determining the concentration of a target specie and water treatment agents in a water system are usually somewhat cumbrous and/or protracted, and/or provide results that are merely estimates and/or variable (for instance, dependent upon a person’s laboratory technique). Long time delays typically exist between changes in system operation and a compensating change in treatment dosage. For example, phosphate concentrations are determined by a spectrophotometric (colorimetric) test. Concentrations of pyrophosphate and organic phosphorus compounds are determined using the same spectrophotometric test with a digestion (reversion) step. Titration methods are routinely employed to determine the concentration of hardness ions, such as calcium and magnesium, and the concentrations of carbonate and bicarbonate, in the water of the water system. Such analysis methods are susceptible to interferences (e.g., turbidity) and/or are subjective (visual observation of color change). These values, and often the ratio therebetween, are then used to manually set the in-system target concentration of the treatment chemicals, such as scale inhibitors and neutralizing amines.

The more accurate a conventional manual (grab sample) analysis technique, the more protracted that technique or its response time can be. Feedback information can at times even be days behind the sampling and hence of little value in providing data from which a dosage-regulation response can be determined. The water system consumption of a water treatment agent may well have changed during the elapsed interval between the taking of the sample and the analysis results.

Even when accurate indications of the mass or volume of a water treatment agent feed delivered to a system are available, and accurate water treatment agent residual concentrations are available, if the residual concentration determinations are based on grab or intermittent samples, any extrapolation therefrom to a value for the system demand and/or system consumption for the water treatment agent is based on fragmentary data and outdated information. A change in the system consumption may not be detected until it has had a significant impact on treatment agent consumption and system performance. When the detection of system consumption change is delayed, the responsive regulation of a treatment agent’s in-system concentration or response to system operation will invariably be late and system performance may suffer. When the responsive regulation of in-system concentration is late, underfeeding or overfeeding of the treatment agent routinely will occur to some extent between the time the system consumption of the water treatment agent has changed and the time the treatment agent in-system concentration and/or system operating parameter (e.g., alkalinity adjustment) is adjusted.

In an industrial water system plant the use of any estimated, variable, intermittent, fragmentary or historic data severely diminishes the sensitivity of any demand-responsive regulation of the water treatment agent in-system concentration and/or diminishes the ability to follow changes in the treatment-agent system demand or system consumption with appropriate compensations to the water treatment agent in-system concentration. Conventional procedures for regulating water treatment agent in-system concentration are further complicated by other imprecise evaluations of operating parameters. The rates at which the water treatment agent is being fed to and/or removed from the industrial water system and/or other operating parameters having an influence on the in-system concentration of the water treatment, may defy precise measurement unless inert tracers and selective analytical methods are used. The readings and/or settings on feed and blowdown equipment and/or lines are seldom
unquestionably reliable and often complicated by multiple sources of blowdown and makeup and changes in composition of these water samples. Fluctuations in the concentrations in the target species and the water treatment agent may stem from a variety of system conditions, such as dilution when other materials are charged to the system, concentration by evaporation or other means, unaccounted loss of fluid from the system and the like, some of which parameters may not be accurately known. Generally all sources of water intake and loss, and all sources of water treatment agent intake and loss, cannot be known precisely and continuously unless inert tracers and selective analytical methods are used.

[0008] US-A-5,132,096 discloses a method of monitoring a water treatment agent performance by the addition of a reagent dye and a transition metal tracer and the subsequent detection of three separate absorbance signals from the reagent dye, the first signal arising from the dye itself, the second from the dye after it reacts unselectively with any stress metals and the third from the dye after it reacts with the tracer.

[0009] A sensitive, selective and rapid demand-responsive control of water treatment agent in-system concentration would render most any industrial water system more efficient. Overfeeding of a water treatment agent is unnecessarily expensive, may at times diminish the recycling potential of waste water discharged from the system and may also at times impair system operation. Underfeeding of a water treatment agent almost inevitably impairs system operation, the imbalance between an underfed water treatment agent and the target species leading to higher levels of deleterious effect(s) from which relief is sought by the water treatment. In some water systems an imbalance between the in-system concentrations of water treatment agents and the system’s water conditions and/or target species can severely diminish the efficiency of the system. For instance the efficiency of a system's temperature conditioning performance, such as heat exchange and steam generation, may be reduced which in turn may diminish the performance of a process to which it is adjuvant.

[0010] A sensitive, selective and rapid demand-responsive regulation of water treatment agent in-system concentration that permits the in-system concentration of water treatment agent(s) to be adjusted in response to real-time system conditions is not provided by the conventional methods.

[0011] It is an object of the present invention to provide a method or process for monitoring the concentration of a target specie(s) in a water system, thereby permitting a responsive regulation of the in-system concentration of one or more water treatment agents. It is an object of the present invention to provide such a method or process that can be conducted on-site in a very short time period. It is an object of the present invention to provide such a method or process further including the regulation of the in-system concentration of at least one water treatment agent in an industrial water system in response thereto. It is an object of the present invention to provide such a method or process that can be conducted on-site in a very short time period, preferably on a continuous basis. These and other objects of the present invention are discussed in detail below.

[0012] The present invention provides a demand-responsive management (regulation or control) of water treatment agent in-system concentration(s) by regulating water treatment agent feed, which includes the monitoring of the value of a target-specie indicator, by fluorescence analysis. The present invention provides a process for the regulation of at least one water treatment agent in-system concentration based on the value of at least one target specie for that treatment agent comprising monitoring a fluorescent characteristic of at least one target-specie indicator that is a combination of an incipient reagent and a target specie to determine the quantity of target species present in the system, monitoring an inert tracer which has been added to the system in a known proportion to the water-treatment agent and adjusting the rate of addition of the water-treatment agent to bring the water-treatment agent presence to an appropriate amount determined from the quantity of target-species present in the system. The target specie for instance may be a chemical specie, scalants, corrosion products, corrosive agents, foulants or a water condition, such as pH, that is targeted by the treatment agent, that is, indicia of system demand and/or system consumption for a water treatment agent or scaling/deposit forming, fouling, or corrosive conditions. In more detail, the target specie may be a chemical specie that is produced by another chemical specie or by a water condition, for instance corrosion products. The target specie may be a system-demanding and/or system consumption condition, for instance system pH. The target specie may be other types of indicia of system consumption for a water treatment agent that in combination with a suitable reagent forms, a target-specie indicator having a fluorescent characteristic which can be correlated to the value of the target specie. That fluorescent characteristic is monitored, preferably on a continuous basis, by at least one fluorescence analysis method and the results of such monitoring preferably are correlated to a regulation of the in-system concentration of such treatment agent.

[0013] In further preferred embodiments, the effects of target-specie responsive adjustments to the treatment agent's in-system concentration are tracked by a continuous monitoring of the target-specie indicator, in combination with a continuous monitoring of an inert tracer, which is described in detail below.

[0014] The system consumption for any specie (subject specie) added to a system in known proportion with an associated inert tracer can be determined from the following Formula.
wherein $C_1$ is the theoretical subject specie concentration determined by correlation to the concentration of an associated inert tracer (added in known proportion with the subject specie), $C_2$ is the actual concentration of the subject specie in the system, and $SC$ is the system consumption upon the subject specie or, in other words, selective impact (s) upon in-system concentration of the subject specie that does not effect the inert tracer's in-system concentration.

**0015** A sensitive and rapid target-specie responsive control of water treatment agent in-system concentration is provided by the on-line continuous monitoring of the value of a target-specie indicator in the water system. The on-line continuous monitoring of the value of a target-specie indicator, for instance a target specie(s) concentration, provides precise and accurate results rapidly and permits the in-system concentration of the water treatment agent(s) to be adjusted in response thereto. The in-system concentration of a water treatment agent or a plurality of water treatment agents can be adjusted by regulation of the rate of feed or delivery of the agent(s) to the system, by regulation of the ratio between rate of delivery versus rate of removal with blowdown and/or the regulation of any means influencing the in-system concentration the water treatment agents.

**0016** The present invention includes the monitoring of the value of a target specie in the water of an industrial water system. By the terminology “monitoring of a target specie” is meant herein, unless expressly indicated otherwise, the determination of at least one fluorescence characteristic of a target-specie indicator in a sample from a water system and the correlation of that characteristic to a value designating the proportion or degree of the target specie in the water system, such as the concentration of a scaling ion or the pH value of the water. That value can in turn be correlated to specified dosage or system consumption for a water treatment agent. By the terminology “regulating” is meant herein, unless expressly indicated otherwise, the setting and/or the adjustment of a system control means, for instance the feed rate of the water treatment agent to a water system, which determines at least in part the in-system concentration of the treatment agent. Such monitoring and/or regulating can be conducted on a singular, intermittent, semi-continuous or continuous basis, and preferably at least the monitoring, and more preferably both the monitoring and regulating is/are conducted on-site (at the site of the industrial water system plant) on a substantially continuous basis.

**0017** By the terminology “in-system concentration” is meant herein, unless expressly indicated otherwise, the concentration of the subject specie within the water phase of the subject water system, generally as a solute. An in-system concentration of a water treatment agent or target specie, for instance, does not include any amounts thereof that are contained in scale deposits or other solid phase material even if such materials are within the confines of the water system.

