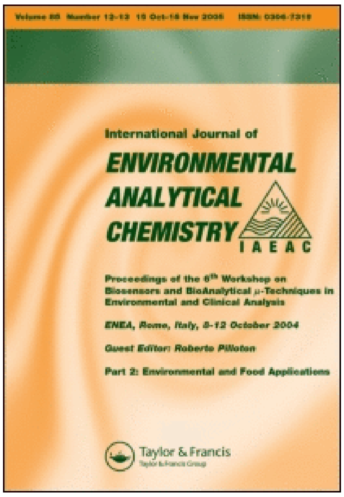

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DETERMINATION OF Fe(II) AND H_2O_2 IN ATMOSPHERIC LIQUID WATER BY PEROXYOXALATE CHEMILUMINESCENCE

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The chemiluminescence reaction of oxygen with bis(2,4,6-trichlorophenyl)oxalate (TCPO) in the presence of Fe(II) has been investigated under the analytical and mechanistic point of view. Its suitability for the determination of Fe(II) as well as H_2O_2 in atmospheric liquid water by using a new static fiberoptic luminometer (FOL) and a flow-injection analysis (FIA) system is demonstrated. Results obtained so far suggest, that chemiluminescence is generated by superoxide ion (O_2^-) produced by autoxidation of Fe(II) through dissolved oxygen. The analytical method based on this reaction shows high sensitivity and detection limits below 100 nM Fe(II). Its application to rain water analysis indicates that Fe(II) and H_2O_2 may be coexistent in the atmospheric liquid phase.

KEY WORDS: Peroxyoxalate chemiluminescence, superoxide radical, speciation, iron(II), rain water.

INTRODUCTION

It is well known that H_2O_2 and iron in its different oxidation states are important components in the chemistry of the atmospheric liquid phase, for example both are involved in possible oxidation reactions of S(IV) species to sulfuric acid[1-7]. Recent investigations indicate, that H_2O_2 and Fe(II) may be produced simultaneously by photoreduction of Fe(III) complexes with organic ligands[8]. Indeed, H_2O_2 production was observed during irradiation of authentic cloud and fog water samples with sunlight[9,10]. In contrast, H_2O_2 and Fe(II) are expected to react with each other according to Fenton's reaction. These interdependencies mean that the chemical characterization of atmospheric liquid water requires methods that allow the determination of H_2O_2 and a speciation of iron at least with respect to its oxidation states. For the latter task, several methods have been reported based on chemiluminescence[11] or absorbance[12-17] measurements, sometimes in combination with preconcentration[11,13] and separation[16,17] techniques.

Sensitive determination of H_2O_2 in atmospheric liquid water has been carried out mostly by an enzymatic catalyzed reaction yielding a highly fluorescent product[18] or by measuring the chemiluminescence (CL) occuring during the reaction of aryloxalates with hydrogen peroxide in presence of a sensitizing fluorophore, known as "peroxyoxalate-CL" (PO-CL)[19-22]. Other analytical applications of this reaction include determination of fluorophores after chromatographic separation[23-25] as well as methods for determination of phenolic compounds[26,27] and free oxalate[28].

The mechanism of the PO-CL proved to be complex and is not completely clarified. Considerable progress has been achieved in the last few years leading to mechanistic models involving multiple intermediates generated in the course of the reaction[29,30]. More recently it has been shown, that PO-CL can be generated also in the absence of H_2O_2 either electrochemically[31] or by laser light stimulation[32,33]. The study presented in this paper was initiated by the observation, that Fe(II) interferes in the H_2O_2 assay reported earlier[22], leading to strong CL under certain circumstances, and thus offering the possibility of being used as an analytical tool for the selective determination of Fe(II). Therefore we have studied this novel type of PO-CL with regard to its applicability for the determination of Fe(II) in atmospheric liquid water.

EXPERIMENTAL

Apparatus

Most investigations were carried out using a specially designed fiber optic luminometer (FOL, Figure 1) allowing batch experiments and time resolved CL recording.The FOL uses standard disposable polypropylene reaction tubes (Eppendorf) as the reaction compartment. Sample and buffer solutions (each 20 µL) are dispensed separated from each other into the lid of such a tube, the reagent solution is injected into the bottom. The tube is closed and inserted into a light tight housing, which is mounted on a turnable rod driven by a spring. An optical fiber bundle, pressed against the lid of the reaction tube, connects the reaction compartment with the detector system consisting of a photomultiplier (Hamamatsu R268), amplifier module (Dr. Seitner 1030 FK-E) and a

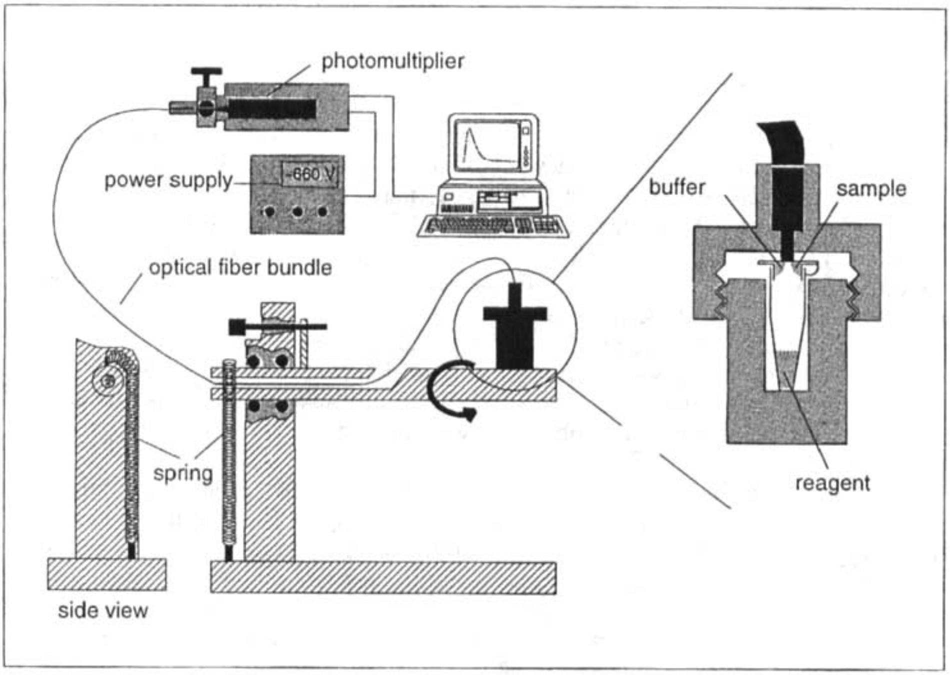

Figure 1 Schematic view of the fiber optic luminometer and its components.

