

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Flow Injection Analysis of Hydrogen Peroxide, Sulfite, Formaldehyde and Hydroxymethanesulfonic Acid in Precipitation Samples

Menno P. Keuken<sup>a</sup>; Frits P. Bakker<sup>a</sup>; Walter A. Lingerak<sup>a</sup>; Jakob Slanina<sup>a</sup>

<sup>a</sup> Netherlands Energy Research Foundation (ECN), Petten, The Netherlands

**To cite this Article** Keuken, Menno P. , Bakker, Frits P. , Lingerak, Walter A. and Slanina, Jakob(1987) 'Flow Injection Analysis of Hydrogen Peroxide, Sulfite, Formaldehyde and Hydroxymethanesulfonic Acid in Precipitation Samples', *International Journal of Environmental Analytical Chemistry*, 31: 2, 263 – 279

**To link to this Article:** DOI: 10.1080/03067318708077145

**URL:** <http://dx.doi.org/10.1080/03067318708077145>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Flow Injection Analysis of Hydrogen Peroxide, Sulfite, Formaldehyde and Hydroxymethanesulfonic Acid in Precipitation Samples

MENNO P. KEUKEN, FRITS P. BAKKER, WALTER A. LINGERAK  
and JAKOB SLANINA\*

*Netherlands Energy Research Foundation (ECN), P.O. Box 1, 1755 ZG  
Petten, The Netherlands*

**Dedicated to Professor W. Haerdi on the occasion of his  
60th birthday**

*(Received 10 June 1987; in final form 22 June 1987)*

Hydroxymethanesulfonic acid (HMSA), the reaction product of sulfite and formaldehyde plays an important part in the aqueous phase conversion of sulfite to sulfate. HMSA is fairly stable under acidic conditions and in presence of hydrogen peroxide. Sulfite is unstable under these conditions.

A flow injection set-up was developed, which allows the determination of  $H_2O_2$ , sulfite, formaldehyde and hydroxymethanesulfonic acid.

$H_2O_2$  analysis by amperometric detection offers the possibility of a simple, robust field instrument. The detection limit is  $5 \mu\text{g/l}$  and the method is linear up to  $5 \text{mg/l}$ .

Based on the 4,4-dithiodipyridine/sulfite reaction selective and sensitive spectrophotometric detections were developed for sulfite, formaldehyde and hydroxymethanesulfonic acid. The detection limit of these compounds is  $50 \mu\text{g/l}$  and the method is linear up to  $5 \text{mg/l}$ .

A large fraction of S(IV) is present as HMSA in fog, dew and precipitation samples in The Netherlands.

**KEY WORDS:** Precipitation samples, flow injection analysis, hydrogen peroxide, sulfite, formaldehyde, HMSA.

---

\*Author to whom correspondence should be addressed.

## INTRODUCTION

In acid precipitation research the aqueous-phase oxidation of  $\text{SO}_2$  is one of the major issues. Hydrogen peroxide is considered to be the most important aqueous-phase oxidant of S(IV) due to fast reaction kinetics in the pH range characteristic of rain, fog and cloud water.<sup>1-3</sup> Recent studies of fog and cloudwater indicate the presence of hydroxymethanesulfonic acid (HMSA), which is resistant to  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  oxidation.<sup>4-5</sup> HMSA is formed from formaldehyde and sulfite most rapidly above  $\text{pH}=5$ . However HMSA is optimally stabilized at acidic conditions.<sup>6</sup> Therefore, S(IV) as HMSA can be found in precipitation samples under acidic conditions and in presence of hydrogen peroxide. Sulfite will be oxidized under these conditions.

In order to evaluate the consequences of HMSA formation for long range transport of S(IV), the scavenging processes of  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  in clouds, fog and dew and possible effects on vegetation, it is necessary to obtain information of the concentrations of hydrogen peroxide, sulfite, formaldehyde and hydroxymethanesulfonic acid. A fast and simple method for the determination of these compounds was developed. Present methods for the determination of  $\text{H}_2\text{O}_2$ , sulfite, formaldehyde and HMSA will be evaluated.

