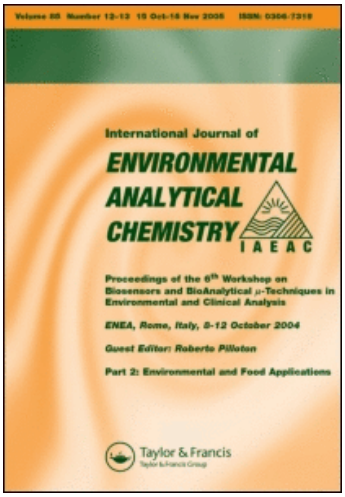

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A new chemiluminescence sensor for hydrogen peroxide determination

Enisa Omanovic[ab]; Kurt Kalcher[b]

[a] Faculty of Agriculture, University of Sarajevo, 71 000 Sarajevo, Bosnia and Herzegovina [b] Department for Analytical Chemistry, Institute for Chemistry, Karl-Franzens University Universitätsplatz 1, A-8010 Graz, Austria

To cite this Article Omanovic, Enisa and Kalcher, Kurt(2005) 'A new chemiluminescence sensor for hydrogen peroxide determination', International Journal of Environmental Analytical Chemistry, 85: 12, 853 — 860

To link to this Article: DOI: 10.1080/14659890500156996

URL: http://dx.doi.org/10.1080/14659890500156996

Intern. J. Environ. Anal. Chem.
Vol. 85, No. 12–13, 15 October–15 November 2005, 853–860

Taylor & Francis
Taylor & Francis Group

A new chemiluminescence sensor for hydrogen peroxide determination

ENISA OMANOVIC*†‡ and KURT KALCHER‡

†Faculty of Agriculture, University of Sarajevo, Zmaja od Bosne 8,
71 000 Sarajevo, Bosnia and Herzegovina
‡Department for Analytical Chemistry, Institute for Chemistry,
Karl-Franzens University Universitätsplatz 1, A-8010 Graz, Austria

(*Received 1 November 2004; in final form 31 January 2005*)

A new sensor based on oxalic acid esters (bis(2,4,6-trichlorophenyl) oxalate-TCPO and bis(2,4-dinitrophenyl) oxalate-DNPO) is presented in this work. The sensor is used for determination of hydrogen peroxide in different samples. Influence of different substances as possible interferences for the determination of new sensor was tested. Water is the biggest interfering substance but it was proved that it does not interfere with determination when it is present in traces. Different organic substances showed influence in different concentration ranges for two esters. Because of this it was possible to choose the system for different determinations depending on the sample matrix. Due to influence of water on esters, the new method was tested on the samples that contain water in traces. Since the samples were washing powders that contained sodium perborate and percarbonate, it was necessary to make calibration curves for both esters. In all cases the calibration curve was linear for concentrations of 1000 $\mu g\,L^{-1}$. The detection limit for the TCPO ester and in the case of sodium perborate was 86 $\mu g\,L^{-1}$ and for the DNPO ester is 48 $\mu g\,L^{-1}$. The lowest concentrations that could be measured were 100 $\mu g\,L^{-1}$ in both cases. Detection limits in the case of sodium percarbonate were 54 $\mu g\,L^{-1}$ (for TCPO) and 48 $\mu g\,L^{-1}$ (for DNPO). The lowest concentrations that could be measured in both cases was 100 $\mu g\,L^{-1}$. The results obtained with the new sensor were compared with results obtained with the standard iodometric method for determination of hydrogen peroxide in per-salts. The results showed that new sensors could be applied successfully for the determination of hydrogen peroxide in the bleaching component of washing powder.

Keywords: Peroxyoxalate chemiluminescence; Single shot sensor; Solid phase

1. Introduction

Hydrogen peroxide (H_2O_2) is a key intermediate in many biological and environmental processes. It has been shown that H_2O_2 is ubiquitous in the hydrosphere [1–7]. Hydrogen peroxide is also significant in both the gas phase and the aqueous chemistry of the atmosphere; thus, the fate of tropospherical H_2O_2 has become a center of attraction.