**0018** The present invention includes the regulating of the in-system concentration of at least one water treatment agent based on the system consumption for the treatment agent by employing the information provided by the monitoring of the target-specie indicator. The water treatment agent in-system concentration is regulated by the process of the present invention based on the present value of a target specie within the industrial water system, and not on estimated, fragmentary or historic data. Since the present invention directly monitors a target-specie indicator, which is correlated to a target specie, it can be considered a method that tracks, and/or obviates the need to quantify, the multitude of influences on the water treatment agent system demand and/or system consumption, such as the introduction of the target specie to the system with makeup water or other added materials, mixing of multiple streams, contamination, leaks between systems, leaks from the system, other dilutions and concentrations, releases of target specie(s) into the water from known and unknown sources, losses of target specie(s) from the water by known and unknown mechanisms and the like.

**0019** The value of a target-specie might alter by system variations independent of treatment agent in-system concentration. In other words, a given treatment agent in-system concentration may be wholly meeting the demands of a target-specie for a time period, and then the value of that target-specie could rapidly change in response to other system variables. An increase in the target-specie in such instance is not an indication that the initial treatment agent in-system concentration was inadequate, and instead is a signal that the water system now requires a higher treatment agent in-system concentration. A decrease in the target-specie similarly could be a signal that continuing the initial treatment agent in-system concentration would be an overfeeding, or instead be a signal that the treatment agent in-system concentration is too low, as described below.

**0020** Variations in the system consumption can occur by virtue of numerous operating conditions. The rate at which the target specie is entering and/or leaving and/or being generated in an industrial water system cannot wholly be predicted or controlled. An industrial water system commonly has unknown sources of material intake and/or losses and/or chemical conversions. The optimal monitoring of such target specie(s) is to quantify their concentration or degree in a water system, rather than attempting to estimate its change in concentration or degree based on other parameters. The method of the present invention can determine the concentration of one or more target specie(s), or other target specie value, from the target-specie indicator value that can be correlated thereto, using one or more fluorescence analysis techniques.
The present invention provides target-specie responsive treatment agent in-system concentration adjustments that are not contingent on water treatment agent residual level determinations, although also performing the analyses necessary for water treatment agent residual level determinations is not excluded.

The water treatment agent in-system concentration is regulated so as to be responsive to the fluorescent characteristic of the target-specie indicator at the sampling site(s), which in turn is correlated to the target specie value, which is proportional or inversely proportional to system demand and/or system consumption for that water treatment agent. A target specie is selected so that its value is proportional/inversely proportional to, or convertible in some respect to, system consumption for (or required dosage of) a water treatment agent. For the purposes of the present invention, a suitable target specie(s), or other target specie for a given water treatment agent, is one that can be correlated to the system consumption for (or required dosage of) that treatment agent. For example, when the treatment agent is an antiscalant, for instance a dispersant, a specie such as calcium and/or iron would be an appropriate target specie. The calcium and/or iron concentrations in a system are correlated to the scaling tendencies or loss of treatment agent within the water of the system, and either calcium or iron concentrations, or both in combination, are useful corollaries of system consumption for antiscalant treatment agent.

The nonfluorescent inorganic ions in this example are the target species, while the effective or final fluorescence reagent is the target-specie indicator, generated by the combination of a target specie with an incipient or first reagent.

The incipient reagent may or may not itself be fluorescent. The target-specie indicator may or may not itself be fluorescent. If both the incipient reagent and target-specie indicator are fluorescent, then the fluorescence analysis technique, including at times the selection of excitation and/or emission wavelengths, is selected to avoid, or at least minimize, interference between any residual incipient reagent and the target-specie indicator. Examples of various combinations of target specie and incipient reagents, and selections of suitable fluorescence analysis techniques for the target-specie indicators formed, are described in more detail below.

Some water systems employ a plurality of water treatment agents for which the monitoring of separate target-specie and/or water consumption for treatment agents. In either instance, such as the refining of aluminate, and the like.

Industrial water systems often are fluid systems that contain at least about 60 weight percent water, the remainder being solids (suspended and/or solutes) are being separated from liquids (for instance the water system of membrane-separation processes), water systems of manufacturing processes, particularly chemical industry manufacturing processes, including without limitation the processes of the pulping and papermaking industries, the steel industry, the metal working industries, the food processing industries, the mining industries, the automotive industry, the textile industry, utilities, chemical processing industries, manufacturing industries, spray paint industries, refining industries such as the refining of aluminate, and the like.

Industrial water systems often are fluid systems that contain at least about 60 weight percent water, the remainder being solids (suspended and/or dissolved) and/or nonaqueous fluids, and which commonly are flowing rather than static. In preferred embodiment the industrial water system of the present invention is an industrial system that contains at least about 65 or 70 weight percent water, the remainder being solids (suspended and/or dissolved) and/or nonaqueous fluids, and preferably which is flowing rather than static.

Some water systems employ a plurality of water treatment agents for which the monitoring of separate target-specie indicators would improve system efficiency. The values of separate target species for the plurality of water treatment agents may be determined by monitoring a plurality of target-specie indicators, each of which may be related to different water treatment agents. In some instances, the system demand and/or system consumption for a plurality of water treatment agents may be related to a single target specie, and the monitoring of a single target-specie indicator may be related to the in-system concentration adjustments for all of the treatment agents. In either instance, such systems.
plurality of water treatment agents may be fed to the water system at the same point or at sites along separate streams.

- A single water treatment agent may be subject to a plurality conditions accounting for system consumption. In some systems, only one of a plurality of target species for a given water treatment agent is crucial, and only the 
- crucial target species needs to be monitored. In other systems, a plurality of target species for a given water treatment agent are significant and the determination of system consumption conditions for each target species would improve system efficiency. Moreover, a plurality of system consumption conditions for a single water treatment agent may be determined by quantifying a plurality of target species, each of which may be related to different system consumption conditions for the water treatment agent.

- Some water systems may have a plurality of zones in each of which a single water treatment agent may encounter distinct system consumption conditions of different severities. Such zones may be disposed sequentially or in parallel, or the water system may have a plurality of streams that each feeds a portion of the water treatment agent to a zone or carries a portion of the water treatment agent residual away from the zone. The present invention can be employed in any of these situations or combinations of situations, provided that the target-specie indicator(s) is monitored across the water system zone for which a separate treatment-agent consumption is to be determined without any intervening water treatment agent-consumption zones.

- The solids and/or solutes within the waters of these water systems may be substantially or mainly organic, or substantially or mainly inorganic, or a mixture of both organic and inorganic materials. The process of the present invention would generally not be applicable to an industrial water system wherein the water system has a high solids loading, for instance a solids loading in excess of 40%.

- A water system may contain dissolved solids or dissolved gases, or it may be a slurry (dilute or concentrated), or it may be a slurry containing dissolved solids and/or gases. A water system may also contain liquids other than water, which liquids may be miscible or immiscible with water.

- An important advantage of the present invention is that by monitoring a target-specie indicator, a given embodiment of the invention may be used on a variety of water systems, in a variety of industries, which employ different water treatment agents. Water treatment agents for controlling scaling, corrosion and the like often differ from industry to industry. The embodiments of present invention, not being tied to the treatment agent itself, may be used in dissimilar industries when the target species are the same. There is a greater distribution of the same target specie among the various industries than the employment of the same water treatment agents.

- To quantify the fluorescent characteristic of a target-specie indicator, a variety of fluorescence analysis methods are available for use singly or in combination. Such fluorescence analysis techniques include, without limitation, techniques that measure and/or indicate:

  1. the appearance or disappearance of fluorescence;
  2. a shift in excitation and/or emission wavelengths of fluorescence;
  3. a fluorescence quenching (by a specific substance) or elimination of quenching;
  4. fluorescence changes based on specific light absorbance changes (increase or decrease);
  5. a well-defined temperature-dependency of fluorescence;
  6. a well-defined pH-dependency or other water condition dependency of fluorescence; and
  7. the exploitation of a temperature-dependency and/or pH-dependency of fluorescence to see or enhance the effects of techniques 1 to 4.

- In general, the concentration of a target-specie indicator or tracer can be determined from a comparison of a sample's emission intensity to a calibration curve of the given target-specie indicator's or tracer's concentration versus emission, for the same set of excitation wavelength/emission wavelengths. Such a concentration-by-comparison method by which the sensed emissions are converted to a concentration equivalent preferably is employed to determine concentrations of a target-specie indicator or tracer that are within the concentration range over which a linear emission response is observed, and this concentration range is referred to herein as the "linear-emission-response concentration range". The linear-emission-response concentration range is to some extent dependent upon the specific target-specie indicator or tracer and the excitation wavelength/emission wavelength set employed. At target-specie indicator or tracer concentrations higher than a given fluorescent target-specie indicator's or tracer's linear-emission-response concentration range, there is a negative deviation from ideal (linear) behavior, the degree of emission for a given concentration being less than predicted by a linear extrapolation. In such instances, the sample can be diluted by known factors until the concentration of the fluorescent target-specie indicator or tracer therein falls within the linear-emission-response concentration range. Two other correction techniques are available when the concentration is higher than the linear-emission-response concentration range. Since the linear-emission-response concentration range is to some extent dependent upon the excitation wavelength/emission wavelength set employed, an alternate excitation wavelength/emission wavelength set could be used. The use of sample cells with shorter pathlengths for the excitation/emission light will also correct or alleviate the problem. If the fluorescent target-specie indicator or tracer is present in the sample...
at only exceptionally low concentrations, there are techniques for concentrating the target-specie indicator or tracer by known factors until its concentration falls within the linear-emission-response concentration range or is otherwise more readily measured, for instance by liquid-liquid extraction. Nonetheless, preferably a calibration curve over the linear-emission-response concentration range would be prepared or obtained before employing a given target-specie indicator or tracer.

