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A chemiluminescence-based continuous flow aqueous ozone analyzer using photoactivated chromotropic acid

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Abstract

Ozone has become the oxidant of choice for water disinfection, especially in large water treatment facilities. This paper describes a fast and sensitive method for the determination of ozone content by reaction with photoactivated chromotropic acid (CA, 4,5-dihydroxynaphthalene-2,7-disulfonic acid), which results in intense chemiluminescence (CL). Freshly ozonated water from a recirculating ozonizer/reservoir is injected into a carrier stream of deionized water in the flow-injection mode. This flow mixes with a stream of photoactivated CA solution in a spiral cell placed directly on top of an inexpensive miniature (8 mm diameter active area) photomultiplier tube (PMT). Alkaline CA is photoactivated by passing it through a FEP-Teflon® coil (residence time ∼ 50 s) wrapped around a 1 W UV lamp emitting at 254 nm; without photoactivation, the signal is ∼70-fold lower. The S/N = 3 limit of detection for aqueous ozone is 3 μg l^{-1} and good response slope is obtained up to an ozone concentration of 1.4 mg l^{-1}, the highest that could be made in this study. The response obeyed a quadratic equation with $r^2 = 0.9984$. No interference from permanganate ion is observed. The proposed system was applied to the monitoring of ozonation status of a playa lake water that exhibited significant ozone demand.

Keywords: Ozone; Photoactivation; Analyzer

1. Introduction

Ozone is one of the most powerful oxidizing agents, and has become the disinfecting agent of choice for water treatment. This is especially true of larger facilities, where the scale permits economically efficient use of an unstable reagent that must be electrically generated in situ. Beyond efficient sterilization, relative to chlorine, advantages of using ozone include minimal formation of trihalomethanes and better taste and odor characteristics. Quality assurance guidelines for the practice of ozonation have been issued [1]. A compromise between ensuring disinfection/deodorization and economy (ozone disinfection is much more expensive than that using chlorine [2] and excess ozone does not lead to a stable disinfectant residual, excessive dosing is thus merely wasteful) must be attained in industrial practice. For water disinfection purposes, minimum dosages are prescribed by regulatory agencies and are expressed in terms of CT (concentration–time product), typically given in mg l^{-1} min. Kill rates depend on the specific organism and the water temperature but lowest CT doses are required for ozone compared to any other oxidant. At 15 °C, 99.9% inactivation of bacteria, vira and cysts (e.g., that of *Giardia lamblia*), respectively, require a CT of ∼0.1, 0.3 and 0.9 mg l^{-1} min [2,3]. The effect of temperature is significant: for most vira, the same degree of removal requires a ∼4 times greater CT at 5 °C than at 25 °C. For most practical cases, immediate post-treatment dissolved ozone concentrations (ozone residual) that need to be measured are below 1 mg l^{-1} [4]; commercially available DPD (*N*,*N*-diethyl-1,4-phenylenediammonium sulfate)-based colorimetric manual kits have an upper measurement

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limit of 2 mg l^{-1} [5]. Similar kits based on the bleaching of indigotrisulfonate (ITS) have an upper measurement limit of 1.6 mg l^{-1} [6].

In pure water, as used in preparing standards, iodometry and UV-absorption are still reliable and constitute recommended methods for measuring ozone concentration [1]. For real samples, the ITS method, which relies on bleaching of the dye by ozone, is the most widely used; this was originally developed by Bader and Hoigne [7–10]. Acid Chrome Violet K has also been similarly used [11]. Membrane-based electrochemical sensors, in which dissolved ozone permeates through a membrane and is then detected by its reduction current on a polarized electrode, are commercially available [12]; however, systematic studies on the response of such sensors to other strong oxidants like chlorine dioxide are not available and membrane fouling can occur. The issue of interference by other oxidants in ozone determination is an important one. While a plethora of colorimetric/bleaching-based methods variously using 1-(2-hydroxy-5-sulfophenylazo)-2-naphthol [13], Fe-Tiron [14], 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)aniline iron(II) [15] have been introduced by one author, it is very doubtful that these methods are selective over other oxidants. The benchmark method based on ITS, which has long been the standard method [16], and has been adapted in the flow analysis format [17], is known to have interferences from permanganate. This is particularly insidious because traces of Mn are present in a variety of feed water samples and are readily concerted to MnO_4^- under typical conditions of ozonation.