home made power supply. Turning the tube by 180° causes the reagent solution to fall into the lid where it mixes with the buffer and sample droplets, generating the CL. In the case of time resolved measurements signals are recorded at 50 s^{-1} by an A/D interface (Bischoff, Leonberg) connected to a personal computer; data are processed by software usually employed for chromatograms (Hyperdata Chromsoft). For most of the measurements reported, only the peak CL intensity was measured using the peakhold option of a standard voltmeter. After completion of the measurement, the reaction tube was rejected or cleaned by carefully sucking it dry. In the latter case the tubes were used 30 to 50 times until they became visually turbid from scratches produced by the capillary used for sucking out the solutions.

Reagents and solutions

All chemicals were of analytical grade and used as purchased exept for the acetone that served as a solvent for the reagent solution. Acetone p.a. (Merck 14) had to be dried further by standing over molecular sieve (Fluka 69829 and Fluka 69832 1:10) for at least 12 h. All aqueous solutions were prepared using deionized destilled water.

CL-Reagent: The reagent solution consisted of 150 mg (334 μmol) of TCPO (Fluka 75707) and 10 mg (39,6 μmol) of perylene (Merck 820969) dissolved in 1 L of acetone treated as mentioned above.

Buffers: Borate buffer solutions (0.2 M) in the pH range of 7.8 to 8.6 were obtained by diluting a solution of 12.32 g H_3BO_3 (Fluka 15660) in 1 L of 1 M NaOH with 0.1 M HCL according to the prescriptions given by Sörensen[34] (pH 7.8 : 53,4 mL of borate solution + 46,6 mL of HCl).

In the same manner phosphate buffer solutions of different pH were prepared by mixing different volumes of stock solutions of HPO_4^{2-} (0.2 M, 35.6 g/L $Na_2HPO_4 \cdot 2\ H_2O$, Merck 6580) and of $H_2PO_4^-$ (0.2 M, 27,2 g/L KH_2PO_4, Fluka 60230).

Standards: Standard solutions of H_2O_2 (0.1 M) were prepared by dilution from 30% hydrogen peroxide (Merck 8797), and Fe(II) standard solution was obtained by dissolving ca. 9 g of $(NH_4)_2Fe(SO_4)_2$ (Merck 3793) in 250 mL of water. Both solutions were standardized regularly by titration with a 0.02 M $KMnO_4$ solution of known titer (Merck 9935). Fe(II) working standards were prepared by appropriate dilution with 1 mM HCl to avoid losses due to autoxidation, which might occur in solutions of higher pH.

Miscellaneous: Catalase (Fluka 60640, 274000 U/mL) and superoxide dismutase (Boehringer 567680) were diluted with water to the activities needed; 1,10-phenanthroline (Merck 7225) was used dissolved in water (1% w/w, 55.5 mM).

RESULTS AND DISCUSSION

Construction and performance of the fiberoptic luminometer (FOL)

Although better detection limits and reproducibility can usually be obtained with a flow injection system[35], static luminometers offer the advantage of easier variation of reaction conditions (pH and composition of buffer solution, relation between sample, buffer and reagent volumes). However, commonly used luminometers are suitable only for relatively slow reactions[36] due to the time needed to mix the reactants that are usually applied in quite large volumes. Furthermore, in the case of the CL of the Fe(II)/TCPO system, all components involved (sample, buffer and reagent) have to be held separated from each other until the reaction is started. Otherwise Fe(II) is subjected to accelerated autoxidation[37] (if sample and alkaline buffer are mixed) or the TCPO reagent is hydrolysed on mixing with an aqueous solution. These demands – low volumes to achieve short mixing times and initial separation of the solutions – are fulfilled by the specially designed fiberoptic luminometer.

The progress of the CL reaction can be followed from the start of the mixing process as shown in Figure 2 for CL signals obtained with different concentrations of Fe(II). A typical single peak shape is observed as expected for peroxyoxalate CL performed in mixed aqueous/organic solvents[29]. According to Orlovic *et al.*[30] the time dependence of CL intensity can be modeled by assuming two consecutive pseudo first order reactions ("pooled intermediates model"):