[0038] A determination of the concentration of a target-specie indicator or tracer in a system can be made when the concentration of the target-specie indicator or tracer in the water system is as low as several parts per million (ppm), or parts per billion (ppb), and at times as low as parts per trillion (ppt). The capability of measuring very low levels is an immense advantage. Such fluorescence analyses (the measurements of the light emitted in response to the light transmitted to the water system sample) can be made on-site, preferably on an almost instant and continuous basis, with simple portable equipment.

[0039] As mentioned above, at times it may be desired to monitor a plurality of fluorescent target-specie indicators or tracers. For instance, it may be desired to monitor more than one target-specie indicator and tracer for each of one or more water treatment agents, or distinct target-specie indicators for more than one water treatment agent. In some instances it may be desired to use a plurality of target-specie indicators and/or tracers solely for a single water treatment agent, for instance to confirm that a target-specie indicator or tracer is not undergoing any selective loss. Such separate and distinct target-specie indicators or tracers can all be detected and quantified in a single water system sample despite all being fluorescent substances if their respective wavelengths of emission do not interfere with one another. Thus concurrent analyses for multiple target-specie indicators or tracers are possible by selection of target-specie indicators or tracers having appropriate spectral characteristics. Preferably separate wavelengths of radiation should be used to excite each of the target-specie indicators or tracers, and their fluorescent emissions should be observed and measured at separate emission wavelengths. A separate concentration calibration curve may be prepared or obtained for each target-specie indicator or tracer.

[0040] A dual-monochromator spectrofluorometer can be used for a fluorometric analysis conducted on an intermittent basis and for on-line and/or continuous fluorescence regulating. Portable or compact fluorometers equipped with appropriate excitation and emission filters and quartz flow through cells are commercially available, for instance from Turner Designs (Sunnyvale, California).

[0041] In general, for most fluorescence emission spectroscopy methods having a reasonable degree of practicality, it is preferable to perform the analysis without isolating in any manner the target-specie indicator or tracer. Thus there may be some degree of background fluorescence in the water system on which the fluorescence analysis is conducted, which background fluorescence may come from chemical compounds in the water system that are unrelated to the present invention. In instances where the background fluorescence is low, the relative intensities (measured against a standard fluorescent compound at a standard concentration and assigned a relative intensity, for instance a relative intensity of 100) of the fluorescence of the target-specie indicator or tracer versus the background can be very high, for instance a ratio of 100/10 or 100/2 when certain combinations of excitation and emission wavelengths are employed even at low target-specie indicator or tracer concentrations, and such ratios would be representative of relative performance (under like conditions) of respectively 10 and 50. In preferred embodiment, the excitation/emission wavelengths and/or the target-specie indicator or tracer are selected to provide a relative fluorescence of at least about 5 or 10 for the given background fluorescence anticipated.

[0042] For instance, for most water system backgrounds, a compound that has a relative performance of at least about 5 at a reasonable concentration is very suitable as a target-specie indicator or tracer. When there is or may be a specific chemical specie of reasonably high fluorescence in the background, the target-specie indicator or tracer and/or the excitation and/or emission wavelengths often can be selected to nullify or at least minimize any interference of the tracer measurement(s) caused by the presence of such specie.

[0043] One method for the continuous on-stream monitoring of chemicals by fluorescence emission spectroscopy and other analysis methods is described in U.S. Patent No. 4,992,380.

[0044] The combination of high-pressure liquid chromatography ("HPLC") and fluorescence analyses of target-specie indicators or tracers is a powerful tool for the present invention, particularly when very low levels of a target-specie indicator or tracer are used or the background fluorescence encountered would otherwise interfere with the efficacy of the fluorescence analysis. The HPLC-fluorescence analysis method allows a target-specie indicator or tracer to be separated from the fluid matrix and then a target-specie indicator or tracer concentration can be measured. The combination of HPLC-fluorescence analysis is particularly effective for measuring minute levels of target-specie indicator or tracer in highly contaminated fluids.

[0045] When the target-specie indicator is nonfluorescent and the incipient reagent is fluorescent, a fluorescence analysis technique, such as those described above, will be focused on the fluorescence of the incipient reagent. The measure of the target specie will be the loss of the incipient reagent, as it is consumed in the formation of the target-specie indicator, as manifested by the change of its fluorescence intensity and/or excitation/emission wavelength characteristics. Similarly, if both the target-specie indicator and the incipient reagent are fluorescent, but have different
fluorescent characteristics, for instance different wavelengths of maximum emission, the fluorescence analysis technique might focus on the loss of light emitted at the incipient reagent's wavelength of maximum emission, or instead on the increase of light emitted at the target-specie indicator's wavelength of maximum emission, as a function of the formation of the target-specie indicator from the interaction between the incipient reagent and target specie.

[0046] An ion selective electrode may be used to determine the concentration of an inert chemical tracer through the direct potentiometric measurement of specific ionic tracers in aqueous systems.


[0048] In a broad embodiment the present invention does not exclude the use of other analysis methods suitable therefor.

[0049] In preferred embodiments, the chemical compound(s) selected as the target-specie indicator or tracer should be soluble or dispersible in the water sample or system in which it is formed or to which it is added and should be either stable in the environment thereof for the useful life expected of the target-specie indicator or tracer, or its loss from the water system due to degradation, deposition, complexation, or other phenomena should be predictable and compensative, particularly since it is desired not merely to detect the presence of some amount of the target-specie indicator or tracer, but also to determine the concentration of both so as to correlate such values to a system demand and/or system consumption for the target specie and regulate water treatment agent in-system concentration based thereon. In preferred embodiment, the combination of the chemical compound(s) selected as the target-specie indicator or tracer and the analytical technique selected for determining the presence of such target-specie indicator or tracer, should permit such determination without isolation of the target-specie indicator or tracer, and more preferably should permit such determination on a substantially continuous and/or on-line basis.

[0050] Chemical species such as sulfide, calcium, iron, (bi)carbonate, manganese, alkalinity, phosphate, silicates, sulfate, fluoride, magnesium and other scaling and/or deposit forming ions, all of these ions may be a target specie. Their concentration in an industrial water system can serve as a measure of system consumption for an antiscalant or other water treatment agent employed to combat deposition formation. Their selective loss from a water system would generally be a sign of scale deposit formation. These ions possess no fluorescence characteristics. Nonetheless all are susceptible to in-system concentration quantification by fluorescence analysis by reaction/interaction with an incipient reagent to form a target-specie indicator. The value to be correlated with target specie system demand routinely would be the in-system concentration of at least one of such ions or a value equivalent and/or proportional to such concentration. The present invention is particularly advantageous when the target specie is one or more scaling and deposit forming ions. The present advantages arise not only from the versatility of the invention in providing both treatment-agent and target-specie system consumption information, but also from the gap between the information here provided and that provided by conventional methods.

[0051] The incipient reagent of the invention may itself be fluorescent, and may be an adduct or a complex or other interaction or reaction product formed between a plurality of target species, forming a target-specie indicator. The interaction between the target specie and the incipient reagent may increase, decrease or alter the fluorescence characteristics of the incipient reagent. The measurement of the fluorescence of the target-specie indicator formed provides a value that can be correlated to the concentration of the target specie in the water system.

[0052] The medium for the formation of the target-specie indicator and/or the fluorescence analysis of the target-specie indicator might be a substantially aqueous medium, a mixed aqueous/nonaqueous medium or substantially nonaqueous medium, although the use of an aqueous medium for the analysis is most often preferred for the present invention if an aqueous medium will suffice. Suitable techniques for the conversion of a water system sample to other than a substantially aqueous sample are known in the chemical analytical field and include conventional techniques such as liquid/liquid extraction, nonaqueous solvent addition, adsorption onto solids, and others.

[0053] The medium for the formation of the target-specie indicator and/or the fluorescence analysis of the target-specie indicator might contain one or more chemical species that enhance or promote the formation of the target-specie indicator and/or the fluorescence analysis of the target-specie indicator.

[0054] Some of the fluorescence analysis techniques utilize responses to pH, temperature or other conditions of the medium in which the target-specie indicator is undergoing fluorescence analysis. For instance, a given fluorescence technique measures an alteration in the fluorescence of a sample upon the formation of a given target-specie indicator. The fluorescence alteration may be observed at a particular pH or temperature to which the target-specie indicator medium would be adjusted. The fluorescence alteration might be the appearance or disappearance of fluorescence at a given pH or temperature, a shift in excitation and/or emission wavelengths of fluorescence at a given pH or temperature, a quenching of fluorescence at a given pH or temperature range or light-absorbance dependent changes of fluorescence at a given pH or temperature range.