To avoid interference, transfer of ozone to the gas phase and monitoring of the ozone by In_2O_3 based sensors [18–20], direct gas phase UV-absorbance measurement with standard instruments used for atmospheric ozone monitoring [21] or with an evanescent wave based UV absorbance sensor [22], have all been proposed. In principle, this is attractive. However, the pitfalls can be gleaned from [21]. These authors eventually ended up exploring discrimination from permanganate either using a gas-permeable membrane or by exploiting the slightly slower decolorization of ITS by permanganate (relative to that by ozone) as the preferred approach.

Ozone is such an energetic oxidant that many of its reactions result in products in the excited state that then emit light, i.e., chemiluminescence (CL) occurs. The use of indigo derivatives for detecting gaseous ozone by CL was reported early on [23]. From this laboratory, Chung et al. [24] explored the feasibility of using the CL reaction with ITS to determine aqueous ozone. However, their study showed that MnO_4^- interferes even more in the CL-based measurement than the colorimetric approach. They also compared several other dyes for CL production with aqueous ozone and found that chromotropic acid (CA) produced four to five times greater sensitivity than ITS. Subsequently, orders of magnitude greater sensitivity were illustrated by McGowan and Pacey using luminol as the CL substrate [25]. Luminol produces CL with a great variety of oxidants. To circumvent the selectivity problems, the authors used a gas diffusion membrane. While this approach is applicable in principle, membrane transfer efficiency is temperature dependent and changes over time and calibration with standard ozone solutions is a nontrivial task. Field testing of a different membrane-based device has shown lower results compared to an alternative method possibly from adsorption of organics on the membrane [21].

Recently, we serendipitously discovered that aging of CA solutions in the presence of light can increase the CL signal from its reaction with ozone by ∼100 times. This was then used to measure gas phase ozone down to parts per trillion levels with ∼100 ms time resolution with an inexpensive miniature photomultiplier tube (PMT) [26]. It was found that great enhancement of the CL signal can be induced reproducibly by modest exposure of the CA solution to UV light en route to its reaction with ozone. Since that time, we have further discovered that unlike ITS, CA solutions produce no CL with MnO_4^- and thus provides an attractive approach to CL-based aqueous ozone determination that does not require the use of a membrane. This is the subject of the present paper.

2. Experimental

Caution: ozone is generated and used in these experiments at levels that represent considerable hazards to health. All experiments were conducted in a well-ventilated hood.

2.1. Instrumentation

A diagram of the experimental system used in this study is presented in Fig. 1. The top left depicts a home made Siemens-type ozone generator (vide infra). The ozone output is directed with a polytetrafluoroethylene (PTFE) tube (except as mentioned, all tubing in the analytical conduit was PTFE) through a fine porosity glass frit to bubble into ∼100 ml water in a reservoir maintained at $22 \pm 1\,^{\circ}C$. A pump with wetted parts of fluorocarbon and ceramic (Fluid Metering Inc., Oyster Bay, NY) aspirated the ozonized water through a timer-controlled 6-port loop injector (200 μl loop volume, reservoir–injector tube: 0.5 mm i.d., ∼40 cm long), a UV-absorbance monitor (Model 757, ABI, Ramsey, NJ, modified to contain a cell made of black Kel-F and quartz windows) and recirculated it back into the reservoir at 5 ml min^{-1} through a 1 mm i.d. tube.

The liquid phase analysis portion consists of a deionized water stream that carries the injected sample to the CL measurement cell at a relatively fast flow rate of 5 ml min^{-1} (Alitea XV peristaltic pump, http://www.flowinjection.com). The injector-CL cell tubing was composed of black PTFE, to eliminate light ingress to the cell. (While our experiments were conducted in the flow injection mode for convenience, the astute reader would appreciate that in real applications the sample stream will be directly mixed with the CA reagent in view of the PMT, the sample would not need to be injected.)