*Corresponding author. Fax: +387-33-667429. Email: eniom77@yahoo.com

International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print: ISSN 1029-0397 online © 2005 Taylor & Francis
DOI: 10.1080/14659890500156996

According to Gunz and Hofmann, who carried out photochemical experiments, H_2O_2 is present in both polluted and clean air [8].

In biological systems H_2O_2 is produced by enzymes (oxidases) and is enzymatically decomposed by catalase and peroxidases. It plays a key role in essential cell processes, many of which were not elucidated until now. Hydrogen peroxide is involved in protein, carbohydrate and fat metabolism, vitamin and mineral metabolism, immunity and in other essential vital processes [8].

Industrial applications of H_2O_2 are connected with forming oxygen in *status nascendi* from decomposition of H_2O_2. The formed oxygen exhibits bleaching and disinfecting properties. The majority of the produced H_2O_2 is used by the washing agent industry for producing washing powders, but it is also used in other industrial processes [9, 10].

The first chemiluminescence sensor for H_2O_2 was described by Freeman and Seitz in 1978, and since then various types of chemiluminescence based sensors have been used extensively for the determination of inorganic, organic and biological/pharmaceutical compounds [11]. Analytical techniques using chemiluminescence as a detection method have received much attention in various fields, owing to their extremely high sensitivity along with extra advantages, such as simple instrumentation, fast dynamic response, wide calibration ranges and easy coupling to separation techniques.

Peroxyoxalate chemiluminescence (PO-CL) provides the most efficient non-enzymatic chemiluminescence yet known with quantum yields up to 34% [12]. The wavelength of the emitted light is determined by the fluorophore. Oxalic acid derivatives react with H_2O_2 to peroxide compound, which form 1,2-dioxetandiones and/or substituted 1,2-dioxetandiones as active intermediates. Subsequently a charge-transfer complex with a fluorescer is formed that dissociates into a fluorophore in the excited state and other products. The resulting emission stems from the fluorophore [13].

Two different types of sensors were developed with two different esters, i.e., bis(2,4,6-trichlorophenyl) oxalate (TCPO) and bis(2,4-dinitrophenyl) oxalate (DNPO).

2. Experimetal

2.1 *Apparatus*

All measurements were done by using an in-house built microprocessor-controlled luminometer, the low-range electric luminescence assay (LELA) version 1.0 [1]. A photodiode detected the released light; the corresponding signal was amplified in four different channels at different amplification factors. The digitalized output of the instrument was transferred to a personal computer interfaced with the luminometer. The measuring cell consisted of a light-tight housing with the light detector (photodiode) and the integrated amplifiers. The upper inner part of the housing was designed to host a Hamilton syringe (25 μL). The sensor consisted of a glass lamella ($18 \times 18 \times 0.4\,mm^3$) with a drop-cast membrane containing the CL reagents (ester, fluorescer and polymer) and was mounted centrically in the cell on the surface of the photodiode. Each sensor was used for one measurement only.

2.2 *Reagents*

DNPO and TCPO, ethyl acetate, cellulose acetate, citric acid, ascorbic acid, ammonium molybdate tetrahydrate, and potassium iodide were purchased from Fluka.

Hydrogen peroxide (30%), sodium perborate, uric acid, xanthin, D(+)-glucose (monohydrat), glutamic acid, potassium iodate, sodium thiosulfate and starch were obtained from Merck, 9,10-diphenylanthracene from Sigma-Aldrich, and sodium percarbonate from Riedel-de Haën.

2.3 *Preparation of membranes*

The solution to cast membranes with TCPO consisted of TCPO (2 mg), 9,10-diphenylanthracene (6 mg), and cellulose acetate (5 mg). All components were mixed together and dissolved in ethyl acetate (2.5 mL).

For DNPO membranes, DNPO (3 mg), 9,10-diphenylanthracene (9 mg), and cellulose acetate (12 mg) were mixed and dissolved in ethyl acetate (2.5 mL).

In both cases 5 μL of the membrane-forming samples were manually cast on the surface of a glass lamella (microscopic cover glass) and dried in a desiccator.