### Hydrogen peroxide determination

Only recently, sensitive procedures were reported to detect hydrogen peroxide in precipitation samples, using the chemoluminescence reaction of  $\text{H}_2\text{O}_2$  with luminol<sup>7</sup> or *bis*-(trichlorophenyl)oxalate (TCPO) in combination with perylene.<sup>8,9</sup> Another very sensitive method is the fluorescence detection with *p*-hydroxyphenylacetic acid (PHOPA) in the presence of the enzyme peroxidase and the use of catalase to improve selectivity.<sup>10</sup> This method was used as a reference procedure for the  $\text{H}_2\text{O}_2$  determination. We have developed an amperometric method,<sup>11</sup> also using the addition of catalase to obtain a selective method. This method is suitable for application in the field and it gives indicative information of other oxidants present in the sample. The amperometric cell consists of a Pt working electrode, a Pt counter electrode and a Ag/AgCl reference electrode.  $\text{H}_2\text{O}_2$  is oxidized at an applied potential of 250 mV. The current is proportional to the concentration of  $\text{H}_2\text{O}_2$ . Recently the use of a Pt

reactor instead of catalase has been described to correct for interference of organic peroxides especially.  $\text{H}_2\text{O}_2$  is decomposed on a Pt column while organic peroxides are not affected.<sup>12</sup> We use this method in the amperometric flow injection analysis (FIA) so a catalase reagent stream can be omitted. In our procedure the sample is injected twice, once analyzed directly and the second time after passing the Pt filled reactor (Figure 1A).

### Sulfite determination

Early methods of sulfite determination were based on the Schiff reaction, utilizing pararosaniline for colour development and a tetrachloromercurate solution for absorption of sulphur dioxide from air.<sup>13</sup> Absorption of sulfur dioxide and stabilization of sulfite by formaldehyde,<sup>14</sup> glycerol,<sup>15</sup> tri-ethanolamine or mono-ethanolamine<sup>16</sup> has been introduced to avoid the use of relatively high concentrations of toxic mercury(II) salts. An improvement of the selectivity of the spectrophotometric method was the application of *p*-aminoazobenzene (PAAB).<sup>17</sup> However drawbacks of the PAAB method are: (1) high spectrophotometric background, (2) critical pH and reaction time dependency for colour development and (3) interference by nitrite implies the addition of reagents. The batch procedure proposed by Humprey *et al.*<sup>18</sup> using 4,4-dinitrodipyrindine (4-PDS) provides a sensitive and simple spectrophotometric method for the measurement of sulfite in precipitation samples. The reaction of sulfite and 4-PDS yields an absorbing thiol which is detected at 324 nm. This method, which seems to have been overlooked since its publication in 1970, was used to develop an automated flow injection procedure with spectrophotometric detection (Figure 1B).

### Formaldehyde determination

Analysis of aldehydes in wet deposition and air samples is commonly made by using 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by HPLC. Spectrophotometric and fluorometric analysis of formaldehyde is based on the Hantzsch reaction using acetylacetonammonium-salt.<sup>19-21</sup> However determination of formaldehyde according to the Hantzsch-reaction is not selective, other aldehydes and amines cause interference.