[0055] The addition of an incipient reagent to the water system itself is generally impractical and unnecessary. A side-stream water sample is taken from the water system routinely, and thus the amount of incipient reagent used is minimized. Seldom would it be desirable to contaminate the entirety of a water system with a substance that is normally
foreign thereto. The present invention does not, however, exclude the use of an incipient reagent, or a precursor thereto, present in the water system itself, particularly when such approach is practical and/or necessary.

[0056] Techniques from various literature sources that can be adapted for the present purposes of formation of the target-specie indicator and/or the fluorescence analysis of the target-specie indicator, when the target specie is a chemical target-specie, are set forth below as exemplific and are not intended as limiting.

[0057] The sulfide anion (S⁻²) is susceptible to quantification by fluorescence analysis and/or fluorometric flow-injection techniques, for instance as described in "Trace Determination of Aqueous Sulfite, Sulfide and Methanethiol by Fluorometric Flow Injection Analysis", P. K. Dasgupta and H. C. Yang, Anal. Chem. 1986, 58(13), p. 2839-2844. The fluorescence analysis is based on the reaction of sulfide with an organic incipient reagent, such as N-acridinylmaleimide, in a water/DMF medium to form a fluorescent product, which fluorescent product has fluorescence characteristics distinguishable from similar reaction products of such organic specie with other sulfur anions, such as the sulfite and methanethiol.

[0058] A fluorometer can be used for fluorescence analysis of the aluminum cation in water systems such as cooling water systems.

[0059] A fluorometric method for determining microamounts of magnesium cation is based on its reaction with 2-quinizarin sulfonate incipient reagent to form 1:1 and 1:2 metal-to-ligand complexes which, in an ethanol/water medium at a pH of about 10, can be quantified fluorometrically using for instance excitation at 545 nm and measuring the emission intensity at 610 nm, as described in "Determination of Magnesium by Spectrofluorometry and Synchronous Scanning First and Second Derivative Spectro-Fluorometry with 2-Quinizarin Sulfonate", F. Salinas, A. M. De la Pena and F. M. De la Pena, Mikrochim. Acta, 1986, 3(5-6), p. 361-368. Synchronous scanned first and second derivative fluorometry can be used to further increase the sensitivity of the method for low levels of magnesium. Linearity between the fluorescence intensity versus concentration was seen for solutions strengths of from 20 to 200 nanograms ("ng") Mg⁺/ml (about 20 to 200 ppb), and for solutions strengths of from 10 to 100 ng Mg⁺/ml (about 10 to 100 ppb) when the first and second derivative approach was used.

[0060] For the fluorescence analysis of calcium cations, a calcein disodium salt or fluorescein can be used as complexing reagents, for instance as described in "Use of the Indicator Calcein Disodium Salt Instead of Fluorescein in Complexometric Titration of Calcium Oxide", N. A. Koxchheeva and L A. Fartushnaya, Zavod. Lab., 1986, 52(6), p. 90-91. A fluorescent solution can be prepared by combining a dilute HCl solution of calcein disodium salt with 0.2% thymolphthalein in 5% KOH and used for the determination of calcium concentrations.

[0061] Another incipient reagent for the fluorescent determination of calcium and other divalent metal ion concentrations is (N-(4-nitrobenzofurazan)monoaza-18-crown-6), a crown ether based fluorophoric reagent, which for example is described in "A New Metal Sensitive Fluorescence Reagent", K. W. Street, Jr. and S. A. Krause, Anal. Lett., 1986, 19(7-8), p. 735-745. Metal cation complexes with this reagent display enhanced fluorescence emissions. The performance of the reagent is sensitive to the solvent system employed, and nonaqueous media provide the most favorable conditions with respect to both sensitivity and complexing ability, although the use of a nonaqueous medium for the analysis is most often undesirable for the present invention if an aqueous medium will suffice. The reagent has been used to determine calcium cation concentrations in the range of (1.5 to 1.9) x 10⁻⁶ M. The detection limit for calcium in H₂C-CN is about 126 ppb.

[0062] Preferable incipient reagents for which literature sources describe methods of fluorescence analysis of analytes relevant to the present invention are set forth below in Table 1.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Fluorescent Reagent</th>
<th>Reference*</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcium</td>
<td>calcein. a.k.a. fluorescein immodiacetic acid, or calcein W (water-soluble disodium salt)</td>
<td>3, page 1741 and 1775</td>
</tr>
<tr>
<td>calcium</td>
<td>1.5-bis (dicarboxymethylaminomethyl)-2,6-dihydroxy-naphthalene</td>
<td>3, page 1747 and 1774</td>
</tr>
<tr>
<td>calcium</td>
<td>3-hydroxy-2-naphthoic acid</td>
<td>3, page 1775</td>
</tr>
</tbody>
</table>

* References corresponding to the numbers listed in Table 1 are: (1) "Molecular Probes - Handbook of Fluorescent Probes & Research Chemicals", 5th Ed., R. P. Haugland, 1992; (2) "Photometric and Fluorometric Methods of Analysis", Part 2, F. D. Snell, 1978 (3) "Photometric and Fluorometric Methods of Analysis", Part 2, F. D. Snell, 1978.
Table 1 (continued)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Fluorescent Reagent</th>
<th>Reference*</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcium</td>
<td>isocein, a.k.a. 8-(bis(carboxymethyl)aminomethyl)-7-hydroxy-2-methyl-isoflavone</td>
<td>3, page 1775</td>
</tr>
<tr>
<td>calcium</td>
<td>8-quinolythydrazone</td>
<td>3, page 1777</td>
</tr>
<tr>
<td>magnesium</td>
<td>o,o'-dihydroxyazobenzene</td>
<td>3, page 1931</td>
</tr>
<tr>
<td>magnesium</td>
<td>2,3-bis(salicylideneamino) benzofuran</td>
<td>3, page 1943 and 1961</td>
</tr>
<tr>
<td>magnesium</td>
<td>calcein</td>
<td>3, page 1953-4</td>
</tr>
<tr>
<td>magnesium</td>
<td>2,2'-dihydroxyazobenzene</td>
<td>3, page 1955</td>
</tr>
<tr>
<td>magnesium</td>
<td>3-hydroxy-3',4'-dimethylflavone</td>
<td>3, page 1956</td>
</tr>
<tr>
<td>magnesium</td>
<td>3,3',4'-trihydroxyflavone</td>
<td>3, p</td>
</tr>
<tr>
<td>magnesium</td>
<td>3-hydroxy-2-naphthoic acid</td>
<td>3, page 1956</td>
</tr>
<tr>
<td>magnesium</td>
<td>8-hydroxyquinoline-5-sulfonic acid</td>
<td>3, page 1956-7</td>
</tr>
<tr>
<td>magnesium</td>
<td>lumomagneson, a.k.a. 5-(5-chloro-2-hydroxy-3-sulfophenylazo) barbituric acid</td>
<td>3, page 1957</td>
</tr>
<tr>
<td>magnesium</td>
<td>morin</td>
<td>3, page 1959</td>
</tr>
<tr>
<td>magnesium iron</td>
<td>2,3-bis(salicylideneamino) benzofuran 1,10-phenanthroline and tetrabromo-, tetraido- dichlorotetraido-fluorescein</td>
<td>2, page 745-6</td>
</tr>
<tr>
<td>iron (ferric)</td>
<td>pontachrome blue black R (a.k.a. mordant black 17) complex with ammonium</td>
<td>2, page 817</td>
</tr>
<tr>
<td>iron</td>
<td>4,4''bis(bis(carboxymethyl)amino) stibine-2,2''-disulfonic acid/ hydrogen peroxide</td>
<td>2, page 853</td>
</tr>
<tr>
<td>iron</td>
<td>4''-(4-methoxyphenyl)-2,2';6','6''-terpyridyl or sulfonate thereof</td>
<td>2, page 853</td>
</tr>
<tr>
<td>copper (cupric ion)</td>
<td>lumocupferron. a.k.a. a-(4-dimethylaminobenzylidene) hippuric acid</td>
<td>2, page 214</td>
</tr>
</tbody>
</table>

Techniques that can be used for the present purposes of formation of the target-specie indicator and/or the fluorescence analysis of the target-specie indicator, when the target specie is a water condition, are set forth below as exemplitive and not limiting. The acid/base sensitivity of the fluorescence characteristics of a incipient reagent may be employed to determine the pH of a water system. Suitable incipient reagents are reagents whose fluorescence intensity increases or decreases, or whose excitation and/or emission wavelength(s) shifts, upon reaction with, or in the presence of, the target specie. Examples of suitable incipient reagents for pH determinations include acridine orange, acridine yellow, acriflavine, 4-aminobenzoic acid, 4-aminobiphenyl, fluorescein, and many others.