$$R \xrightarrow{r} I \xrightarrow{f} P \qquad (1)$$

R. I, P : pools of reactants, intermediates and products, resp.
r. f : pseudo first order rate constants (rise and fall)

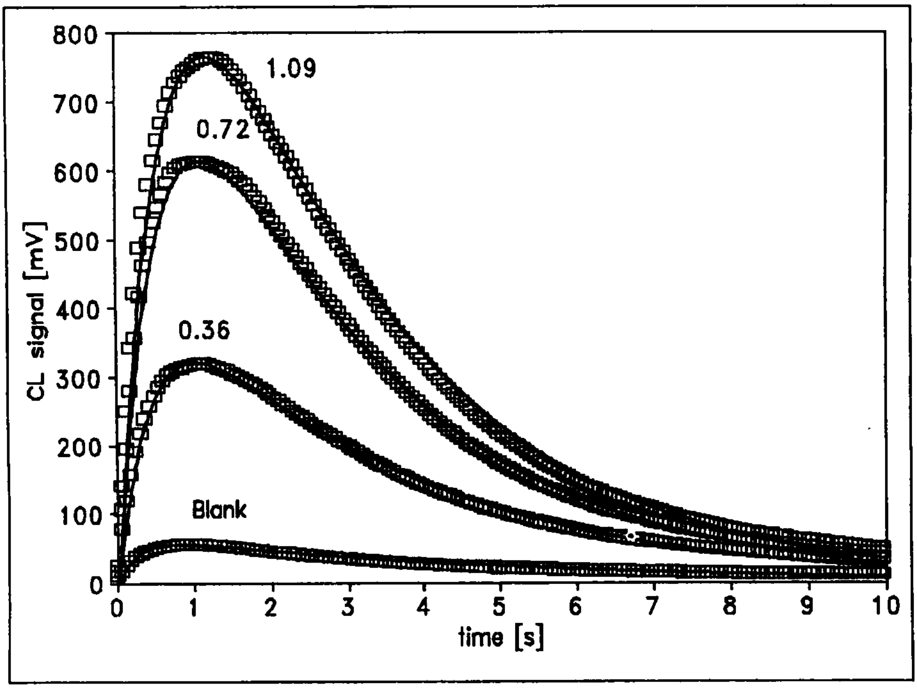

Figure 2 Time resolved CL measurements made with the FOL for solutions of different Fe(II) concentrations [μM]. Lines are results of calculations according to the pooled intermediates model. Conditions: 20 μL sample solution, 20 μL buffer (phosphate, pH 9), 300 μL reagent solution.

If the CL intensity at time t, CL(t), is proportional to the concentration of intermediates, I, a kinetic expression is obtained[29]

$$CL(t) = \{M * r/(f-r)\}\ \{e^{-rt} - e^{-ft}\} \qquad M = \text{const.} \tag{2}$$

where the constant M corresponds to the maximum intensity achieved when the reactants are completely converted into chemiluminescent intermediates. M is connected to the measured CL maximum by

$$CL_{max} = M * (f/r)^{(f/|r-f|)} \tag{3}$$

Combining eq. 2 and eq. 3 under elimination of M and evaluating the rate constant f from a ln(CL(t)) vs. t plot of the experimental data, a least squares fit to the data points is obtained by variation of the residual unknown parameter r. These fits are also shown as lines in Figure 2; good agreement with the experimental data is obtained especially in the first seconds of the reaction indicating rapid and homogeneous mixing of the components during FOL measurements. With longer reaction time (> 10 s) the calculated intensities deviate significantly from the experimental data. This may be the result of some heterogeneous processes arising through the cristallization of buffer salts which are less soluble in the acetone/water mixture; however, a perfect fit over the whole reaction period would be surprising in view of the mechanistic simplifications used in the pooled intermediate model.

Conditions of analysis

The FOL was used to investigate the influence of buffer composition, pH, concentration of TCPO/perylene and acetone/water ratio on the sensitivity of H_2O_2 and Fe(II) determinations.

The analytical sensitivity was nearly equal for both analytes when using borate buffer at a pH of 7.8. This is in agreement with results reported earlier for H_2O_2 FIA measurements[22]. However, Fe(II) could be determined with much better sensitivity in phosphate buffer, which only led to low CL intensities in the case of H_2O_2. Figure 3 shows the influence of the pH of phosphate buffer solution on the relative CL intensities measured with test solutions of 0.8 μM Fe(II) and 2000 μm H_2O_2. For Fe(II) the optimum pH was found in the range between 8 and 9, while the maximum signal for H_2O_2 was obtained at pH 11, which is considerably higher than in the case of borate buffer. Consequently, a borate buffer of pH 7.8 was chosen for H_2O_2 determination and a 0.2 M Na_2HPO_4 solution of pH 9 for the analysis of the Fe(II) test solutions.

The influence of the volume ratio of organic and aqueous phase was investigated by varying the reagent volume at fixed sample and buffer volumes of 20 μL each. From the data presented in Figure 4, a reagent volume of 150 μL appeared to be suitable for further experiments with H_2O_2, while 300 μL of reagent solution proved to be preferable for Fe(II) determinations. It has to be mentioned that under the conditions chosen for Fe(II) a similar dependence of blank CL on the amount of reagent solution has been observed. This means that only the sensitivity, but not the limit of detection (LOD) is improved with increasing volume of reagent solution.

Finally, the effects of different concentrations of TCPO and perylene were investigated. As expected, sensitivity increases with increasing concentrations of either component (Figure 5a and 5b); however, the signal/blank ratio — taken as an indicator

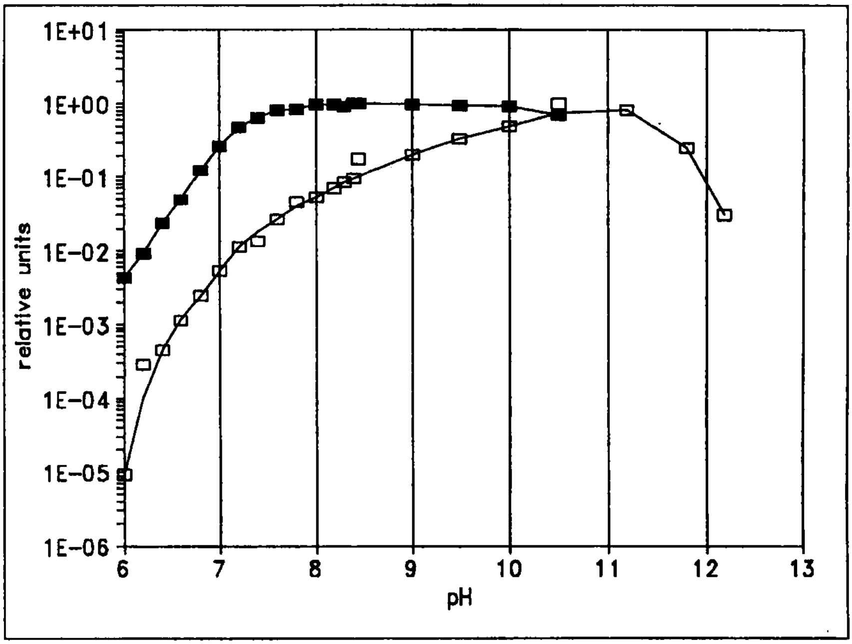

Figure 3 Dependence of CL intensity on pH of the phosphate buffer solution. ■: 0.8 µM Fe(II), □: 2 mM H_2O_2.