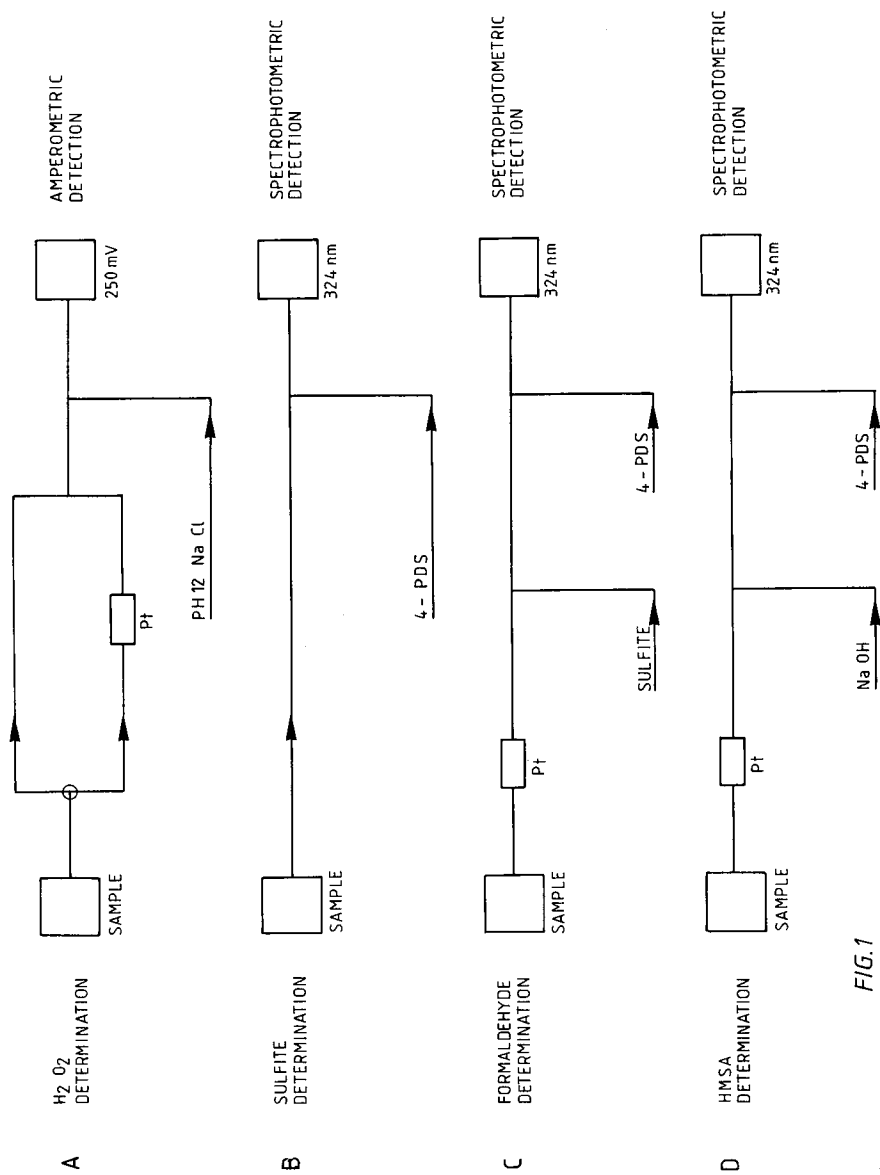


FIG. 1

**Figure 1** Procedures used in the determination of hydrogen peroxide (A), sulfite (B), formaldehyde (C) and hydroxymethanesulfonic acid (D).

In the proposed set-up formaldehyde determination is based on destruction of sulfite present in the sample by means of a platinum reactor, followed by adding a constant sulfite background and measurement of the decrease in the sulfite signal by 4-PDS caused by HMSA formation (Figure 1C).

### HMSA determination

For the determination of hydroxymethanesulfonate Munger *et al.*<sup>5</sup> briefly describe a method based on ion-pairing chromatography, followed by a cation-exchange suppressor column in the  $\text{Ag}^+$  form and conductivity detection. In our procedure the measurement of HMSA is based on destruction of sulfite present in the sample by the platinum reactor, followed by dissociation of HMSA under alkaline conditions ( $\text{pH} > 9$ ) and detection of the resulting sulfite by 4-PDS (Figure 1D).

So in the proposed procedure 4-PDS is used for the determination of sulfite, formaldehyde and HMSA. The pH is the controlling parameter in this system. A Pt reactor is employed for several purposes. This reactor is used in the  $\text{H}_2\text{O}_2$  determination instead of catalase to improve selectivity and in the formaldehyde and HMSA determination to eliminate interference of respectively  $\text{H}_2\text{O}_2$  and sulfite.

Flow injection procedures are used so sample consumption, time of analysis and contamination due to handling are reduced. Furthermore the reaction parameters for the selective destruction of  $\text{H}_2\text{O}_2$  and sulfite have to be kept fairly constant, which is easy in case of continuous flow procedures.

## EXPERIMENTAL SECTION

### Reagents

Sodium hydroxymethanesulfonate and 4,4-dithiodipyridine (4-PDS) were obtained from Aldrich Chemical Co. Sodium sulfite (98% minimum  $\text{Na}_2\text{SO}_3$ ) and formaldehyde (37%  $\text{CH}_2\text{O}$ ) were Baker Analyzed reagent grade. Horse radish peroxidase (1120 U/mg) was obtained from Serva. Other chemicals used for preparation of buffers and evaluation of interferences were reagent grade materials.

