

CHEMICAL ANALYZER

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 12/514,610, which is a National Phase filing under 35 U.S.C. §371 of PCT/AU2007/001801 filed Nov. 23, 2007, claiming priority to Patent Application No. 2006906573, filed in Australia on Nov. 24, 2006. The entire contents of each of the above-applications are incorporated herein by reference.

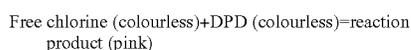
This invention relates to a method and apparatus for chemical analysis, especially analysis entailing the automatic detection of substances in solution, for example by reagent addition and titrimetry. The invention is especially suited to on-line analysis and control of chlorine content and the measurement and control of pH in pools and air conditioning towers.

BACKGROUND

Field of the Invention

The detection of substances in solution has long been determined by a variety of known techniques. A sensor such as a pH electrode may be inserted in a sample solution and the millivolts generated can be output as a pH measurement. Another known technique involves pumping a known volume or series of volumes of reagent into a defined volume of sample. The reagent and sample solutions are then mixed and a property of a component of the mixture, for example, a reaction product, is measured by a suitable detector.

As one example of the latter technique, the concentration of disinfectant such as free chlorine can be determined by the addition of a stoichiometric excess of N,N-Diethyl-p-phenylenediamine (DPD) in a suitable pH buffer:



The concentration of the coloured reaction product can be measured by the level of absorbance of light in the green to blue range. This directly relates to the concentration of free chlorine.

As a second example of the latter technique, the pH of aqueous samples can be determined by the addition of an indicator whereby the indicator varies in colour according to the pH. The colour at a particular pH is due to the ratio of different forms of the indicator. For example the pH of swimming pool water can be ascertained by the addition of a small amount of phenol red.

The extension of the above described techniques to automated analysis especially for on-line analysis and process control has been accomplished by a number of known devices. In the case of direct sensing, a pH electrode can be connected to a measuring instrument or process controller. This has the advantages of simplicity and low cost, but suffers from the disadvantage of not being able to diagnose malfunction or fouling in real time. This is especially serious for process control, which relies on reliable measurement.

In the case of the reagent addition technique, a typical state of the art apparatus for the measurement of free chlorine by DPD is described in Hanna Instruments Volume 25 (details) page T48 Model PCA 300. This device is expensive and complex in that it contains an incoming pressure regulator, sample inlet solenoid valve, multi-channel peristaltic pump, magnetic mixer and drain valve. The device requires two reagent containers which are open to the atmosphere. One

contains DPD at low pH because DPD is air sensitive at the reaction pH of 6.3, and a separate pH buffer to fix the reaction pH at 6.3. The device also consumes considerable quantities of reagents. This results in a considerable operating expense and significant operator time to replace reagent containers. The peristaltic pump tubing requires periodic replacement, requiring additional operator time. Furthermore, an (optional) on-line filter is preferred to "prolong the life of the meter".

U.S. Pat. No. 5,132,096 is an early example to methods of monitoring water treatment performance by resolving optical voltage analogs using a tracer metal added to the reagent.

U.S. Pat. No. 5,242,602 discloses a system for analysing aqueous systems using spectroscopic and pattern recognition techniques based on pre-calibrated databases

U.S. Pat. No. 5,925,572 discloses a continuous spectrophotometric pH sensor for sea water. It uses a flow through cell with three wavelength channels. A calibration routine is carried out every 15 minutes.

U.S. application 2002/0054828 discloses a waste water analysis unit immersed in the water, using removable reagent cartridges.

U.S. Pat. No. 6,627,450 discloses a method of measuring free chlorine content which provides an inline cartridge of a solid reagent. It is concerned with a total chlorine detection system using a combination of an iodide salt and a proton donating compound such as bicarbonate without lowering the pH of the sample.

It is an object of this invention to provide a reliable cost effective online chemical analysis instrument.

It is also an object of this invention to provide a system which is able to use an air sensitive reagent.

SUMMARY

To this end, the present invention provides a method of analysing a liquid sample to determine the presence of a target chemical, in which a sample is added to a measurement cell of known volume and a reagent is incrementally added to the cell until a detectable change is observed, the improvement comprising the incorporation in the reagent of a known concentration of a reference compound that does not take part in the reaction and measuring the concentration of the reference compound to determine the amount of reagent added.

One of the contributors to the high cost of other available on-line analysers which automate standard methods, is accurate volume dispensing means. In knowing the volume of reagent added and the cell volume, the final concentrations of reagents can be determined. The approach in this invention is to use a reference compound to deduce the final concentration and the volume dispensed can be determined retrospectively or regulated by monitoring the level of reference.

Internal standards have been used in chemical analysis, where a compound is added in a known concentration to the sample and undergoes the same sample preparation and reaction steps as the analyte. The resultant detected signal for the target chemical is then calibrated against the reacted product signal of the known concentration of internal standard. In this invention a reference compound is added to the reagent solution, rather than directly to the sample to be analysed, in a known proportion to the other chemicals in the reagent solution and does not undergo any subsequent chemical changes. The purpose of the reference compound is purely as an indicator of how much reagent solution has been added. Reagent solution is added to the sample in the measurement cell and the final concentration of the reference compound is measured via its absorbance. The concentrations of other reagent