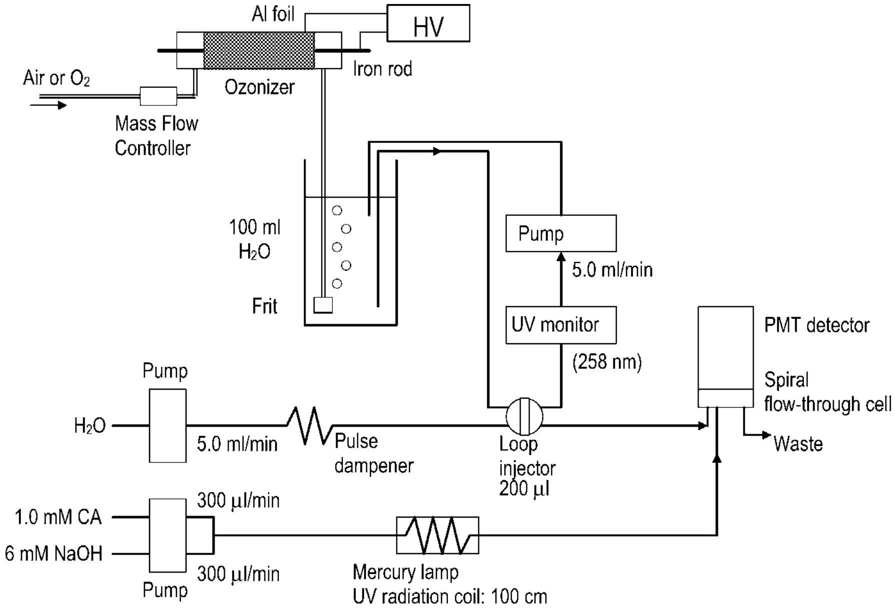

Fig. 1. Schematic diagram of the ozone generation and flow injection–chemiluminescence detection system.

A second identical peristaltic pump first merged the flow streams of 1 mM CA and 6 mM NaOH (300 µl min^{-1} each, alkaline CA is unstable over long periods and is best made in situ) and then put it through an irradiation coil (fluorinated ethylene propylene copolymer, 0.8-mm i.d., 0.05-mm wall, 100 cm long, FEP type 20 LW, Zeus Inc.) that provides a computed residence time of ∼50 s and finally through a black PTFE tube (0.8 mm i.d.) to the CL cell. The irradiation coil is wrapped around an inexpensive tubular UV lamp 8 mm in diameter and 10 cm long (BF-8100-UVC, JKL Components, Pacoima, CA) powered by a miniature power supply from the same manufacturer (BXA 12577). The lamp consumes an input power of 1 W and although the principal emission is at 254 nm, little of the emitted radiation makes it out through the glass enclosure. Overall irradiation power is thus quite limited (30 µW/cm^2, as stated by the manufacturer). The coil was wrapped on the outside with Al-foil to act as a reflector.

Except as mentioned, all liquid flow conduits were 0.50 mm in i.d. The injector-UV detector tube length (the UV detector provides the basis for the known ozone concentration), and the injector-CL cell tube length (0.80 mm i.d.) were kept as small as possible (15 and 10 cm, respectively) to minimize ozone loss.

The flow-through CL detection cell is shown in Fig. 2. It consists of two pieces, both made from polymethylmethacrylate (PMMA). A square transparent piece with a circular step (22 mm × 22 mm × ∼3 mm) fits on the PMT window, the circular protrusion fitting snug in the window recess of the PMT (see Ref. [27] for a picture of the PMT). The second piece, made from an opaque black PMMA polymer, was 22 mm × 22 mm × 7 mm containing a spiral groove of trapezoidal cross section (0.35 mm at top, 0.1 mm at bottom, 0.2 mm deep) ∼125 mm in total length (total volume ∼5.5 µl) and wholly contained within the 8 mm diameter view window of the PMT. An O-ring groove (12 mm diameter) surrounded the flow path and prevented liquid leakage. Two angled 10–32 threaded inlets, bearing respectively the sample/carrier and the reagent solution met at the center beginning of the spiral. A similarly threaded outlet aperture was provided at the end of the spiral. We had originally planned to machine the second piece from transparent PMMA as well, with heavy external silvering to provide opacity and to direct more of the generated light to the PMT. In practice, the opaque top provided more than adequate sensitivity and the mirrored alternative was not pursued. The CL-cell was installed on top of a miniature metal package PMT-based photosensor module (PSM, 22 mm × 22 mm × 60 mm, Hamamatsu H5784-00, peak response 320–500 nm) using the four M-2 threaded screw holes to anchor and seal the cell. The whole assembly was securely covered with aluminum foil to shield from external light. Except as noted, a gain control voltage of 0.925 V was applied