By the terms “tracing” is meant herein, unless expressly indicated otherwise, the determination of the concentration of an inert tracer(s) in a water aqueous system. Such tracing could be conducted on a singular, intermittent or semi-continuous basis for the purpose of the present invention, but preferably on a substantially continuous basis, and, more preferably, the concentration determination is conducted on-site (at the site of the water system). Inert tracers are at times referred to herein simply as a “tracer”.

Generally the dosage of a tracer to a water treatment agent feed or makeup water will be at least sufficient to provide a concentration of tracer at the downstream sampling/monitoring station of at least about 50 ppt (parts per trillion), and more commonly at least about 5 ppb (parts per billion) or higher, up to about 100 or 1,000 ppm (parts per million), in the water system.

A water treatment agent feed is commonly, but not always, comprised of one or more active water treatment agents and one or more inert diluents. A diluent is frequently a solvent for the water treatment agent(s), and such solvent can be, and in many instances is, water. A diluent is frequently included in the water treatment agent feed to facilitate the rapid and substantially homogeneous distribution of the active water treatment agent(s) in the water system to which the water treatment agent feed is charged. The concentration of the active water treatment agent(s) in the water treatment agent feed is generally from about 0.5 to about 50 weight percent and at times higher. The weight ratio of active water treatment agent(s) to tracer in the water treatment agent feed is often within the range of from about

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Fluorescent Reagent</th>
<th>Reference*</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper (cuprous)</td>
<td>ternary complex of 1,10-phenanthroline and rose bengal</td>
<td>2, page 230</td>
</tr>
<tr>
<td>copper (cupric)</td>
<td>thiamine</td>
<td>2, page 238</td>
</tr>
<tr>
<td>copper (cupric)</td>
<td>1,1,3-tricyano-2-amino-1-propene</td>
<td>2, page 241</td>
</tr>
<tr>
<td>copper (cupric)</td>
<td>2-hyroxy-1-naphthaldehyde/4-chlorobenzylediethio-carbamate in DMF</td>
<td>2, page 256</td>
</tr>
<tr>
<td>copper (cupric)</td>
<td>1-(2-hydroxypropyl)anabasine/hydrogen peroxide reaction product</td>
<td>2, page 257</td>
</tr>
<tr>
<td>copper</td>
<td>1,10-phenanthroline and tetrabromo-, tetraiodo- or dichlorotetraiodofluorescein</td>
<td>2, page 262-3</td>
</tr>
<tr>
<td>chloride</td>
<td>N-(sulfopropyl)acridinium</td>
<td>1, page 145</td>
</tr>
<tr>
<td>chloride</td>
<td>N-(6-methoxyquinolyl)acetic acid</td>
<td>1, page 145</td>
</tr>
<tr>
<td>chloride</td>
<td>N-(6-methoxyquinolyl)acetoethyl ester</td>
<td>1, page 145</td>
</tr>
</tbody>
</table>

The weight ratio between the active water treatment agent and the tracer in a system ahead of any selective water treatment agent-consuming site is of course substantially the same as that of the water treatment agent feed, and thereafter that weight ratio would fall as the water treatment agent is selectively consumed in the water system, for instance to the extent of approaching a 1:1 weight ratio or less. A selective release of water treatment agent, which is also a factor in its system consumption, would of course have the opposite effect on this ratio.

The tracer is preferably selected from among those that are easily quantifiable by a fluorescence analysis method, a preferred analytical technique for the purposes of the present system. Other analysis methods not excluded for use in quantifying the tracer are described elsewhere herein.

An inert tracer preferably is both soluble and stable in the water treatment agent feed and transportable with the water of the system and thus wholly water-soluble therein at the concentration it is used, under the temperature and pressure conditions to be encountered. Preferably the selected inert tracer also meets the following criteria:

1. Be thermally stable and not decompose at the temperature within the given system;
2. Be detectable on a continuous or semicontinuous basis and susceptible to concentration measurements that are accurate, repeatable and capable of being performed on system water;
3. Be substantially foreign to the chemical species that are normally present in the water of the water systems in which the inert tracer may be used;
4. Be substantially impervious to interference from, or biasing by, the chemical species that are normally present in the water of the water systems in which the inert tracer may be used;
5. Be substantially impervious to any of its own potential specific losses from the water of the water system, including selective carry-over;
6. Be compatible with all treatment agents employed in the water of the water systems in which the inert tracer may be used, and thus in no way reduce the efficacy thereof;
7. Be compatible with all components of the water treatment agent feed formulation or makeup water despite the concentrations of the tracer and/or other components in such a formulation, and despite any storage and/or transportation conditions encountered; and
8. Be reasonably nontoxic and environmentally safe, not only within the environs of the water of the water system in which it may be used, but also upon discharge therefrom.

The chemical compound(s) selected as an inert tracer(s) should not be one that is consumed or selectively lost to the water of the system, for instance due to degradation, deposition, complexation, or other phenomena, unless such loss is at a rate that is predictable and proportional to a non-system-consumption loss of the water treatment agent or target-specie indicator being monitored. An inert tracer(s) used in the present invention is preferably substantially unconsumed in the water system environment. An inert tracer(s) that is wholly inert in the water system environment would not react to a substantial degree with any of the components in the water of the water system to which it is added, would not degrade in the environment of the water of the water system, would be incapable of coupling and/or depositing in any manner within such system and would not appreciably be effected by other system parameters such as metallurgical composition, heat changes or heat content. There are water-soluble inert tracer(s) that are wholly inert, or substantially inert, in the aqueous environments likely to be encountered in industrial water systems. Further, it is believed that an inert tracer(s) having a degree of inertness such that no more than 10 weight percent thereof is lost due to reaction, degradation, coupling and/or deposition during the time that elapses between its addition and its final analysis, is sufficiently, or substantially, inert for the purpose of the present invention for most, if not all, water treatment agent monitirings.

As noted above, an inert tracer must be added to the makeup water and/or water treatment agent feed in known proportion to the water treatment agent, and an inert tracer is introduced into the water system together with the water treatment agent at a known and constant concentration therein which is at a known and constant proportion to the water treatment agent therein. The preferred method of achieving such proportionality is to formulate an inert tracer together with water treatment agent concentrate if the water treatment agent feed is to be prepared by on-site dilution and if an inert tracer is stable in such concentrate. The concentrate may be an aqueous solution or other substantially homogeneous admixture that disperses with reasonable rapidity in the dilution fluid which is added. Since in most any instance a water treatment agent and an inert tracer would both be added to a system as components of a fluid feed formulation, rather than as a dry solid or individual neat liquids, the tracer concentration may be correlated not to the numerical concentration of an inert tracer itself or the water treatment agent itself, but instead to the concentration of a formulated product containing the water treatment agent, which in turn can be correlated to the concentration of an inert tracer and/or water treatment agent when and if such information is required. Therefore the proportionality of the tracer to the water treatment agent feed for the purposes of the present invention can be equivalent to a proportionality of tracer to the active water treatment agent component of the feed.

Among the substantially water-system inert fluorescent compounds are the mono-, di- and trisulfonated naph-
thalenes, including their water-soluble salts, particularly the various naphthalene mono-, di-, and tri-sulfonic acid isomers, which are preferred inert tracers for use in the present invention. The naphthalene mono- di- and tri-sulfonic acid isomers are water-soluble, generally available commercially and easily detectable and quantifiable by known fluorescence analysis techniques. Preferred naphthalene mono- and disulfonic acid isomers are the water-soluble salts of naphthalene sulfonic acid ("NSA"), such as 1-NSA and 2-NSA, and naphthalene disulfonic acid ("NDSA" or "NDA"), for instance 1,2-NDSA, 1,3-NDSA, 1,4-NDSA, 1,5-NDSA, 1,6-NDSA, 1,7-NDSA, 1,8-NDSA, 2,3-NDSA, 2,4-NDSA and so forth. Many of these inert tracer(s) (mono-, di- and trisulfonated naphthalenes and mixtures thereof) are extremely compatible with the environments of most systems. Among these preferred fluorescent tracers, 2-NSA and 1,5-NDSA have been found to be thermally stable (substantially inert) at temperatures up to at least about 540 °C (1004 °F), for at least 24 hours at 285 °C (545 °F) and at pressures up to about 1,500 psig for time periods at least commensurate with, and often well in excess of, commercial water system holding times. Such inert fluorescent tracers are not volatilized into steam. Another group of inert fluorescent tracers that are preferred for use in the process of the present invention are the various sulfonated derivatives of pyrene, such as 1,3,6,8-pyrene tetrasulfonic acid, and the various water-soluble salts of such sulfonated pyrene derivatives.

In preferred embodiment an inert tracer is one of the above sulfonated fluorescent tracers and is employed at concentration levels of from about 0.5 ppb, and more commonly at least about 5 ppb or higher, up to about 10 ppm in the water system. Fluorescent chemical tracers and monitoring techniques are now known, for instance as disclosed in U.S. Patent No. 4,783,314 wherein fluorescent tracers are employed in combination with a fluorescence monitoring, such as the sodium salt of 2-naphthalenesulfonic acid.