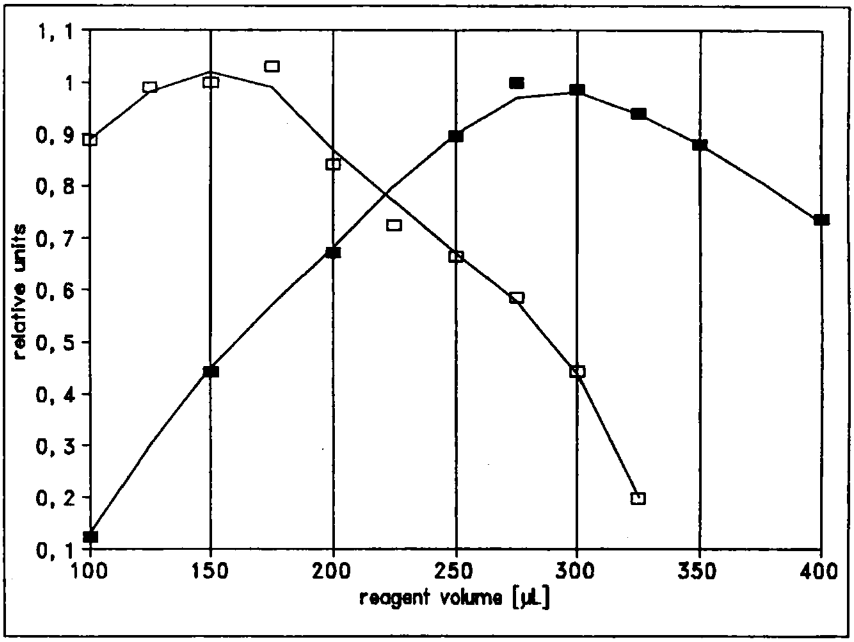

Figure 4 Influence of reagent volume on the CL intensity. Sample and buffer volumes were held constant at 20 µL. ■: 0.8 µM Fe(II), phosphate buffer □: 3,9 µM H_2O_2, borate buffer.