*H<sub>2</sub>O<sub>2</sub> determination* For electrochemical H<sub>2</sub>O<sub>2</sub> detection a solution, containing 1 M NaCl and 0.25 M Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, is adjusted to pH 12 with 10 M NaOH. In case of fluorescence H<sub>2</sub>O<sub>2</sub> detection this solution was exchanged by a solution of 11 mg *p*-hydroxyphenylacetic acid (PHOPHA) and 3 mg peroxidase in 250 ml 0.1 M sodiumphthalate buffer pH 5. A stock 1000 mg/l H<sub>2</sub>O<sub>2</sub> solution was prepared monthly by diluting a 30% H<sub>2</sub>O<sub>2</sub> solution and stored at 4°C in glassware. The exact concentration was determined by KMnO<sub>4</sub> titration. Working standards of hydrogen peroxide were prepared daily by serial dilution of the stock solution.

*Sulfite determination* A 1000 mg/l sulfite stock solution was prepared by dissolving Na<sub>2</sub>SO<sub>3</sub> (Baker) in 0.001 M Na<sub>2</sub>EDTA solution. Working standards of sulfite were prepared by weight dilution in 0.001 M Na<sub>2</sub>EDTA. These solutions are stable for one week. The 4-PDS solution was prepared by dissolving 44 mg 4-PDS in 5–10 ml ethanol (95%) and diluting to 200 ml with 0.5 M phosphate buffer pH 4. The 4-PDS solution was prepared daily.

*Formaldehyde determination* A 20 mg/l sulfite solution for use as the sulfite background in the determination of formaldehyde was diluted by weight from the sulfite stock solution in 0.001 M Na<sub>2</sub>EDTA and 0.25 M sodium phosphate buffer pH 7. This solution is stable for two weeks. Working standards of formaldehyde in the range 0.050–5.0 mg/l were diluted with water by weight from a 37% (CH<sub>2</sub>O) solution. The exact concentration was determined by titration.<sup>22</sup>

*HMSA determination* A 1000 mg/l hydroxymethanesulfonate stock solution was prepared by dissolving an accurately weighted amount of NaOHCH<sub>2</sub>SO<sub>3</sub> in one liter of water. Working standards of hydroxymethanesulfonate in the range 0.050–5.0 mg/l were diluted by weight from this stock solution. All solutions were prepared from water purified by deionization and removal of organics (Millipore-Q system).

## Apparatus

The FIA system was constructed using a Gilson peristaltic pump, Technicon flow-certified pump tubes, Teflon 0.3 mm i.d. tubing and

Chem inert valves (Figure 2). The Pt reactor was made of 4 cm length 0.15 cm i.d. Teflon tubing, 2 cm packed with Pt sponge and Teflon wool at each end to prevent loss of material. The heating of the reaction coil is provided by standard 25 Ohm resistance (5 watt). Spectrophotometric detection was performed by means of a Uvikon 740 C detector, the amperometric detector was a Dionex Potentiostat. A Merck/Hitachi Fluorescence detector was used for fluorescence measurements.

A microcomputer Apple IIc controls the autosampler (LKB) and the valves, measures peak heights and is used for data storage.