When the tracer is 2-NSA, one of the water-soluble salts of naphthalene sulfonic acid ("NSA"), its concentration in the water system can be fluorometrically measured by excitation at 277 nm and emission measurement at 334 nm, and the emissions observed referenced to a standard aqueous solution containing 0.5 ppm 2-NSA, as acid actives. Unless expressly indicated otherwise herein, the inclusion of a prefix or suffix in parenthesis designates the word with such prefix or suffix as an alternative. For instance, "specie(s)" means "specie and/or species", "determination(s)" means "determination and/or determinations", "technique(s)" means "technique and/or techniques", "chemical(s)" means "chemical and/or chemicals", "component(s)" means "component and/or components", "tracer(s)" means "tracer and/or tracers", and the like. By "ppm" is meant "parts per million" by weight. By "ppb" is meant "parts per billion" by weight. By "ppt" is meant "parts per trillion" by weight.

The present invention is applicable to industries employing water treatment agents for the treatment of aqueous systems, mixed aqueous/nonaqueous systems and substantially nonaqueous system, including industries employing boiler water systems, cooling water systems, and so forth.

Examples

Unless indicated otherwise, the water employed to prepare the synthetic industrial water solutions in the following Examples 1 to 5 had the following initial chemistry, which is prototypical of, for instance, industrial cooling waters and is thus referred to herein as "synthetic industrial water":

200 ppm Ca²⁺ (as CaCO₃)
200 ppm Mg²⁺ (as CaCO₃)
200 ppm HCO₃⁻ (as CaCO₃)
140 ppm Cl⁻ (as Cl)
194 ppm SO₄²⁻ (as SO₄)
90 ppm Na⁺ (as Na)
pH 8.4

Example 1

To demonstrate the application of the present process to an orthophosphate (PO₄³⁻) target specie, the fluorescence analysis of a series of synthetic industrial water solutions, also containing from 0 to 10.0 ppm PO₄³⁻ (as PO₄), in the presence of an incipient reagent were conducted and percent relative fluorescence of the target-specie concentration indicators in each solution were determined in comparison to such a solution without that target specie. The incipient reagent was 1-pyrenesulfonic acid in a highly acidic vanadomolybdate aqueous solution. This solution (fluorescent reagent) contains 1.0 ppm 1-pyrenesulfonic acid, (ppm, as acid actives), 2.35 wt./vol. percent ammonium molybdate, 0.125 wt./vol. percent ammonium metavanadate, and 33 vol./vol. percent concentrated hydrochloric acid.

The fluorescent reagent (10 ml.) was admixed with 100 ml. of each of the orthophosphate-containing solutions. The fluorescence analysis was conducted after one minute using a Gilford Fluoro IV dual monochromator, with a 1.0 cm x 1.0 cm cuvette. An excitation wavelength of 380 nm and an emission wavelength of 405 nm were used. The solution
containing the fluorescent reagent but not the orthophosphate was assigned a percent relative fluorescence of 100. The change in the fluorescence characteristic of the incipient reagent when it interacted with the orthophosphate was a decrease in fluorescence intensity under these conditions. The fluorescence characteristic that can be correlated to the target-specie concentration is the emission intensity decrease as the analyte (PO$_4^{3-}$) concentration increases. The fluorescence being measured is affected by that of the complex between incipient reagent and target-specie. The concentration of PO$_4^{3-}$ versus the percent relative fluorescence determined for each sample are set forth in Table 2 below. Such data exhibits a coefficient of linear correlation ($r$) of 0.98. Perfect linearity would exhibit an $r$ of 1.000.

### Table 2

<table>
<thead>
<tr>
<th>PO$_4^{3-}$ Concentration (ppm, as PO$_4$)</th>
<th>Percent Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 ppm</td>
<td>100 %</td>
</tr>
<tr>
<td>2.5 ppm</td>
<td>72.6 %</td>
</tr>
<tr>
<td>5.0 ppm</td>
<td>55.4 %</td>
</tr>
<tr>
<td>10.0 ppm</td>
<td>29.7 %</td>
</tr>
</tbody>
</table>

#### Example 2

[0078] To demonstrate the application of the present process to a ferrous ion (Fe$^{2+}$) target specie, the fluorescence analysis of a series of synthetic industrial water solutions, also containing from 0.0 to 1.0 ppm Fe$^{2+}$ (as Fe), in the presence of an incipient reagent were conducted and percent relative fluorescence of the target-specie concentration indicators in each solution were determined in comparison to such a solution without that target specie. The incipient reagent was 1,10-phenanthroline, employed in this Example 2 in aqueous solution. This solution (fluorescent reagent) was prepared by adding 1,10-phenanthroline to distilled (DI) water to form a solution containing 1,000 ppm of 1,10-phenanthroline. The fluorescent reagent (1.0 ml.) was admixed with 100 mL of each of the target-specie-containing solutions, and the fluorescence analysis was conducted after one minute using a Gilford Fluoro IV dual monochromator, with a 0.2 cm diameter cuvette (flowcell). An excitation wavelength of 293 nm and an emission wavelength of 360 nm were used. The solution containing the fluorescent reagent but not the target specie was assigned a percent relative fluorescence of 100. The change in the fluorescence characteristic of the incipient reagent when it interacted with the target specie was a decrease in fluorescence intensity under these conditions. The fluorescence characteristic that can be correlated to the target-specie concentration is the emission intensity decrease as the analyte (Fe$^{2+}$) concentration increases. The concentration of Fe$^{2+}$ versus the percent relative fluorescence determined for each sample are set forth in Table 3 below. Such data exhibits a coefficient of linear correlation ($r$) of 0.9999.

### Table 3

<table>
<thead>
<tr>
<th>Fe$^{2+}$ Concentration (ppm, as Fe)</th>
<th>Percent Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 ppm</td>
<td>100 %</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>79.1 %</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>59.9 %</td>
</tr>
<tr>
<td>0.75 ppm</td>
<td>39.0 %</td>
</tr>
<tr>
<td>1.0 ppm</td>
<td>19.4 %</td>
</tr>
</tbody>
</table>

#### Example 3

[0079] To demonstrate the application of the present process to a cupric ion (Cu$^{2+}$) target specie, the fluorescence analysis of a series of synthetic industrial water solutions, also containing from 0.0 to 2.0 ppm Cu$^{2+}$ (as Cu), in the presence of an incipient reagent were conducted and percent relative fluorescence of the target-specie concentration indicators in each solution were determined in comparison to such a solution without that target specie. The incipient reagent was bicinchoninate (which is also known as 2, 2'-biquinoline-4,4'-dicarboxylic acid, dipotassium salt), employed in this Example 3 in aqueous solution. This solution (fluorescent reagent) of bicinchoninate was prepared by adding bicinchoninate to DI water to form a solution containing 1,000 ppm bicinchoninate. For samples containing 0 to 0.5 ppm Cu$^{2+}$, the fluorescent reagent (0.2 ml) was admixed with 100 ml of each of the target-specie-containing solutions, and the fluorescence analysis was conducted after one minute using a Gilford Fluoro IV dual monochromator, with a 0.2 cm diameter cuvette (flowcell). An excitation wavelength of 260 nm and an emission wavelength of 410 nm were used. For samples containing 0.5 to 2.0 ppm Cu$^{2+}$, the fluorescent reagent (0.6 ml) was admixed with 100 ml of each of the target-species-containing solution, and the fluorescence analysis was conducted after one minute development...
time as before. The synthetic industrial water solution containing the fluorescent reagent but not the target specie was assigned a percent relative fluorescence of 100. The change in the fluorescence characteristic of the incipient reagent when it interacted with the target specie was a decrease in fluorescence intensity under these conditions. The fluorescence characteristic that can be correlated to the target-specie concentration is the emission intensity decrease as the analyte (Cu$^{+2}$) concentration increases. The concentration of Cu$^{+2}$ versus the percent relative fluorescence determined for each sample are set forth in Table 4 below. Such data exhibits a coefficient of linear correlation ($r$) of 0.994.

<table>
<thead>
<tr>
<th>Cu$^{+2}$ Concentration (ppm, as Cu)</th>
<th>Percent Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 ppm</td>
<td>100 %</td>
</tr>
<tr>
<td>0.05 ppm</td>
<td>94.3 %</td>
</tr>
<tr>
<td>0.10 ppm</td>
<td>90.0 %</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>65.8 %</td>
</tr>
<tr>
<td>0.5 ppm</td>
<td>42.1 %</td>
</tr>
</tbody>
</table>

[0080] Additional tests were conducted to determine the compatibility of bicinchoninate with industrial water conditions and chemistries other than those already demonstrated by the use of synthetic industrial water in Example 3 above. The conditions/chemistries tested and the effect thereof on bicinchoninate in aqueous solution is set forth below in Table 5.