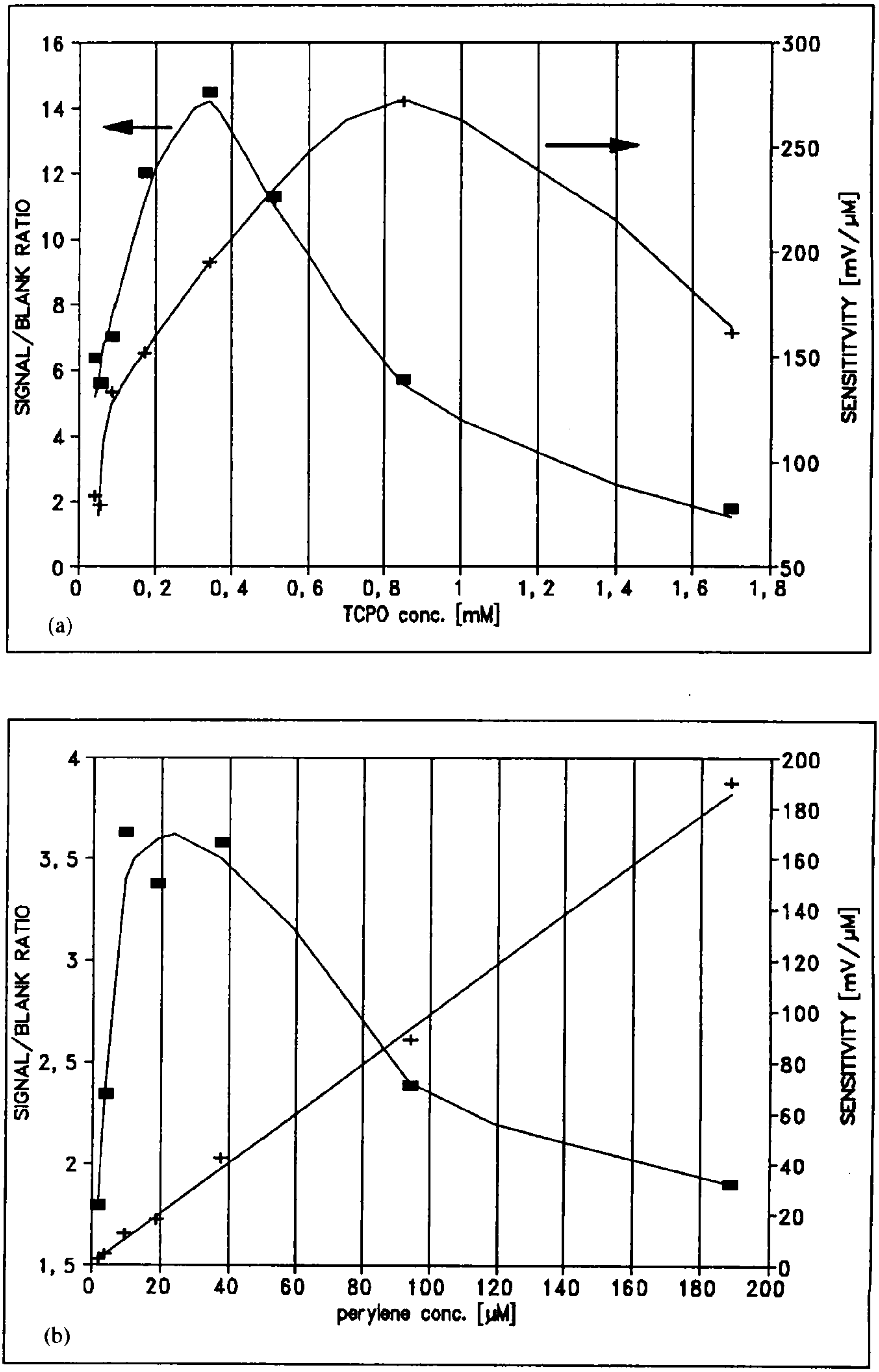

Figure 5a and 5b: Variation of CL intensity and signal/blank ratio with concentration of a) TCPO ([perylene] = const. = 190 µM) and b) perylene ([TCPO] = const. = 1,7 mM). [Fe(II)]: 0.8 µM.

of LOD — shows maxima at relatively low concentrations of perylene and medium concentrations of TCPO. Based on these maxima the composition of the reagent solution was set to the concentrations mentioned under "Experimental". The decrease in sensitivity at high TCPO contents can be explained by precipitation of reaction components in the resulting acetone/water mixture.

Selectivity

As mentioned before, the sensitivities for Fe(II) and H_2O_2 were nearly equal if measured in the presence of borate buffer. Thus it would not be possible to distinguish between Fe(II) and H_2O_2 in unknown samples. In contrast, the use of phosphate buffer results in a Fe(II)/H_2O_2 selectivity factor of about 400. However, this value is not high enough for reliable analysis of atmospheric water, if one takes into consideration that the concentration of iron found in rain water is in the order of 1 µM[3], whereas H_2O_2 may exhibit concentrations of more than 100 µM[4]. Furthermore, CL signals obtained in experiments where both analytes were present in the reaction mixture simultaneously, were less than those expected for the sum of CL intensities of the corresponding single component solutions. This means that losses of analytes occur due to Fenton's reaction, which is known to be accelerated in alcaline solution. Therefore, additional steps had to be taken to enhance selectivity.

Hydrogen peroxide can be removed easily by adding the enzyme catalase to the sample containing hydrogen peroxide and Fe(II). A slight decrease of Fe(II)-CL was observed with increasing activities of the enzyme; however, 500 U/mL of catalase present in the sample proved to be enough to achieve determination of 0.8 µM Fe(II) in presence of 120 µM H_2O_2 without significant losses.

For the purpose of suppressing the Fe(II) interference in the determination of H_2O_2. 2,2'-bipyridine (dipy) and 1,10-phenanthroline (phen) were tested as masking agents. Applied in concentrations of 1 mM neither influenced the CL of test solutions containing only H_2O_2; phen was chosen due to higher stability of the complex formed. In the presence of Fe(II), significant quenching of H_2O_2-CL was observed only at Fe(II) concentrations above 50 µM. Different reaction tubes had to be applied for Fe(II) and H_2O_2 determinations, because of interferences caused by residues of catalase and phen, respectively.

Further experiments were done to evaluate the influence of organic peroxides that have been found in atmospheric liquid water[38], and of metal ions. While methylhydroperoxide (MeOOH) exhibited CL signals only at millimolar concentrations, bis(hydroxymethyl)peroxide (BHMP) could not been distinguished from equimolar solutions of H_2O_2. Obviously BHMP is hydrolyzed rapidly in the alkaline reaction medium to formaldehyde and H_2O_2, which then reacts with TCPO.

The influence of metal ions — Cu(II), Ni(II), Al(III), Pb(II), Mn(II), Zn(II) — was investigated by adding them to a test solution containing 0.6 µM Fe(II). The concentrations of the ions tested ranged from 6 µM to 150 µM. Only Cu(II) showed a significant effect by quenching the CL intensity to 25% of the non-spiked Fe(II) solution. This is most probably due to the oxidation of Fe(II) shown in eq. 4. However, the mean concentrations of Cu(II) found in atmospheric liquid water are 2 orders of magnitude less than those of iron[3]. Therefore we conclude, that the interference of Cu(II) is not important for the intended analysis of rain water.

$$Fe^{2+} + Cu^{2+} \rightarrow Fe^{3+} + Cu^{+} \qquad (4)$$

Reproducibility and calibration plot

Figure 6 shows results of repeated measurements of samples taken from the same test solution containing 0.6 μM Fe(II) and 548 U/mL catalase over a period of 50 minutes. The slight overall decrease in signal intensity is caused by slow autoxidation of Fe(II), although the test solution had been acidified. The overall relative standard deviation obtained by treating the data shown in Figure 6 as a series of triple determinations is 3.4%. In Figure 7 log-log calibration plots for Fe(II) and H_2O_2 analyses are given. The calibration curve for Fe(II) turned out to be non-linear. Linearity may be assumed only up to 10 μM (regression coefficient 0.9991), whereas H_2O_2 can be determined linearly over at least 4 orders of magnitude in concentration (r = 0.9995). It should be emphasized here that the sensitivity, i.e. the slope of the calibration plot, depends on the photomultiplier amplification as determined by the voltage applied. The latter was held rather low so as to collect data at a single voltage even at high concentrations. With higher amplification, concentrations well below 1 μM are detectable. The LOD depended on the intensity and variation of blank signals (1 mM HCl or pure water, resp.) and were 0.052 μM for Fe(II) and 0.6 μM for H_2O_2 (3 σ, n = 5).