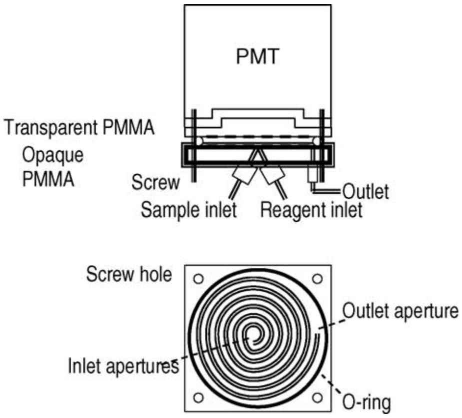

Fig. 2. Structure of the flow-through chemiluminescence detection cell, shown with the photosensor module.

to the PMT and the output was processed with a 2-s time constant RC filter prior to acquisition at 1 Hz on a laptop-type PC equipped with a 12-bit data acquisition board (PCM-DAS16D12/AO, Measurement Computing, Middleboro, MA).

A Siemens-type ozone generator was constructed from a used neon sign transformer (NST) bought from a local neon sign supply and a Liebig condenser (30 cm effective length, LG-5150-104, http://www.labdepotinc.com). An iron rod (40 cm long, 5 mm diameter) was inserted to protrude through one end of the 8 mm i.d. condenser and the outside of the condenser was wrapped with Al foil. The NST output (60 Hz, up to ∼14 kV) was applied between the iron rod and the aluminum foil. Feed gas (air or O_2) was dried and cleaned by successively passing through silica gel, activated carbon, and soda lime columns, and metered by a mass flow controller (FC-280, Tylan General, Torrance, CA). The discharge occurring between the glass surfaces results in ozone production as feed gas traverses the discharge. The ozone concentration was a function of the feed gas (air/O_2), its flow rate, and the discharge current. The last parameter was varied by feeding different primary voltages to the NST with the help of a variable transformer.

2.2. *Reagents*

Aqueous ozone was generated as shown in Fig. 1. Chromotropic acid was prepared as a 10 mM stock solution in water from the reagent grade chemical (Aldrich) and stored in foil-wrapped bottles. NaOH used was also reagent grade. Water used was distilled and deionized (18 MΩ cm).

2.3. *Standard procedure*

Feed gas passed through the ozone generator (operated typically at an applied voltage of 9 kV) at 0.70 standard liters per minute (SLPM). The ozonated water was circulated at a high flow rate to reach the injector loop in <3.8 s to minimize loss of ozone (through self-decomposition [28]). The injector was switched between load and inject positions every 10 s with a valve switching timer (DVSP-4, Valco Instruments Inc.) resulting in a sample injection every 20 s.

3. Results and discussion

3.1. *Preparation of aqueous ozone standards and its stability*

Even in deionized water ozone undergoes self-decomposition [28]; aqueous ozone solutions must therefore be freshly prepared and used essentially in situ. As shown in Fig. 1, neither the recirculation pump nor the carrier pump contacted the aqueous ozone solution before it was used. Experiments showed that at recirculation and carrier flows $\geq 3.0\ \mathrm{ml\ min^{-1}}$, ozone loss was negligible and stable responses were obtained. We henceforth used recirculation and carrier flow rates of $5.0\ \mathrm{ml\ min^{-1}}$ each.

Ozone concentration in purified water was determined by from the absorbance at 258 nm; ε_{258} was taken to be $3100\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ [28]. The maximum dissolved ozone concentration generated in this study was $1.4\ \mathrm{mg\ l^{-1}}$ (∼30 μM); as indicated in Section 1, this adequately covers the need for ozone measurement in water treatment applications. The Henry's law constant for the dissolution of ozone in water is $0.015\ \mathrm{M\ atm^{-1}}$ at 293 K [29].