<table>
<thead>
<tr>
<th>Water Condition or Chemistry</th>
<th>Effect on Bicinchoninate</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH from 6 to 13</td>
<td>no effect</td>
</tr>
<tr>
<td>highly acidic pH</td>
<td>tends to precipitate</td>
</tr>
<tr>
<td>5 ppm Fe$^{+2}$</td>
<td>no effect</td>
</tr>
<tr>
<td>10 ppm Zn$^{+2}$</td>
<td>no effect</td>
</tr>
</tbody>
</table>

Example 4

[0081] To demonstrate the application of the present invention to Total Alkalinity as a target species, the fluorescence analysis of a synthetic industrial water was conducted and percent relative fluorescence of the Target Species concentration indicators in each solution were determined in comparison to such a solution without that Target Species. The incipient fluorescent reagent was 1,000 ppm 4-aminobenzoic acid aqueous solution. The fluorescent reagent (0.1 ml) solution was added to 100 ml of each of the target-species-containing solutions. The fluorescence analysis was conducted with a Gilford Fluoro IV dual monochromator, with 0.2 cm diameter cuvette (flow cell). An excitation wavelength of 275 nm and an emission wavelength of 340 nm were used. The solution containing the fluorescent reagent but 0 ppm (bi)carbonate alkalinity was assigned a percent relative fluorescence of 0% and solution containing fluorescent reagent between pH 6.4 - 8.9 (without any sulfuric acid neutralizing agent present) was assigned a percent relative fluorescence of 100%. The change in fluorescence character of the incipient reagent was measured after one minute and as it reacted with the total alkalinity was an increase in fluorescence intensity under these conditions. The fluorescence character that can be correlated to the Target Species concentration is the emission intensity increase as the analyte increases. The concentration of Total Alkalinity versus the percent relative fluorescence was determined for each sample and is set forth in Table 6 below.

<table>
<thead>
<tr>
<th>Total Alkalinity Added (as CaCO$_3$)</th>
<th>% Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 ppm (initial)</td>
<td>4.0%</td>
</tr>
<tr>
<td>250 ppm</td>
<td>8.6%</td>
</tr>
<tr>
<td>275 ppm</td>
<td>14.7%</td>
</tr>
<tr>
<td>300 ppm</td>
<td>85.8%</td>
</tr>
<tr>
<td>325 ppm</td>
<td>91.6%</td>
</tr>
</tbody>
</table>
Example 5

To demonstrate the application of the present process to a (hydrogen) sulfide target specie, the fluorescent analysis of a series of synthetic industrial water solutions also containing 0.0 to 2.24 ppm (hydrogen) sulfide, in the presence of an incipient reagent were conducted and percent relative fluorescence of the target-specie concentration indicators in each solution were determined in comparison to such a solution without that target specie. The incipient reagent was N,N-dimethyl-p-phenylenediamine solution (1,700 ppm in 8M aqueous sulfuric acid). For samples containing 0 ppm to 0.056 ppm (hydrogen) sulfide, the fluorescent reagent (1.0 ml) was admixed with 25 ml of each of the target-specie-containing solutions and then 1.0 ml of aqueous potassium dichromate (1600 ppm as H₂Cr₂O₇) was admixed with the fluorescent reagent + target-specie-containing solution. The fluorescence analysis was conducted after five minutes development time using a Gilford fluoro IV dual monochromator, with a 0.2 cm diameter cuvette (flowcell). An excitation wavelength of 660 nm and an emission wavelength of 680 nm were used.

For samples containing 0.56 to 2.24 ppm (hydrogen) sulfide, the same procedure was used, except that fluorescence analysis was conducted at an excitation wavelength of 690 nm and an emission wavelength of 710 nm. The synthetic, industrial water solution containing the fluorescent reagent, chromate and highest level of target specie (for each group of analysis) was assigned a percent relative fluorescence of 100. The change in the fluorescence characteristic of the incipient reagent when it interacted with the target specie was a change in excitation and emission wavelengths and corresponding increase in fluorescence intensity under the stated analysis conditions the concentration of (hydrogen) sulfide versus the percent relative florescence determined for each sample are set forth in Tables 7 and 8 below. Such data exhibits a coefficient of linear correlation (r) of 0.999 for (hydrogen) sulfide concentration at or below 0.56 ppm and r=0.991 for (hydrogen) sulfide concentration from above 0.56 to 2.24 ppm.

<table>
<thead>
<tr>
<th>(Hydrogen) Sulfide Concentration</th>
<th>Percent Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 ppm</td>
<td>0.0%</td>
</tr>
<tr>
<td>0.11 ppm</td>
<td>21.2%</td>
</tr>
<tr>
<td>0.28 ppm</td>
<td>53.3%</td>
</tr>
<tr>
<td>0.56 ppm</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

Table 7

<table>
<thead>
<tr>
<th>(Hydrogen) Sulfide Concentration</th>
<th>Percent Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 ppm</td>
<td>0.0%</td>
</tr>
<tr>
<td>1.12 ppm</td>
<td>61.9%</td>
</tr>
<tr>
<td>1.68 ppm</td>
<td>82.2%</td>
</tr>
<tr>
<td>2.24 ppm</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

Table 8

Example 6

The hardness ion calcium

A method for the detection of calcium was developed using the reagent 1,2-bis(o-aminophenoxy)ethane-N, N,N', N'-tetraacetic acid (BAPTA). A 5 x 10⁻³ M BAPTA reagent was prepared by dissolving 314 mg of K₂BAPTA in 100 ml of water. A 1 x 10⁻² M tris(hydroxymethyl)aminomethane (TRIS) buffer containing 0.1 M KCl was prepared by dissolving 1.21 g tris (hydroxymethyl)aminomethane and 7.4 g KCl in approximately 800 ml of deionized water adjusting pH to 7.4 using NaOH then diluting to 1 liter with deionized water. A solution containing 2 x 10⁻⁴ M Ca⁺² (8 ppm Ca⁺²) was prepared by dissolving CaCl₂ 2H₂O in water. Appropriate aliquots of the 2 x 10⁻⁴ M Ca⁺² solution were added to 100 ml volumetric flasks. 2 ml of the TRIS buffer was added to the flask along with enough deionized water so that the total volume was approximately 75 ml. Finally, 2 ml of the BAPTA reagent was added along with deionized water. A stable fluorescence had developed when the sample was analyzed. Several samples in the range of 0 - 3.2 ppm final concentration of Ca⁺² were analyzed. The excitation was at 295 nm and emission at 365 in a 1.0 cm x 1.0 cm cuvette. The response is monotonic and fluorescence decreases predictably as calcium is complexed by the BAPTA reagent. The results are summarized below in Table 9. Such data exhibits a coefficient of linear correlation (r) of 0.985.
Claims

1. A fluorometric method regulating the dosage of a water treatment agent present in an industrial water system to combat a target-species wherein said target-species is not itself fluorescent and which treatment agent is consumed in that combatting comprising:

   using a fluorometer to detect the fluorescent emissions in a sample of an industrial water system;
   determining from the quantity of target-species present in said industrial water system whether an appropriate amount of water-treatment agent is present;
   adding water-treatment agent to said industrial water system in a known proportion of inert tracer to said water-treatment agent;

   characterized in adding to the sample a reagent to react with said target-species either to create a moiety with a detectable fluorescent emission or to create a moiety that quenches detectable fluorescent emission of said reagent, and determining the quantity of target-species present from said fluorescent emissions; and
   monitoring the inert tracer to determine the amount of water-treatment agent present, and adjusting the rate of addition of water-treatment agent to bring the water-treatment agent presence to said appropriate amount.

2. The method of claim 1 wherein said industrial water system comprises at least about 70 weight percent water.

3. The method of claim 2 wherein said industrial water system is a cooling water system or a boiler water system.

4. The method of any one of the preceding claims wherein said monitoring of said subject target-specie indicator is conducted at the site of said industrial system on a continuous basis.

5. The method of any one of the preceding claims wherein said target specie is sulfide, calcium, iron, carbonate, copper (bi)carbonate, alkalinity, copper, sulfate, fluoride, magnesium or phosphate.

6. The method of claim 5 wherein said industrial fluid system contains a plurality of said target species and system consumption conditions for the plurality of target species are determined by monitoring a plurality of subject target-specie indicators.

7. The method of claim 1, claim 2 or claim 3 wherein said target-specie is calcium.

8. The method of claim 7 wherein said target-specie indicator is a complex formed between calcium and 1,2-bis(o-aminophenoxy) ethane-N,N,N',N'-tetraacetic acid.

9. The method of claim 1 wherein

   a) when said target-species is orthophosphate, said reagent is 1.0 ppm 1-pyrenesulfonic acid, 2.35 wt./vol. percent ammonium molybdate, 0.125 wt./vol. percent ammonium metavanadate and 33 vol./vol. percent concentrated hydrochloric acid;


Table 9

<table>
<thead>
<tr>
<th>Final Concentration</th>
<th>% Relative Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (ppm)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>0.4</td>
<td>99.4%</td>
</tr>
<tr>
<td>0.8</td>
<td>89.6%</td>
</tr>
<tr>
<td>1.6</td>
<td>68.7%</td>
</tr>
<tr>
<td>2.4</td>
<td>43.4%</td>
</tr>
<tr>
<td>3.2</td>
<td>7.6%</td>
</tr>
</tbody>
</table>
b) when said target-species is ferrous ion (Fe$^{+2}$), said reagent is 1000 ppm 1,10-phenanthroline in deionized water;

c) when said target-species is Cu$^{+2}$, said reagent is 1000 ppm bicinechinoninate(2,2'-biquinoline-4,4'-dicarboxylic acid);

d) when said target-species is Total alkalinity, said reagent is 1000 ppm 4-aminobenzoic acid aqueous solution;

e) when said target-species is hydrogen sulfide, said reagent is 1700 ppm N,N-dimethyl-p-phenylenediamine solution in 8M aqueous sulfuric acid and 1.0 ml of aqueous potassium dichromate; and

f) when said target-species is Ca$^{+2}$, said reagent is 1,2-bis(o-aminophenoxy)ethane-N,N,N',N'-tetracetic acid buffered by a 1 x 10$^{-2}$M tris(hydroxymethyl) aminomethane buffer.