2.4 *Procedure*

The membrane-coated sensor was put directly on the light sensitive area of the photodiode and fixed by self-adhesive strips. The sample solution (5 μL) was applied via the Hamilton syringe which was mounted on the upper inner part of the housing. Immediately after triggering the instrument to start recording the data the sample was injected. The whole procedure was done as quickly as possible in order to minimize possible decomposition of H_2O_2 during this step. At the same time, the response curves were recorded and transferred to a personal computer with corresponding software. The reaction was finished after a few seconds. The signals were usually evaluated by integration over the whole response.

2.5 *Indirect iodometric reference method*

Sulphuric acid (100 mL, 1+19) was added to the sample solution (25 mL), followed by three drops of ammonium molybdate solution (3%). The liberated iodine was immediately titrated with standard thiosulphate solution (0.05 M), adding 2 mL starch solution (1%) when the color of the iodine had nearly vanished [14].

3. Results and discussion

In this work, the new sensors were investigated for their possible application to determine perborate and percarbonate, either in pure form or as components of washing powders. The optimized conditions for the determination of H_2O_2 are given in section 2 and have been evaluated elsewhere [15].

The sensor with TCPO is capable of practically detecting up to 2.5 $\mu g\,L^{-1}$ H_2O_2; whereas the detection limit was calculated at the 3σ value of 1.4 $\mu g\,L^{-1}$. The lowest concentration which could be measured for the sensor with was DNPO 16 $\mu g\,L^{-1}$ and detection limit, calculated at the 3σ value of 12.8 $\mu g\,L^{-1}$ [15, 16].

Relative standard deviations of the measurements are higher due to the manual preparation of the membranes. The problem will be solved with future work and with automatic preparation of the membranes.

3.1 *Interferences*

The influence of different substances (water, citric acid, uric acid, glucose, xanthine, ascorbic acid, glutamic acid, benzoyl peroxide) on the determination with the new sensor was investigated.

The main interfering substance for both sensors is water. Water, as a nucleophilic solvent, attacks the oxalate ester and consumes it in non-chemiluminescent hydrolysis. Water also interferes with significant amounts of the esters to be hydrolyzed, whereas traces of water will not interfere with the determination. Thus, aqueous media have to be avoided with the samples which constitute the main drawback of PO-CL in general, whereas the presence of small concentrations (low ppm concentration range) does not show negative effects.

Due to the influence of water we did not investigate the influence of metal ions, due to the insolubility of the corresponding salts in organic solvents, which show as 'saturated' solutions with no practical influence on the chemiluminescence.

The influence of some organic compounds on the determination with the new sensor is presented in tables 1 and 2.

As can be expected organic peroxides, such as benzoyl peroxide, interfere with the determination of H_2O_2 with the new sensors in the concentration range 10–1000 $\mu g\,L^{-1}$. Organic peroxides react with both esters in the same way as H_2O_2; thus if they are present together with the analyte the sum of peroxides will be determined.

Ascorbic acid reduces the signal in all concentration ranges and for both esters. This influence was expected due to the fact that ascorbic acid is a reducing regent. Except below concentrations of 10 $\mu g\,L^{-1}$ for the DNPO sensor, uric acid was a strong

Table 1. Influence of different organic compounds at various concentrations on the signal obtained with 100 $\mu g\,L^{-1}$ of H_2O_2; the signal produced by H_2O_2 corresponds to 100%; TCPO sensor.

	10 $\mu g\,L^{-1}$ (%)	100 $\mu g\,L^{-1}$ (%)	1000 $\mu g\,L^{-1}$ (%)
Uric acid	−14	+31	+47
Ascorbic acid	−34	−49	−66
Glucose	−20	−22	−30
Xanthin	−2	−5	+6
Citric acid	+59	+50	−32
Glutamic acid	−14	−13	+4
Benzoyl peroxide	100	100	100

Table 2. Influence of different organic compounds at various concentrations on the signal obtained with 100 $\mu g\,L^{-1}$ of H_2O_2; the signal produced by H_2O_2 corresponds to 100%; DNPO sensor.