### Procedure

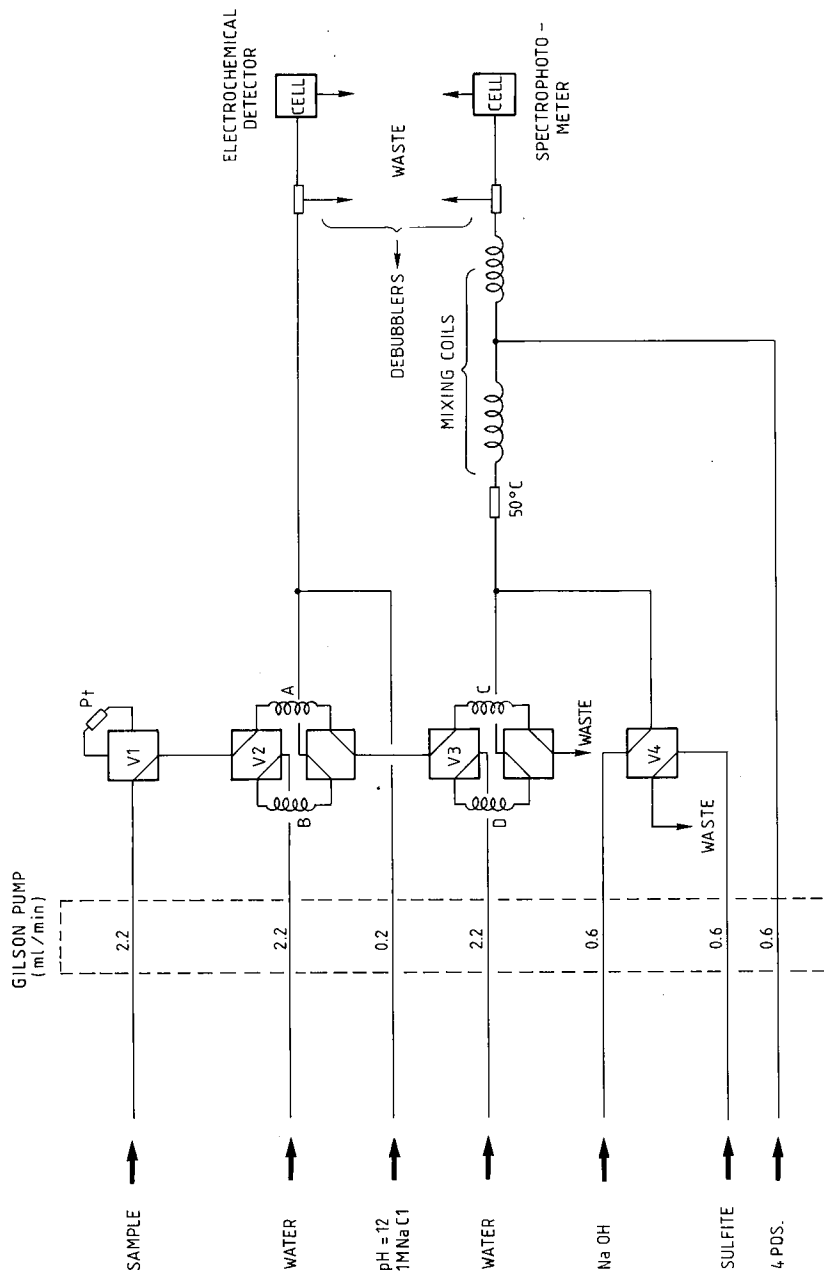
To measure sulfite and  $\text{H}_2\text{O}_2$  the Pt reactor is bypassed. The sample is loaded from an autosampler into loops A and C (Figure 2A). By switching the valves V1, V2 and V3 the content of these loops is injected into the detection systems, while the sample is loaded into loops B and D after passing the Pt column, destroying sulfite and  $\text{H}_2\text{O}_2$  in the sample. The volumes of loops A and B are identical ( $250 \mu\text{l}$ ) as are the loops C and D ( $500 \mu\text{l}$ ).

In the case of amperometric hydrogen peroxide detection, the carrier stream is adjusted to pH 12 by the phosphate buffer. The current of the amperometric cell—ECN design (Figure 3)—is detected at the applied potential of 250 mV. The reference potential is maintained by the chloride concentration in the phosphate buffer.

In case of fluorescence hydrogen peroxide detection the phosphate buffer is exchanged by the PHOPA/peroxidase solution and after a 4 turn Teflon mixing coil, a 0.1 N NaOH solution is added (Figure 2B). The amperometric cell is exchanged by the fluorometer and the fluorescence is detected (excitation 330 nm, emission 420 nm). Details on the fluorescence detection are described by Lazrus *et al.*<sup>10</sup> The  $\text{H}_2\text{O}_2$  concentration is determined by the differences in amperometric (or fluorescence) signal, followed by injection of loops A and B.

In case of sulfite detection (loop C) and HMSA detection (loop D), sodium hydroxide and spectrophotometric 4-PDS reagent are sequentially added. The sample stream passes through a 4 turn Teflon mixing coil. The reaction of sulfite and 4-PDS yields an absorbing thiol, which is detected at 324 nm.





