

A chemiluminescence sensor for the determination of hydrogen peroxide

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Abstract

A chemiluminescence one-shot sensor for hydrogen peroxide is described. It is prepared by immobilization of cobalt chloride and sodium lauryl sulphate in hydroxyethyl cellulose matrix cast on a microscope cover glass. Luminol, sodium phosphate and the sample are mixed before use and applied on the membrane by a micropipette. The calibration graph is linear in the range 20–1600 $\mu\text{g/L}$, and the detection limit of the method (3σ) is 9 $\mu\text{g/L}$. A relative standard deviation of 4.5% was obtained for 100 $\mu\text{g/L}$ H_2O_2 ($n=11$). The sensor has been applied successfully to the determination of hydrogen peroxide in rainwater.

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1. Introduction

Hydrogen peroxide, H_2O_2 , plays an important role in atmospheric and biochemical processes. It is formed in the reaction of hydroperoxyl radicals (HO_2^\bullet) and their hydrated form, produced by the photochemical reactions of atmospheric trace gases, such as ozone and volatile organic compounds [1]. Hydrogen peroxide is considered as the most efficient oxidant for the conversion of dissolved sulphur dioxide (SO_2) to sulphuric acid (H_2SO_4) as the main contributor to the acidification of rainwater [2–6]. H_2O_2 can be decomposed by various aqueous chemical processes such as reaction with dissolved SO_2 , catalyzed destruction by transition metals such as Fe, Cu, Mn, oxidation by OH radicals, and photolysis [3,7–9]. Concentrations of H_2O_2 within a range 0.01–199 μM for continental rainwater were reported in studies [2]. Generally, the levels of hydrogen peroxide are higher in the summer and lower in the winter [10–12]. It was found that levels of H_2O_2 were higher in the afternoon and low at night [10,12,13].

Different researches have studied the effects of meteorological and chemical factors that can effect the concentration of hydrogen peroxide in clouds and rainwater [2,8,10,13,14].

A number of methods have been used for the determination of hydrogen peroxide, spectrophotometry [15–17], fluorimetry [18,19], amperometry [20,21], and chemiluminescence (CL) [10,22–24]. Chemiluminescence has many advantages in comparison to other methods due to its high sensitivity, low cost, and simple instrumentation.

Chemical sensors with immobilized or solid-state reagents have been used for the determination of hydrogen peroxide; most of them are based on chemiluminescence with luminol or oxalic esters as reagents [25–27]. The Co(II) catalyzed CL reaction of luminol with hydrogen peroxide in alkaline solution has been used quite widespread for the determination of hydrogen peroxide. This reaction has been applied to the determination of gaseous hydrogen peroxide [28], hydrogen peroxide in seawater [29] and rainwater [30] with detection limits in the nanomolar and sub-nanomolar range in seawater [24].

Chemiluminescence flow sensors with immobilized luminol and Co(II) ions onto ion-exchange columns using hydrolysis technique have been applied to the determination of hydrogen peroxide in rainwater [31]. The reported detection limit was 1.2×10^{-8} mol/L.

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An approach with immobilization of the Co(II)–ethanolamine complex on a resin, Dowex-50W, lead to the construction of sensitive flow sensors for the determination of hydrogen peroxide in rainwater allowing the use of luminol in neutral or weakly alkaline solutions with a detection limit of 1×10^{-7} mol/L [32].

The use of periodate in designing sensitive and interferences free flow-through sensors for the determination of hydrogen peroxide in rainwater by immobilization of the reagents on an ion-exchange resin have been also reported by the same author [33]. The detection limit of the method was 1×10^{-7} mol/L.

Although some disadvantages of the CL method have been reported due to the interfering effect of transition metal ions [10], this reaction offers some advantages in comparison to enzyme based sensors. Enzymes are usually expensive, pH sensitive, and enzyme based biosensors are often difficult to store over a longer period.

The aim of this work was to develop low cost disposable sensors for the determination of hydrogen peroxide in rainwater based on the reaction of luminol in the presence of Co(II) ions as a catalyst. The sensors are simple and sensitive with a rapid response.