3.2. *UV irradiation to sensitize the chromotropic acid chemiluminescence reaction*

Among eight dyes examined, CA was previously found to provide the best sensitivity [24]. Very recently, we found that the CL reaction sensitivity with CA can be vastly increased further by aging in light or better, by a short reproducible UV exposure [26]. Alkaline CA solution passed through a semi-UV-transparent FEP Teflon coil wrapped around a UV lamp resulted in a photoactivated CA solution that produced ozone-reaction CL intensity ∼100 times greater than virgin CA solution; this was used for the fast sensitive measurement of gaseous ozone [26]. We exploited these findings to construct a aqueous ozone monitoring system except that a much lower power and low-cost UV-lamp and a longer irradiation coil was used; this combination produced a ∼70× sensitivity gain over the use of virgin CA and adequate sensitivity for aqueous ozone measurement in water ozonation applications.

Typical CL responses to aqueous ozone with and without UV radiation are shown in Fig. 3. The high voltage was turned on to generate ozone during the intervals 1–6 and 11–16 min in (a) and (b), which respectively represent experiments with the UV lamp being on and off. It takes ∼2 min to saturate the water with ozone and result in a stable signal. Similarly, it took ∼4 min for the ozone signal to disappear after the high voltage was turned off (gas sparging of ozone reservoir was continued during this period). When the CA solution is used without photoactivation, the signal is weak; the inset in

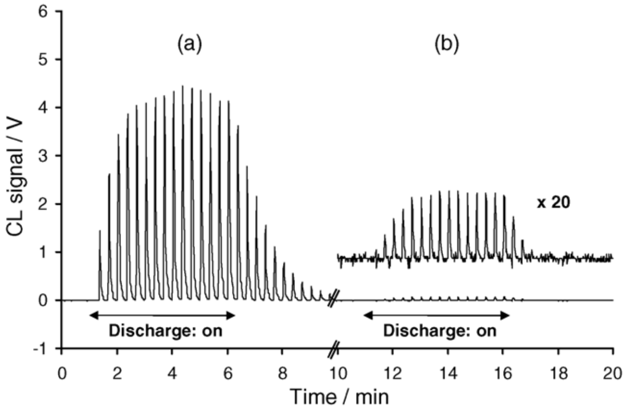

Fig. 3. Typical system output for $1.3\ \mathrm{mg\ l^{-1}}$ aqueous ozone, discharge voltage: 12 kV. Photoactivation of CA solution: (a) on and (b) off.

Fig. 3(b) is shown after 20-fold amplification. With the photoactivation operative, the relatively low cost PMT provides excellent sensitivity.

Effect of the radiation coil length on the sensitivity of the CL reaction was examined. From a coil length of 25–100 cm (which length completely covered the tube), the sensitivity increased linearly:

$$\text{CL signal (V)} = 0.0235 \times \text{irradiation coil length (cm)} \\ \text{X} - 0.383, \quad r^2 = 0.9980\ldots \qquad (1)$$

We did briefly examine a more powerful low-pressure Hg lamp (Analamp 80-1178-01, BHK Inc., Claremont, CA), the CL intensity with a 150 cm coil on this lamp was 4× greater than our default conditions using the UV-8100C lamp (~US$ 20, including power supply). Given the specific needs of residual ozone monitoring in water treatment applications, we did not deem the use of the more powerful lamp worthwhile.

3.3. Optimization of operational parameters

3.3.1. pH

In previous experiments dealing with the measurement of gaseous ozone in air [26]; the CL intensity reached a plateau value at pH ≥ 11.5 of the CA solution (corresponding to ~3 mM NaOH in solution). In the present case, the reagent stream is diluted ~10× by the sample stream in the detection cell; the effect of pH was hence studied again with the NaOH concentration ranging from 0.1 to 100 mM. The CL intensity increased with increasing pH and reached a plateau at [NaOH] ≥1 mM in the mixed reagent stream. The slightly lower [NaOH] content at which the plateau value is reached in the present case suggests that in the gaseous ozone experiments CO_2 present in the air may have played a role. The relative constancy of the optimum pH, despite the large dilution in the present case, also suggests that the reaction is extremely rapid and takes place at the interface of the two streams. In any case, it is prudent to allow for some buffer capacity of the aqueous sample and we have, therefore, continued to operate at a final NaOH concentration of 3 mM in the mixed stream.

3.3.2. CA concentration

Concentrations of CA ranging from 25 to 2500 μM (final concentration in mixed reagent) were examined at pH 11.5; the results are shown in Fig. 4. The maximum CL response was obtained at 0.5 mM CA. The concentration of the photoactivated species produced by the radiation is too low at low concentrations of CA. At high concentrations of CA, the solution in the center of the tube is not efficiently photoexposed because of self-filtering but subsequently dilutes the active ingredient. Based on these results, a CA concentration of 0.5 mM was chosen for further experiments.