Mechanistic considerations

The nonlinearity of the Fe(II) calibration curve is an indicator of significant differences between the reaction mechanisms of the H_2O_2/TCPO and the Fe(II)/TCPO system. Thus

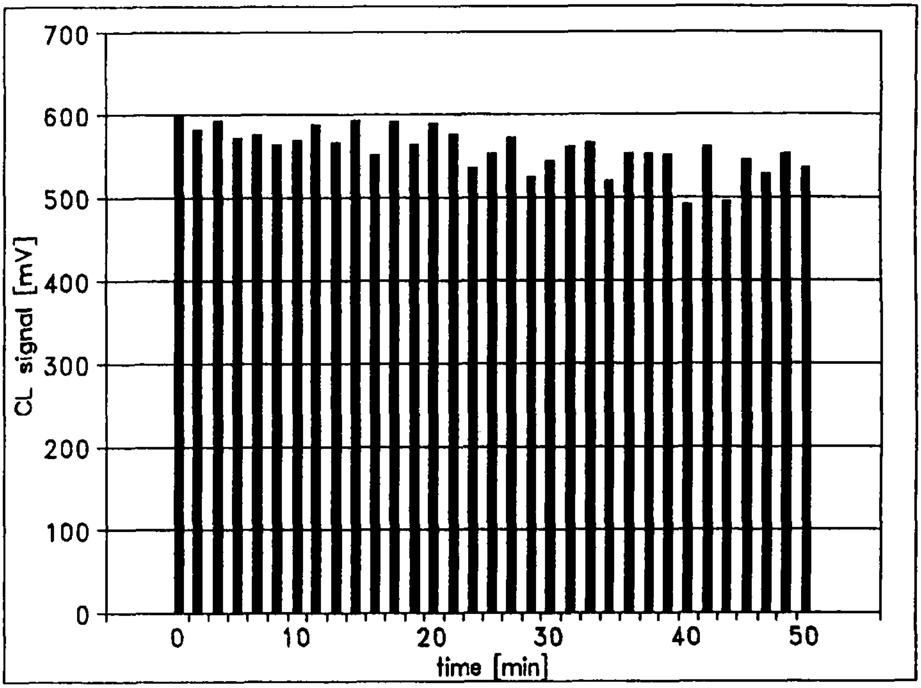

Figure 6 Reproducibility of CL signals obtained from repeatedly measured Fe(II) test solutions containing 548 U/mL catalase. [Fe(II)]: 0.6 μM.

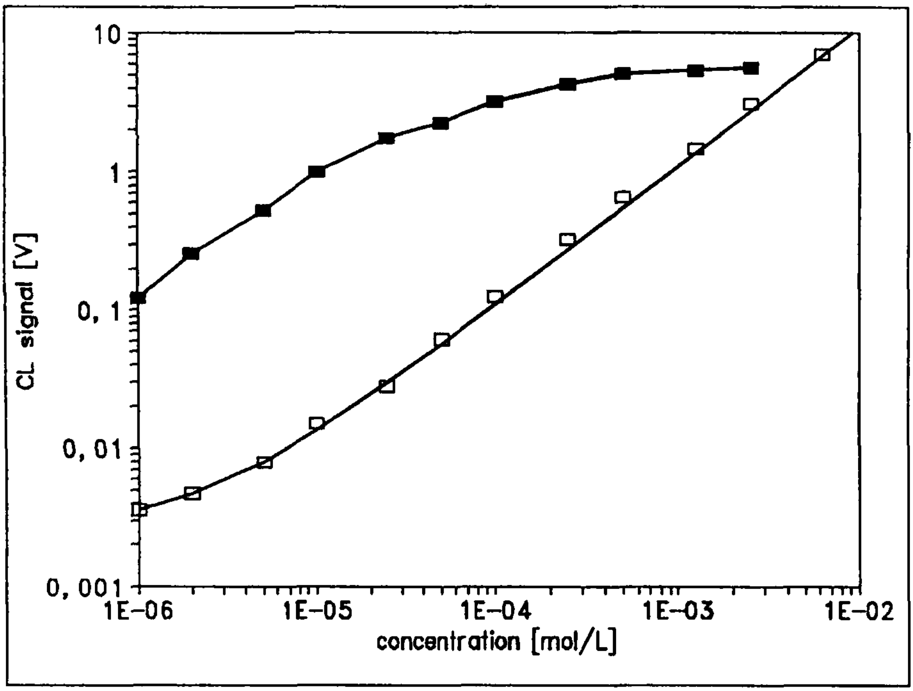

Figure 7 Log-log calibration plots for FOL measurements. ■: Fe(II), phosphate buffer □: H_2O_2, borate buffer.

we tried to obtain some insight into possible reaction paths of the Fe(II)-CL reaction. Preliminary experiments revealed that oxygen is a necessary component in this reaction system, because the CL intensity decreased significantly when the solutions used were purged with nitrogen. Therefore we concluded that some intermediate formed by reaction of Fe(II) with oxygen is the chemiluminescence generating species rather than Fe(II) itself. Three highly reactive oxygen species, superoxide (O_2^-), H_2O_2 and the OH-radical, are formed during Fe(II) autoxidation[37] by consecutive and parallel reactions:

$$\begin{aligned}
&(a)\quad Fe^{2+} + O_2 \leftrightarrows Fe^{3+} + O_2^{-}\cdot \\
&(b)\quad Fe^{2+} + O_2^{-}\cdot + 2H_2O \rightarrow Fe^{3+} + H_2O_2 + 2\,OH^- \\
&(c)\quad Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \\
&(d)\quad Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^-
\end{aligned} \qquad (5)$$

H_2O_2 most probably is not the intermediate in question, because addition of catalase resulted only in a minor decrease of the CL, as mentioned above. This observation also excludes OH radical as relevant species because it is produced from H_2O_2 via reaction 5,c). In contrast, addition of superoxide dismutase to the buffer solution caused a dramatic decrease of Fe(II)-CL (Figure 8). Therefore, it is suggested that the superoxide radical ion is the species which reacts with TCPO yielding CL. Strong support for this