2. Experimental

2.1. Apparatus

A portable laboratory-built luminometer was employed in this work [34]. It consists of a measurement cell and the main electronic board, placed in a separate box. The body of the measurement cell was made from aluminium in two parts, a cylindrical containment for the photodiode (light-sensitive detector) and another cylindrical support for a micropipette. The latter can be mounted on the former, where light tightness and mechanical stability was achieved by using rubber sealings. The amplifiers were designed in a way that four circuits with different gains amplified simultaneously the signal obtained from the detector, thus allowing the monitoring of the signal without changing the sensitivity range of the instrument. The printed circuit boards were assembled in surface mounted technology and directly incorporated in the measurement cell in order to avoid electrical disturbances.

The photodiode was a type (OSD35 mm, Centronics) offering enhanced sensitivity in the near ultraviolet to blue range of the electromagnetic spectrum making it suitable for measurements with luminol (emission maximum at around 425 nm). The photocurrent of the photodiode was converted into four differently amplified voltages (channels) by four operational amplifiers (LTC 1050CS8, Linear Technology). The amplification ratio between ensuing channels was around 10. The main electronic board with four microprocessors (PIC 16F874, Microchip) provided digitalization (10 bits A/D converter on chip) and storage of the signals, as well as data transfer to a personal computer via a serial interface (RS 232). The tasks were performed with four microprocessors allowing the measurements of all channels simultaneously. Data were evaluated on a personal computer with a laboratory-made soft-

ware written in Visual Basic. The maximum height of the peak and the integration area were calculated by the software. Usually the two channels with highest sensitivity were used for the data evaluation.

Spectrophotometric determinations were carried out by a UV–VIS spectrophotometer (Hitachi, model V-1500, $\lambda = 200$ –1100 nm).

2.2. Reagents

A stock solution of H_2O_2 (10,000 mg/L) was prepared by diluting a standardized 30% solution of hydrogen peroxide. The solution was standardized by titration with KMnO_4 . Standard solutions of lower concentrations were prepared daily by appropriate dilution of the stock. A 56.4 mmol/L luminol solution was prepared by dissolving appropriate amount of luminol and 0.250 g of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in water to 10 mL volume. The solution was allowed to stand for 48 h before use at 4 °C in the refrigerator.

An aqueous solution of cobalt chloride (0.1 mol/L) was prepared by dissolving $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.1896 g) in water up to 50 mL.

Aqueous solutions of EDTA (0.1 mol/L) were prepared by dissolving proper amounts of $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ in water. Hydroxyethyl cellulose (HEC) was purchased from Fluka. A stock solution of potassium titanium oxalate (25.0 g) was dissolved in 400 mL of warm water. After cooling, the solution was diluted to 500 mL. The surfactant, sodium lauryl sulphate (SLS, 100 mg), was dissolved in water and made up to 10 mL.

All other chemicals were of analytical grade. Highly purified water prepared with a Milli-Q system (Brenstend, USA) was used for the preparation of solutions.

Trisodium phosphate dodecahydrate was purchased from Fluka.

2.3. Preparation of the sensor

Hydroxyethyl cellulose (150 mg) was weighed into a centrifuge tube, and then cobalt chloride solution (100 μL , 0.1 M) was added, and filled up to 8 mL with water. The solution was placed on a vertical shaker for 48 h. Afterwards 400 μL of the solution of sodium lauryl sulphate was added and the volume was adjusted to 10 mL; the final solution was shaken for additional 30 min.

Ten microlitres of polymer solution was dispensed onto a microscope cover glass (18 mm \times 18 mm, Menzel-Gläser, Germany) which was previously rinsed thoroughly with ethanol (96%). The glass was equipped with a self-adhesive reinforcement ring (polypropylene, inner diameter 5.2 mm; Avery Zweckform 5308) in order to get a defined area for the membrane formation. The membranes were dried in the drying oven at 70 °C for 4 h. They were stored in a desiccator over sodium hydroxide at room temperature protected from ambient light. Sodium hydroxide was used as a drying agent in order to prevent possible influence of gasses present in the atmosphere such as CO_2 .

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