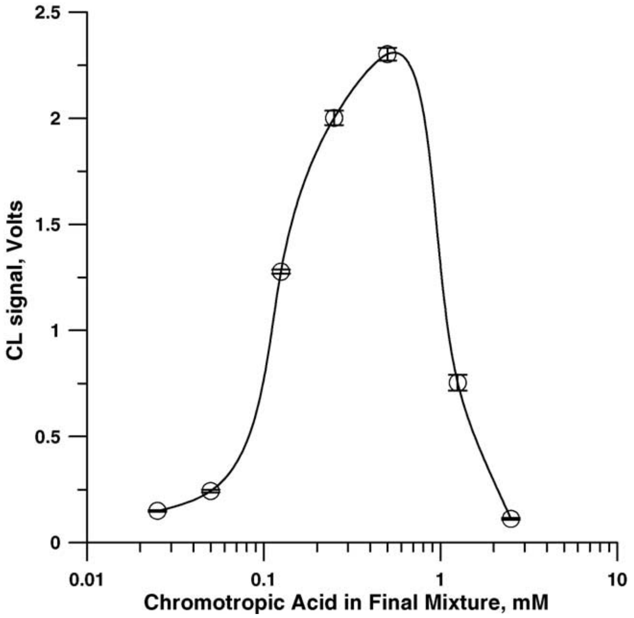

Fig. 4. Effect of chromotropic acid concentration on CL response.

3.3.3. Reagent flow rate

The flow rate of the reagent solutions, CA and NaOH, affect the photoactivation period, given a definite irradiation coil volume. However, given definite reagent concentrations, too low a flow rate will result in inadequate reagent availability. Under the optimized conditions described above, the maximum CL intensity was obtained in the 300–400 μl min^{-1} flow rate range; 300 μl min^{-1} flow rates for each reagent were henceforth chosen.

3.3.4. PMT gain

The maximum permissible gain control voltage of the particular PMT used is 1 V. Based on observed response between control voltages between 0.800 and 0.975 V, we chose a control voltage of 0.925 V, which provided good sensitivity and a stable baseline. No additional secondary amplification was used in this work.

3.4. Determination range, response and reproducibility

Varying the discharge voltage and the source gas changes the gaseous ozone concentration and hence the corresponding concentration in the ozonated water. Fig. 5(a) shows how the generated ozone concentration changes with the discharge voltage with air and ozone as the feed gas. At applied voltages <6 kV, no discharge took place and ozone was not generated. At higher voltages, increasing amounts of ozone were produced with increasing voltage, asymptotically approaching plateau values. The response behavior for aqueous ozone in the present CA–CL system is shown in Fig. 5 (b). Up to an ozone concentration of 0.8 mg l^{-1}, the response is adequately described by a linear equation ($r^2 = 0.9906$). We believe that the slight curvature at higher concentrations is due