**Patentansprüche**

1. Fluorimetrisches Verfahren, das die Dosis eines Wasserbehandlungsmittels reguliert, das in einem Industriewassersystem enthalten ist, um eine Zielspezies zu bekämpfen, worin die Zielspezies selbst nicht fluoreszierend ist und wobei das Behandlungsmittel bei der Bekämpfung verbraucht wird, umfassend:

   die Verwendung eines Fluorimeters zum Detektieren der Fluoreszenzemissionen in einer Probe eines Industriewassersystems;

   das Bestimmen anhand der im Industriewassersystem enthaltenen Menge an Zielspezies, ob eine geeignete Menge an Wasserbehandlungsmittel enthalten ist;

   die Zugabe von Wasserbehandlungsmittel zum Industriewassersystem in einem bekannten Verhältnis zwischen inertem Tracer und dem Wasserbehandlungsmittel;

   dadurch gekennzeichnet, dass der Probe ein Reagens zur Reaktion mit der Zielspezies zugesetzt wird, um entweder eine Gruppe mit einer detektierbaren Fluoreszenzemission zu erzeugen oder eine Gruppe zu erzeugen, die eine detektierbare Fluoreszenzemission des Reagens löscht, und die Fluoreszenzemissionen die Menge an enthaltener Zielspezies bestimmt wird; und

   dass der inerte Tracer kontrolliert wird, um die Menge an enthaltenem Wasserbehandlungsmittel zu bestimmen, und die Zuführerate von Wasserbehandlungsmittel so eingestellt wird, dass der Gehalt an Wasserbehandlungsmittel auf die geeignete Menge gebracht wird.

2. Verfahren nach Anspruch 1, worin das Industriewassersystem zumindest etwa 70 Gew.-% Wasser umfasst.

3. Verfahren nach Anspruch 2, worin das Industriewassersystem ein Kühlwassersystem oder ein Kesselwassersystem ist.

4. Verfahren nach einem der vorangegangenen Ansprüche, worin das Kontrollieren des vorliegenden Zielspezies-Indikators am Standort des Industriesystems auf kontinuierlicher Basis erfolgt.

5. Verfahren nach einem der vorangegangenen Ansprüche, worin die Zielspezies Sulfid, Calcium, Eisen, Carbonat, Kupfer(bi)carbonat, Alkalinität, Kupfer, Sulfat, Fluorid, Magnesium oder Phosphat ist.

6. Verfahren nach Anspruch 5, worin das Industrieflüssigkeitssystem mehrere Zielspezies enthält und die Systemverbrauchsbedingungen für die mehreren Zielspezies durch Kontrollieren mehrerer vorliegender Zielspezies-Indikatoren bestimmt werden.

7. Verfahren nach Anspruch 1, 2 oder 3, worin die Zielspezies Calcium ist.

8. Verfahren nach Anspruch 7, worin der Zielspezies-Indikator ein zwischen Calcium und 1,2-Bis(o-aminophenoxy) ethan-N,N,N',N'-tetaessigsäure gebildeter Komplex ist.

9. Verfahren nach Anspruch 1, worin:

   a) wenn die Zielspezies Orthophosphat ist, das Reagens 1,0 ppm 1-Pyrensulfonsäure, 2,35 % (Gew./Vol.) Ammoniummolybdat, 0,125 % (Gew./Vol.) Ammoniummetavanadat und 33 % (Vol./Vol.) konzentrierte Salzsäure ist;

   b) wenn die Zielspezies das Eisen(II)-ion (Fe$^{+2}$) ist, das Reagens 1.000 ppm 1,10-Phenanthrolin in entioni-
siertem Wasser ist;
c) wenn die Zielspezies Cu^{2+} ist, das Reagens 1.000 ppm Bicinchoninat (2,2'-Bichinolin-4,4'-dicarbonsäure) ist;
d) wenn die Zielspezies Gesamt-Alkalinität ist, das Reagens 1.000 ppm wässrige 4-Aminobenzoesäure-Lösung ist.
e) wenn die Zielspezies Schwefelwasserstoff ist, das Reagens 1.700 ppm N,N-Dimethyl-p-phenyldiamin-Lösung in 8 M wässriger Schwefelsäure und 1,0 ml wässriges Kaliumdichromat ist; und
f) wenn die Zielspezies Ca^{2+} ist, das Reagens 1,2-Bis(o-aminophenoxy)ethan-N,N,N',N'-tetraessigsäure, gepuffert mit einem 1 x 10^{-2} M Tris(hydroxymethyl)aminomethan-Puffer, ist.

Revendications

1. Méthode fluorométrique régulant le dosage d’un agent de traitement de l’eau présent dans un système d’eaux industrielles pour combattre une espèce cible, où ladite espèce cible n’est pas elle-même fluorescente et lequel agent de traitement est consommé par le fait que le combat consiste à :
   - utiliser un fluoromètre pour détecter les émissions fluorescentes dans un échantillon d’un système d’eaux industrielles ;
   - déterminer à partir de la quantité de l’espèce cible présente dans ledit système d’eaux industrielles si une quantité appropriée d’agent de traitement de l’eau est présente ;
   - ajouter de l’agent de traitement de l’eau audit système d’eaux industrielles à une proportion connue d’un traceur inerte audit agent de traitement de l’eau ;

   caractérisée en ce qu’on ajoute à l’échantillon un réactif pour réagir avec ladite espèce cible soit pour créer une fraction avec une émission fluorescente détectable ou pour créer une fraction qui arrête l’émission fluorescente détectable audit réactif, et on détermine la quantité de l’espèce cible présente à partir desdites émissions fluorescentes ; et on surveille le traceur inerte pour déterminer la quantité de l’agent de traitement de l’eau présent, et on ajuste le taux d’addition de l’agent de traitement de l’eau pour porter la présence de l’agent de traitement de l’eau à ladite quantité appropriée.

2. Méthode de la revendication 1 où ledit système d’eaux industrielles comprend au moins 70% en poids d’eau.

3. Méthode de la revendication 2 où ledit système d’eaux industrielles est un système d’eau de refroidissement ou un système d’eau de chaudière.

4. Méthode de l’une des revendications précédentes où ladite surveillance audit indicateur de l’espèce cible sujet est entreprise au site audit système industriel sur une base continue.

5. Méthode de l’une quelconque des revendications précédentes où ladite espèce cible est sulfure, calcium, fer, carbonate, bi(carbonate) de cuivre, alcalinité, cuivre, sulfate, fluorure, magnésium ou phosphate.

6. Méthode de la revendication 5 où ledit système de fluide industriel contient un certain nombre des espèces cibles et lesdites conditions de consommation du système pour les espèces cibles sont déterminées en surveillant un certain nombre d’indicateurs d’espèces cibles sujets.

7. Méthode de la revendication 1, de la revendication 2 ou de la revendication 3 où ladite espèce cible est le calcium.

8. Méthode de la revendication 7 où ledit indicateur d’espèce cible est un complexe formé entre calcium et acide 1,2-bis-(o-aminophénoxy) éthane-N,N,N',N'-tétraacétique.

9. Méthode de la revendication 1 où

   a) quand ladite espèce cible est un orthophosphate, ledit réactif est 1,0 ppm d’acide 1-pyrènesulfonique, 2,35% poids/volume de molybdate d’ammonium, 0,125% poids/volume de métavanadate d’ammonium et 33% volume/
volume d'acide chlorhydrique concentré ; et

b) quand ladite espèce cible est l'ion ferreux (Fe$^{2+}$), ledit réactif est 1000 ppm de 1,10-phénanthroline dans de l'eau désionisée ; et
c) quand ladite espèce cible est Cu$^{2+}$, ledit réactif est 1000 ppm de bicinchoninate (acide 2,2'-biquinoléine-4-4'-dicarboxylique) ;
d) quand ladite espèce cible est l'alcalinité Totale, ledit réactif est 1000 ppm d'une solution aqueuse d'acide 4-aminobenzoïque ;
e) quand ladite espèce cible est du sulfure d'hydrogène, ledit réactif est 1700 ppm d'une solution de N,N-diméthyl-p-phénylènediamine dans de l'acide sulfurique aqueux 8M et 1,0 ml de dichromate de potassium aqueux ; et
f) quand ladite espèce cible est Ca$^{2+}$, ledit réactif est l'acide 1,2-bis (o-aminophénoxy)éthane-N,N,N',N'-téra-cétique tamponné par un tampon tris(hydroxyméthyl) aminométhane $1 \times 10^{-2}$ M.