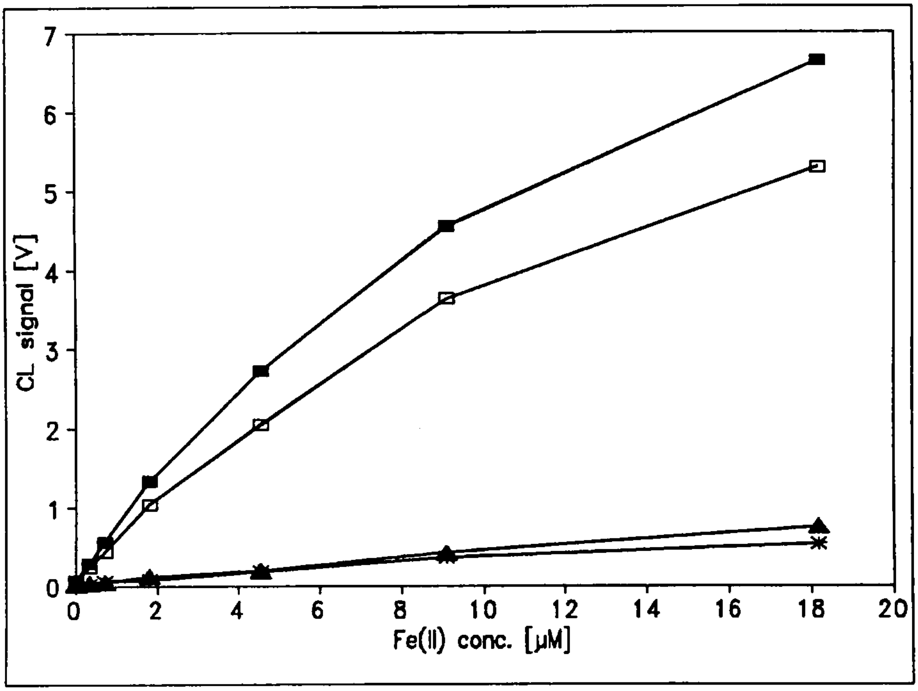

Figure 8 Influence of catalase (CAT) and superoxid dismutase (SOD) on the Fe(II)-TCPO-reaction. ■: no enzyme, □: 5000 U/mL CAT, ▲: 5000 U/mL SOD, *: CAT + SOD.

assumption is provided by the observation of intense CL when a granule of KO_2 is used instead of the Fe(II) test solution, even in presence of high activities of catalase. Finally, with O_2^- as the actual reactive component the shape of the Fe(II) calibration curve can be explained in terms of competition between the reactions of superoxide with TCPO and with Fe(II) (reaction 4b). Increasing relevance of the latter reaction with increasing concentration of Fe(II) will result in losses of analyte and hence in the observed decreasing slope of the calibration graph.

Flow injection system

Using the results described above, a FIA system (Figure 9) was constructed, suitable for the determination of either H_2O_2 or Fe(II). In this apparatus, reagent solution, buffer and sample carrier are transported continuously by a peristaltic pump (Ismatec); after the buffer and the sample carrier (water) have been mixed in a T-piece, the reagent solution is introduced just in front of the photomultipier tube, which is of the same type as used in the FOL. Signal output is monitored by a chart recorder and baseline corrected peak heights are used for further calculations.

This system is a modification of that one previously described[22] for determination of H_2O_2. In this method the sample solution was buffered to pH 7.8 (borate) and then injected into a flow of a similar buffer. This procedure could not be applied to the determination of Fe(II) due to its accelerated autoxidation in the alkaline medium as

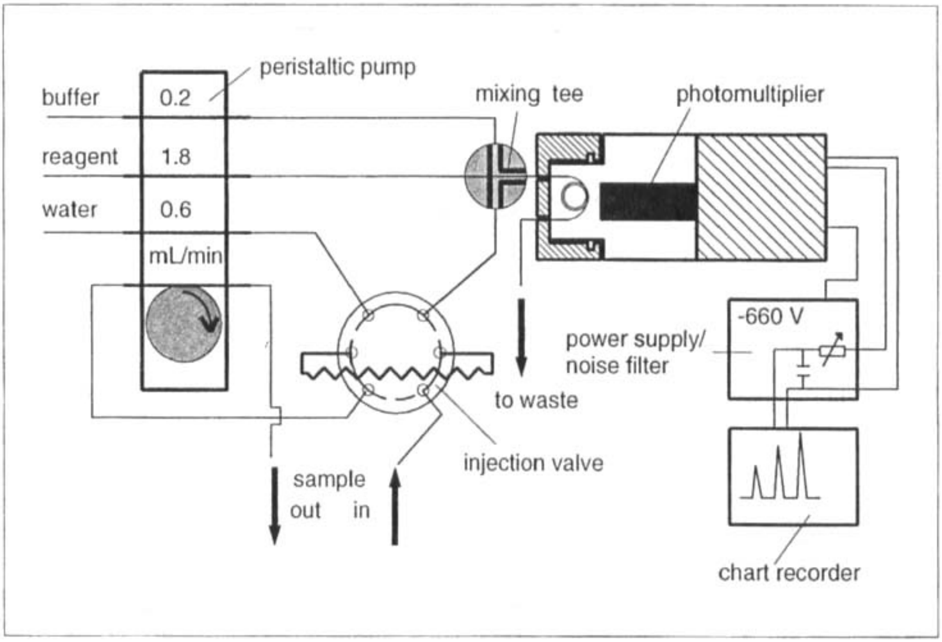

Figure 9 Construction of the flow injection system used for determination of Fe(II) and H_2O_2.

mentioned above. Therefore the contact time between buffer and sample solution had to be held as low as possible and was measured to be less than 1 s in the FIA system described here.