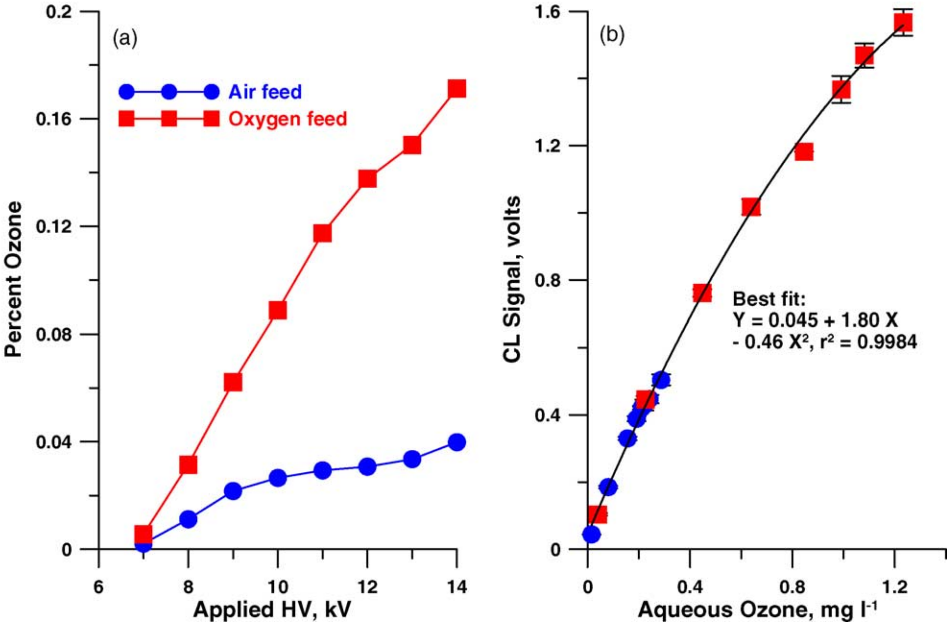

Fig. 5. (a) Generated ozone concentration as a function of discharge voltage, feed 0.7 SLPM, (%) O_3 computed from absorbance of water in equilibrium and $K_H = 0.015\,M^{-1}\,atm^{-1}$ and (b) CL response as a function of aqueous ozone, the best fit quadratic equation describing the response is shown. The error bars depict ±1S.D.

to an inadequate amount of photoactivated CA, which can be changed through a change in the experimental parameters, e.g. the UV lamp intensity. However, the availability of inexpensive microprocessors that are imbedded in virtually all present-day instrumentation and their ability to handle quadratic responses (as long as there is an adequate slope), makes it superfluous in our judgment to strive for a perfectly linear response. It will also be observed that the calibration behavior is identical whether air or O_2 is as the feed gas, although obviously the use of O_2 results much greater (3.5–4×) concentration of generated O_3.

The mass of ozone generated is essentially constant at the same discharge voltage. The concentration of ozone in the output gas thus, varies inversely with the gas flow rate. The CL signal elicited by the sample water, which in this range is linearly related to the aqueous ozone concentration (and hence by Henry's law to the gaseous ozone concentration), is shown in Fig. 6 as a function of the reciprocal gas flow rate. The linear relationship establishes that ozone generation is inversely proportional to the flow rate of the feed gas.

Reproducibility was examined with 30 successive injections using $1.3\,mg\,l^{-1}$ aqueous ozone; the relative S.D. was 1.8%. This of course reflects variations in the reproducibility of the ozone generation system as well. We did not attempt to push the limits of detection (LOD) in this work because the levels attained were adequate for practical application. Nevertheless, the lowest concentration of aqueous ozone in Fig. 5 was $15\,\mu g\,l^{-1}$. The noise at this level was bit noise from the A/D board and would doubtless have been lower if a secondary amplifier was used. Regardless, if we take the A/D noise as the real noise and consider the signal for the $15\,\mu g\,l^{-1}$ sample, we calculate an S/N = 3 LOD of $3\,\mu g\,l^{-1}$.

No opacity of the CL cell made of PMMA developed over several months of use. In this and other experiments, we have found PMMA to be resistant to aqueous ozone.

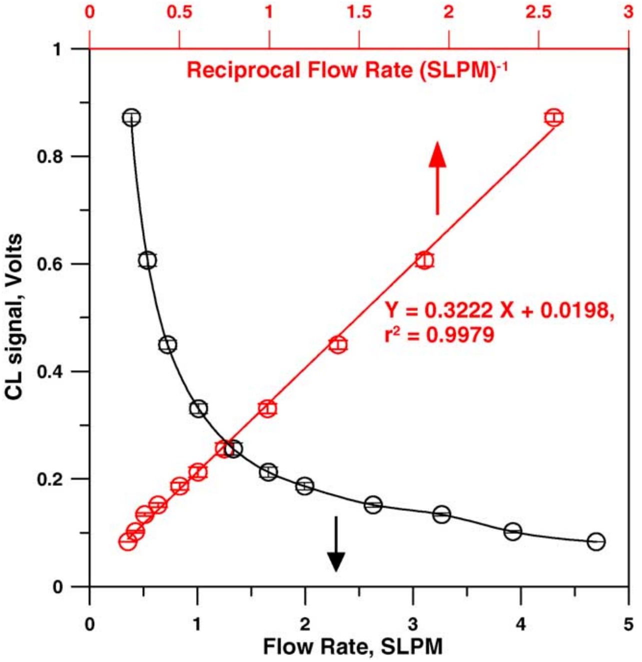

Fig. 6. The CL signal of ozonated water (12 kV applied) vs. the ozonizer gas flow rate (bottom abscissa). The straight line depicts the best linear fit against the reciprocal flow rate (top abscissa). The error bars depict ±1S.D.