	10 $\mu g\,L^{-1}$ (%)	100 $\mu g\,L^{-1}$ (%)	1000 $\mu g\,L^{-1}$ (%)
Uric acid	+12	+16	−56
Ascorbic acid	−46	−52	−62
Glucose	−12	−21	−38
Xanthin	−5	−1	+72
Citric acid	+5	+44	−4
Glutamic acid	−25	−51	−60
Benzoyl peroxide	100	100	100

interferent for both sensors in concentrations higher than $10\,\mu g\,L^{-1}$. Also, glucose interfered with the determination of the latter ester. The determination with the TCPO sensor was also interfered by glucose. Xanthin shows no adverse effects in the investigated concentration range, except for concentrations higher than $1000\,\mu g\,L^{-1}$ with the nitroester. Citric acid was a strong interferent for the TCPO sensor, but was less pronounced for DNPO. Glutamic acid interfered determination with both sensors, but was less pronounced with TCPO.

Somehow the different behavior of the esters in the presence of some substances can be explained with some cross-reactions between the esters and the interferent, but more probable with the influence of these substances on intermediates in the chemiluminescence reaction.

As model analytes, washing powders were tested as target samples of the new sensors. Sodium perborate and sodium percarbonate were the most common oxidizing agents in washing powders. In dry form they contained only negligible amounts of water, and were soluble in some organic solvents.

3.2 *Calibration curves for hydrogen peroxide in sodium perborate*

Standard solutions of sodium perborate were prepared in ethyl acetate and left for 12 h. Then, the calibration curves were established (figures 1 and 2). Water (10 μL) was added in prepared standard solutions due to effectively releasing H_2O_2 from per-salts.

With TCPO, the peak area increases linearly up to a perborate concentration of $1000\,\mu g\,L^{-1}$. Above this concentration the curve starts to level off. The lowest concentration that can be unambigously measured is $100\,\mu g\,L^{-1}$. The detection limit calculated at the 3σ value was $86\,\mu g\,L^{-1}$. A concentration of $100\,\mu g\,L^{-1}$ showed a relative standard deviation of ±8%.

Similar results were obtained with DNPO. The detection limit (3σ) was $48\,\mu g\,L^{-1}$. The lowest concentration which could be measured was $100\,\mu g\,L^{-1}$. Standard deviation corresponding to the concentration of $100\,\mu g\,L^{-1}$ was ±9%.

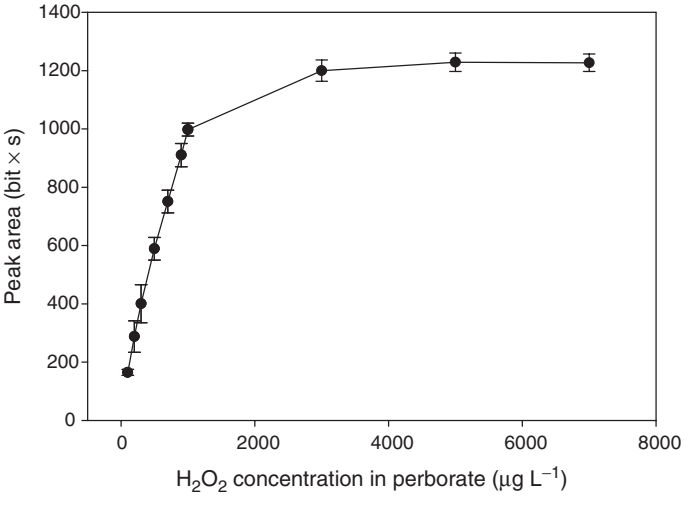

Figure 1. Calibration curve for H_2O_2 in sodium perborate with TCPO sensor.