**Figure 2A** Diagram of the procedure with amperometric detection of  $\text{H}_2\text{O}_2$  and spectrophotometric detection of sulfite, formaldehyde and hydroxymethanesulfonic acid.

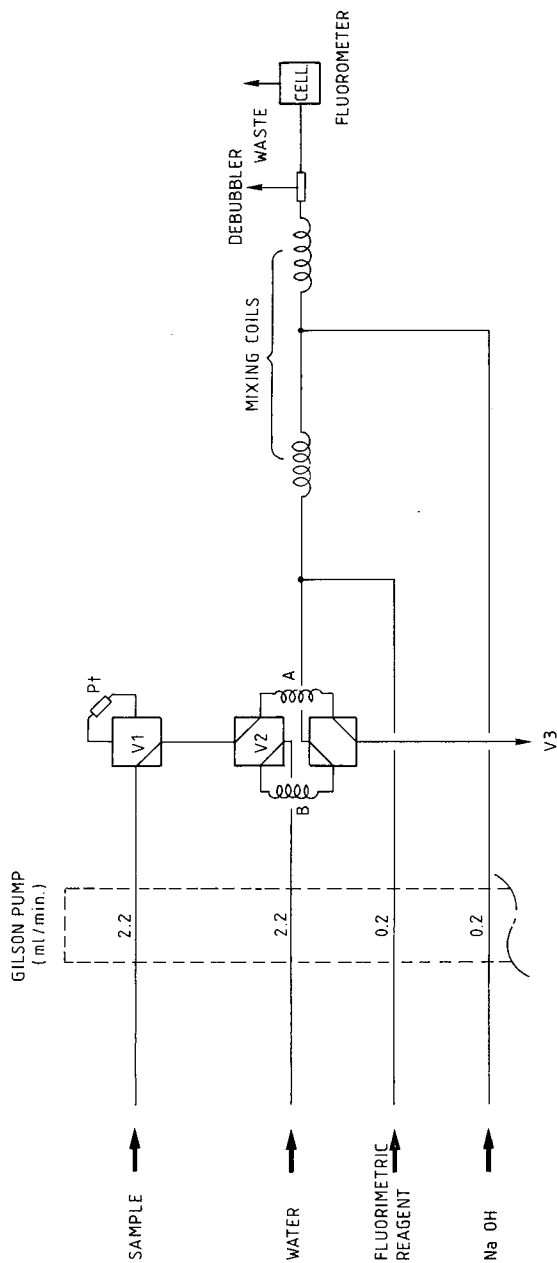


Figure 2B Diagram of the procedure with fluorimetric detection of  $H_2O_2$ .

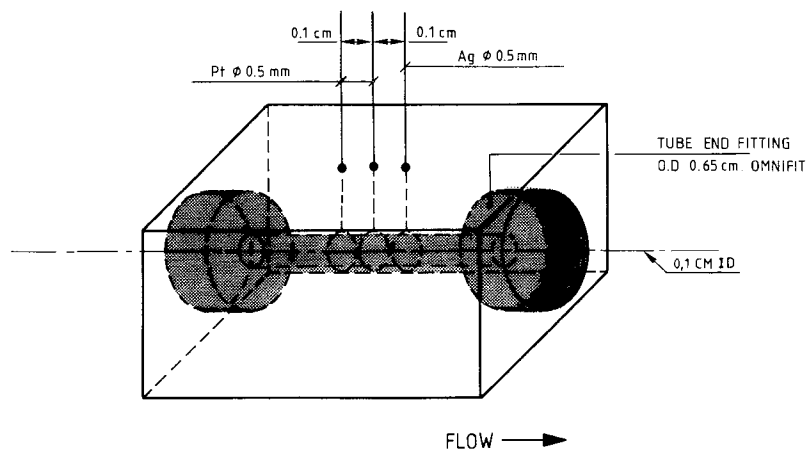


Figure 3 The amperometric cell.

In case of formaldehyde detection loop C is loaded after passing the sample through the Pt reactor to eliminate sulfite and  $\text{H}_2\text{O}_2$  interferences. By switching valve V4 a 20 mg/l sulfite solution is added. The pH of the sample is adjusted to pH 7 by means of the phosphate buffer even for samples with an original pH 3. The pH 7 is required for fast reaction kinetics between sulfite and formaldehyde to form HMSA. After a 4 turn reaction coil, maintained at  $50^\circ\text{C}$ , the spectrophotometric reagent added reacts with the remaining sulfite. The absorbance is measured at 324 nm.