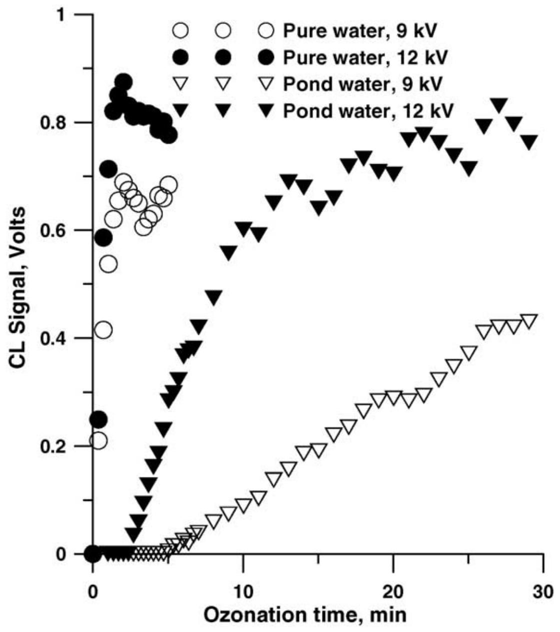

Fig. 7. Monitoring of residual ozone with pure water or pond water used as sample.

3.5. Interferences

In water treatment plants where ozone is used as the primary disinfectant, auxiliary oxidants such as chloramine are only well added after ozonation to maintain a disinfectant residual. The primary concern for interference is thus from secondary oxidants, notably MnO_4^-, which form as a result of ozonation. A solution of potassium permanganate was introduced into the detection cell instead of the aqueous ozone. No chemiluminescence was observed with 0.1 mM or 1.0 mM $KMnO_4$, even when the permanganate solution was made acidic (0.01 M H_2SO_4). Therefore, the CL reaction with photoactivated chromotropic acid has no interference from MnO_4^- and a gas-diffusion or other analyte separation step is not necessary. The present approach would provide a reliable Mn-interference free instrument for the measurement of aqueous ozone in water disinfection applications.

3.6. Ozonation of a sample with high chemical oxygen demand

The system was applied to the monitoring of ozonation status of a sample with high ozone demand. Water from a playa lake (Maxey park pond, Lubbock, TX) was sampled in February 2003. The sample was filtered with a coarse fiber filter and aliquots were ozonated at two different ozone concentrations (discharge voltage 9 and 12 kV, respectively). The results are shown in Fig. 7.

When pure water was used as the sample, within the fluctuations observed in the experiment, saturation occurred within 2 min (gas flow rate 0.7 SLPM). Note that the saturation ozone levels were different for the two different discharge voltages because the generated gaseous ozone concentrations are different. On the other hand, it took approximately >20 min for the pond water sample at 12 kV applied voltage to reach the corresponding saturation value. At 9 kV, the corresponding saturation value was not reached by 30 min. It is also seen that that ozone was completely consumed in the initial stages of ozonation of the pond water. The data suggests that the rate of ozone consumption of such samples is dependent on the ozone concentration on a more than first order basis, such that it is more economic (in terms of total amount of ozone consumed) to use a higher rather than a lower concentration of ozone.

As may be expected, the pond water had significant ultraviolet absorbance at 258 nm (much higher relative to absorbance from saturation levels of dissolved ozone). This absorbance decreased during ozonation, suggesting oxidative destruction of some of the compounds responsible for absorption. In the higher level ozonation case (12 kV) even after complete ozonation, when the dissolved ozone level was the same as the saturation level in pure water, A_{258} remained much higher than that for pure water, suggesting UV-absorbing compounds that are stable to ozone remain.

4. Conclusion

A highly-sensitive continuous determination method for aqueous ozone is proposed. The method relies on the CL reaction of aqueous ozone with chromotropic acid. Reproducible on-line photoactivation of choromotropic acid greatly increases the sensitivity. A limit of detection of 3 $\mu g\,l^{-1}$ and a determination range at least up to 1.4 $mg\,l^{-1}$ were attainable.

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