The use of different buffer solutions, as in the case of FOL, cannot be adapted easily to FIA measurements. Attempts made in this direction were without success. Sample throughput was decreased dramatically, because after each buffer change it took at least 5 minutes to achieve again a stable baseline. Such a change, however, would have been nescessary after each measurement, because sample storage would not have been advisable due to the instability of the compounds to be determined. Thus borate buffer was used for both analytes at the cost of non optimum sensitivity for Fe(II) determination. However, the LOD's achieved with the FIA system (H_2O_2: 38 nM, Fe(II): 28 nM) proved to be lower than those obtained by FOL measurements, because in the case of FIA they depended on fluctuations of the baseline rather than on blank signals.

Rain water analyses

Rain water samples were collected during spring 1993 on the roof of the ISAS. Samples were taken at time intervals of 15 to 20 minutes during each rain event and were analysed immediately after collection using the FIA system. Distinction of the analytes was made possible as described above by pretreatment of the samples with catalase or phen, respectively. It has to be mentioned, that the addition of catalase or phen to the samples led to contamination of the injection port with these agents causing underestimation of the real concentrations. This was revealed by control experiments conducted later, and it turned out that the maximum error was less than 30% of the results. These problems could be overcome by rinsing the injection valve after each sample or by using different valves for H_2O_2 and Fe(II) measurements.

Figure 10 shows the variation of the concentrations of Fe(II) and H_2O_2 with time in rain samples collected during two rain events on April 13., 1993. Additionally, the H_2O_2/Fe(II) ratio is plotted showing clearly, that each of the components may be dominating. No distinct correlation or anticorrelation could be found, neither between the measured concentrations of H_2O_2 and Fe(II) nor between the concentrations and the rain intensity. Similar results have been reported recently for water samples collected from fog or stratus clouds[39].

The results obtained demonstrate the usefulness of the proposed method. Furthermore, they indicate that H_2O_2 and Fe(II) may be coexistent in the atmospheric liquid phase in micromolar concentrations thus emphazising the influence of reducing (photo)chemical processes[8].

CONCLUSIONS

The chemiluminescence arising during the reaction between oxygen and bis(2,4,6 trichlorophenyl)oxalate (TCPO) in the presence of Fe(II) has been studied with respect to its analytical applicability. To our knowledge, this type of PO-CL has not been described before. However, a similar CL system using luminol as CL reagent has been investigated several years ago by Seitz and Hercules and other research groups[40–42].

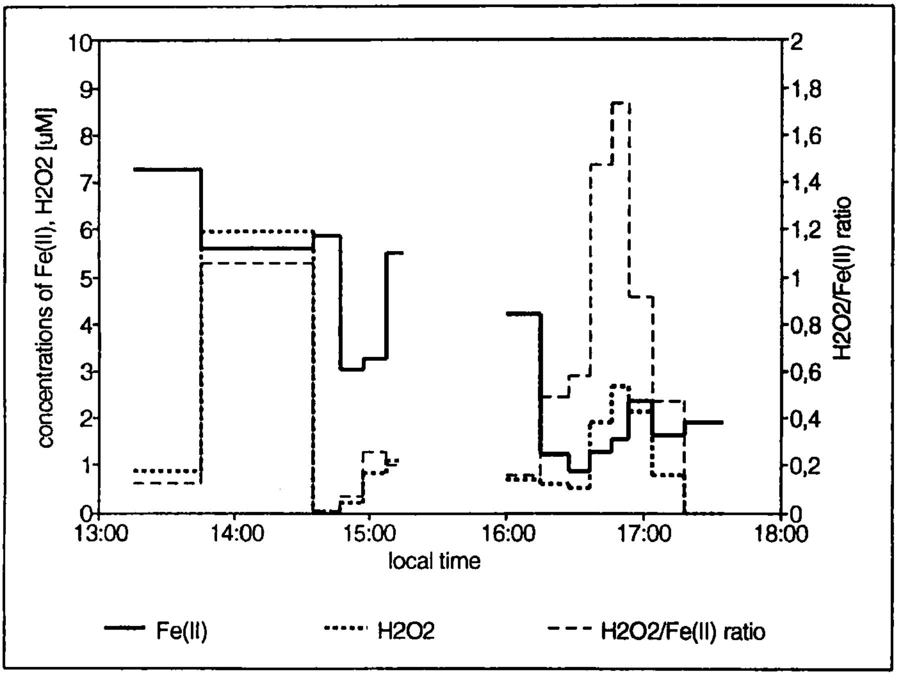

Figure 10 Concentrations of Fe(II) and H_2O_2 and H_2O_2/Fe(II) ratio measured in rain water samples of two rain events on April, 13., 1993. The period of sampling for each analysis is indicated by the width of the steps.

With the developed fiberoptic luminometer and an appropriate buffer solution determination of Fe(II) is possible at submicromolar concentrations. A higher sensitivity was observed compared to the well known H_2O_2/TCPO reaction, but the dependence of the chemiluminescence intensity on Fe(II) concentration proved to be nonlinear. This supports the assumption of a mechanism involving superoxide ions as actual reactive compounds, as is indicated by the decrease of the CL signal in presence of superoxide dismutase serving as O_2^- scavenger. The superoxide radical ion has also been brought into discussion as actual reactant in the luminol/O_2/Fe(II) system, but it was not made clear, if oxygen is needed in this reaction at all[42].

For analytical purposes, distinction between H_2O_2 and Fe(II) can be achieved by masking the metal ion with 1,10-phenanthroline and removing H_2O_2 by catalase, respectively. While this approach is not critical in the case of FOL measurements, it introduces a source of error in the FIA system that was designed to be suitable for determination of both analytes, H_2O_2 and Fe(II). Modifications had to be made to avoid these difficulties.

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