## RESULTS AND DISCUSSION

To optimize the electrochemical detection,  $500\ \mu\text{g/l}$   $\text{H}_2\text{O}_2$  solutions were injected and the current was measured as function of pH, buffersystem, bufferstrength and cell potential. Sodiumphosphate buffer 0.25 M, adjusted to pH 12 gave the best results in terms of signal to noise ratio. At the applied voltage of 250 mV the method is free of interference by nitrite and formaldehyde and by sulfite at concentrations lower than 10 mg/l.

The application of a Pt reactor to improve the selectivity of the  $\text{H}_2\text{O}_2$  analysis depends on residence time in the reactor, too long

contact with platinum will result in destruction of organic peroxides and too short will incompletely remove  $\text{H}_2\text{O}_2$ . To keep the pressure drop as low as possible we used the smallest column, which completely removed  $\text{H}_2\text{O}_2$  at concentrations up to 5 mg/l. The selectivity of the Pt reactor was compared with the well established catalase method in combination with the PHOPA fluorescence detection. The tests were performed using rain water, as it is hardly possible in the laboratory to prepare standards of organic peroxides in the range and variety encountered in environmental samples. Sampled rainwater in the period April–June 1986 was injected using fluorescence detection and the Pt reactor or catalase (Table 1). In the range up to 240  $\mu\text{g}$   $\text{H}_2\text{O}_2$  per liter the analysis gave the following results: correlation coefficient 0.9994, slope 1.01 and intercept  $-1.9 \mu\text{g}$   $\text{H}_2\text{O}_2$  per liter. These results show that the Pt reactor is suitable to remove selectively  $\text{H}_2\text{O}_2$  in atmospheric deposition.

**Table 1** Comparison of  $\text{H}_2\text{O}_2$  destruction in rainwater (April–June 1986) by Pt or catalase. Results are obtained by PHOPA fluorescence detection in  $\mu\text{g}/\text{l}$   $\text{H}_2\text{O}_2$

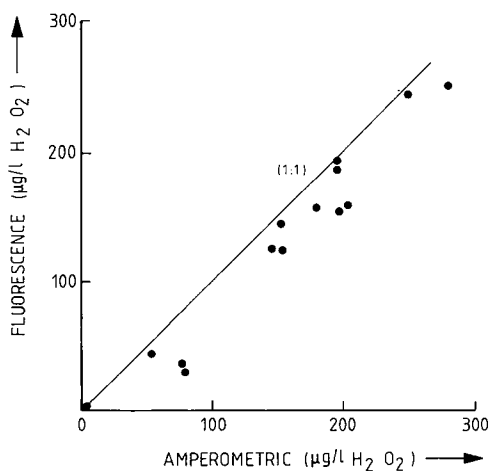
Sample No.	I Injection	II	III	I–II	I–III
	Direct	+ Catalase	+ Pt	$\text{H}_2\text{O}_2$ (Catalase)	$\text{H}_2\text{O}_2$ (Pt)
1	200	5	8	195	192
2	188	3	3	185	185
3	194	3	3	191	191
4	252	4	6	248	246
5	265	5	6	260	259
6	190	2	4	188	186
7	184	3	5	181	179
8	218	8	8	210	210
9	286	6	6	280	280
10	146	5	3	141	143
11	167	4	4	163	163
12	105	21	21	84	84
13	21	20	21	1	< d.l.
14	116	32	24	84	92

d.l.: detection limit.

Intercomparison  $\text{H}_2\text{O}_2$  analysis of rainwater and dew were performed using the presented electrochemical detection and the fluorescence detection. Results are shown in Figure 4 with correlation coefficient 0.9775, slope 0.98 and intercept  $-20 \mu\text{g H}_2\text{O}_2$  per liter. The amperometric results for unknown reasons are systematically higher than the fluorescence results. In the laboratory we use the fluorescence detection for reasons of sensitivity and the possibility to stabilize samples by addition of the fluorescence reagent in the field.<sup>23</sup> The amperometric method is applied for *in situ* measurements in view of the simple set-up.