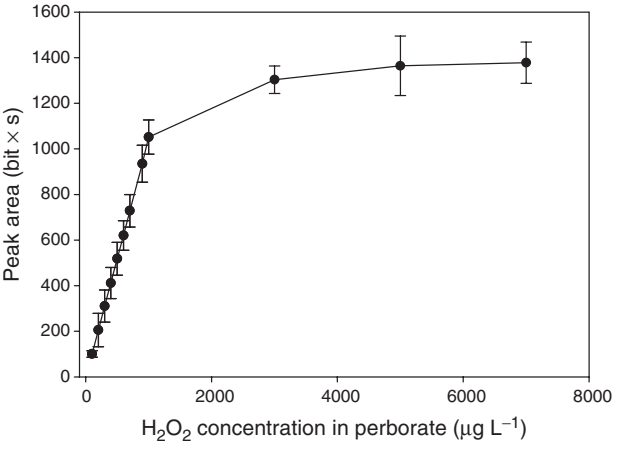

Figure 2. Calibration curve for H_2O_2 in sodium perborate with DNPO sensor.

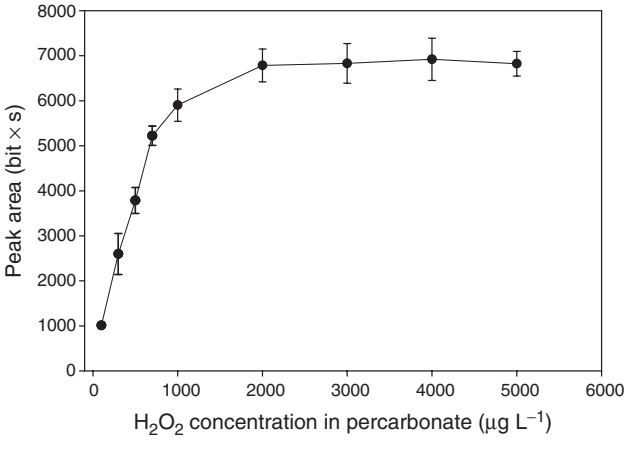

Figure 3. Calibration curve for H_2O_2 in sodium percarbonate for the TCPO sensors.

3.3 *Calibration curves for hydrogen peroxide in sodium percarbonate*

Standard solutions of sodium percarbonate are prepared in ethyl acetate. The solutions are left for 4 h. Hydrogen peroxide was determined afterwards. Water (10 μL) was added in prepared standard solutions due to effectively releasing hydrogen peroxide from per-salts.

The resulting calibration curves are presented on figures 3 and 4.

The peak area increases linearly up to a concentration of 1000 μg L^{-1}. With higher concentration the curve starts to level off. The lowest concentration that could be measured was 100 μg L^{-1}. The detection limit, calculated at the 3σ value was 54 μg L^{-1}. The standard deviation of the concentration of 100 μg L^{-1} was ±8%.

Again, a similar situation was found with DNPO. The lowest concentration that could be measured was 100 μg L^{-1}. The detection limit of the method was 49 μg L^{-1} and the standard deviation of concentration of 100 μg L^{-1} was ±9%.

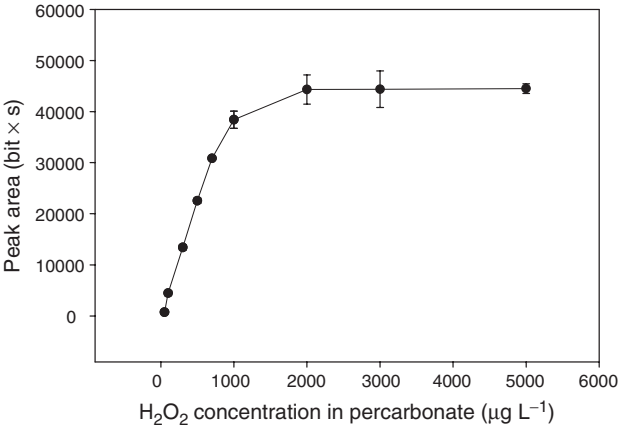

Figure 4. Calibration curve for H_2O_2 in sodium percarbonate for the DNPO sensor.

Table 3. Results of the washing powders analysis; washing powders (samples 1 and 2) contain perborate; washing powders (samples 3 and 4) contain percarbonate.

Washing powder	TCPO Determination with sensor (%)	DNPO Determination with sensor (%)	Titration (%)
Sample 1	12.7 ± 0.8	12.6 ± 0.9	12.6 ± 0.6
Sample 2	18.0 ± 0.8	17.4 ± 0.8	17.6 ± 0.7
Sample 3	9.4 ± 0.7	9.2 ± 0.8	9.2 ± 0.6
Sample 4	15.8 ± 0.8	15.8 ± 0.9	15.1 ± 0.6

3.4 *Determination of perborate/percarbonate concentration in washing powder samples*

Four different samples were dissolved in ethyl acetate. Two of the samples contained perborate as a bleaching component and the other two percarbonate. Determination of the hydrogen peroxide was done after 12 h for the samples containing perborate and 4 h for samples containing percarbonate. Water (10 µL) was added in all sample solutions.

The final H_2O_2 concentrations were evaluated by the corresponding calibration curves for the respective ester (TCPO, DNPO) and the proper analyte (perborate, percarbonate). Reference determinations were performed with iodometric titrations.

The results obtained by the new sensors showed very good correlation with the results obtained by the standard method (table 3).

The new sensors could be successfully applied for the determination of H_2O_2 in perborate and percarbonate of washing powders.

4. Conclusions

New sensors based on the chemiluminescence of two oxalic acid esters, i.e., bis(2,4-dinitrophenyl) oxalate (DNPO), and bis(2,4,6-trichlorophenyl) oxalate (TCPO), have been investigated for their application in determining inorganic peroxides, namely

percarbonate and perborate, in washing powders. They exhibit good stability over a few days and are able to determine peroxides reliably. Potential applications as biosensors are in progress.

References

[1] H. Moderegger. Development of one-shot sensors based on chemiluminescence, PhD thesis, Faculty of Natural Science, Karl-Franzens University, Graz, Austria (2003).
[2] D. Price, J.P. Worsfold, R. Fauzi, C. Mantoura. *Trends Anal. Chem.*, **11**, 379 (1992).
[3] W.J. Cooper, R.G. Zika, R.G. Petasne, J.M.C. Plane. *Environ. Sci. Technol.*, **22**, 1156 (1988).
[4] E. Yamada, K. Tomozawa, Y. Nakanishi, Y. Fuse. *Bull. Chem. Soc. Jpn.*, **75**, 1385 (2002).
[5] W.J. Cooper, E.S. Saltzman, R.G. Zika, *J. Geophys. Res.*, **92**, 2970 (1987).
[6] B. Palenik, O.C. Zafiriou, F.M.M. Morel. *Limnol. Oceanogr.*, **32**, 1365 (1987).
[7] J.W. Moffet, O.C. Zafirou, *Limnol. Oceanogr.*, **35**, 1221 (1990).
[8] D.W. Gunz, M.R. Hoffmann. *Atmos. Environ. Part A*, **24**, 1601 (1990).
[9] C.E. Housecroft, A.G. Sharpe, *Inorganic Chemistry*, Pearson Education Limited, Harlow, Essex, UK (2001).
[10] R.D. Jones, A.H. Morice, R.M. Wadsworth. *Pharmacol. Therapeut.*, **88**, 153 (2000).
[11] X.R. Zhang, W.R.G. Baeyens, A.M. Garcia-Campana, J. Ouyang. *Trends Anal. Chem.*, **18**, 384 (1999).
[12] S.G. Schulman. *Molecular Luminescence Spectroscopy; Methods and Applications: Part 3*, John Wiley & Sons, Inc., New York/Chichester.
[13] A.M. Garcia-Campana, W.R.G. Baeyens, *Chemiluminescence in Analytical Chemistry*, Marcel Dekker Inc., NY, USA (2001).
[14] J. Basset, R.C. Denney, G.H. Jeffery, J. Mendham. *Vogel's Textbook of Quantitative Inorganic Analysis*, Longman Group Limited, London (1981).
[15] E. Omanovic, K. Kalcher. *Sci. Paper Univ. Pardubice*, Seria A, **54**, 10 (2004).
[16] J.C. Miller, J.N. Miller. *Statistics for Analytical Chemistry*, Ellis Horwood Limited, West Sussex (1993).