The detection limit of the amperometric method is 5 microgram per liter, the method is linear up to 5 mg/l.

The greatest source of error in the sulfite determination is the instability of sulfite in samples generally due to oxidation catalyzed by metal ions. Losses of sulfite in samples stored at ambient temperature can reach 50% of the original concentration. Since the delay between sampling wet atmospheric deposition and analysis may be days, a technique for fixing sulfite is needed. The possibility of forming the 4-PDS/sulfite product with reagent addition in the collecting vessel was investigated. However at ambient temperature the background absorption increases with a factor 3 after one day.



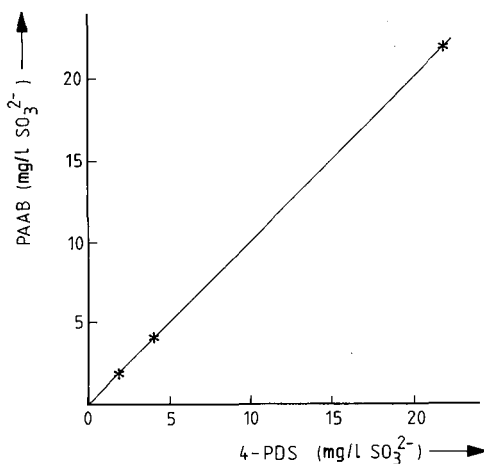
**Figure 4** Comparative analysis of rainwater for  $\text{H}_2\text{O}_2$  by amperometric detection or fluorescence detection and the use of catalase.

Stabilizing sulfite by means of EDTA gave good results, losses of only 5% per year were encountered. Preservation of sulfite in wet atmospheric deposition by addition of EDTA will be further investigated. The results of an evaluation of the presented method in comparison to the *para*-aminoazobenzene method are given in Figure 5.

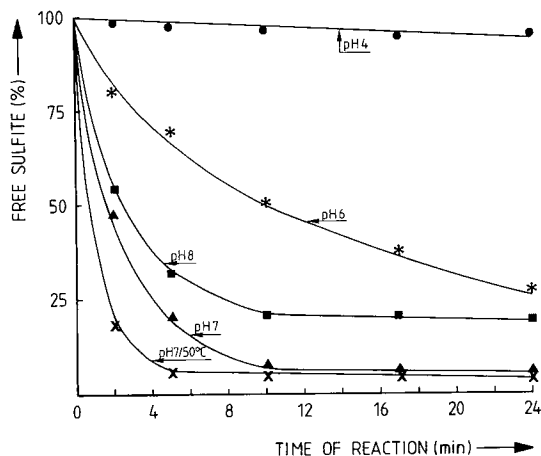
The calibration graph is linear up to 5 mg/l, the detection limit is 50  $\mu$ g sulfite per liter.

The indirect formaldehyde determination is quite selective, acetaldehyde concentrations up to 4 mg/l were not detected. Several authors reported optimal reaction kinetics at pH 7 for HMSA formation.<sup>5,6</sup> Increasing temperature from ambient up to 50°C enhances the speed of reaction at pH 7 significantly, as shown in Figure 6. HMSA formation is complete within a few seconds at the applied sulfite concentration in our FIA set-up, the conditions being pH 7 and a reaction temperature of 50°C.

The reaction of sulfite with 4-PDS proceed rapid and complete over the pH range of 4 to 7. HMSA is stable at decreasing pH, so the 4-PDS reagent to detect remaining sulfite is added at pH 4. The linear range of formaldehyde detection is limited by the loop volume and the background concentration of sulfite. Optimal sulfite con-



**Figure 5** Comparative analysis of sulfite standards ( $N=4$ ) by the proposed procedure (4-PDS) and the *p*-aminoazobenzene method (PAAB).



**Figure 6** HMSA formation as function of pH (4–8) and temperature (ambient – 50 °C) by measuring free sulfite after mixing equimolar concentrations of sulfite and formaldehyde.

centration in the reagent stream is 20 mg/l in terms of signal to background ratio. In our experimental set-up the calibration is linear up to 5 mg CH<sub>2</sub>O per liter. The detection limit is 50 µg CH<sub>2</sub>O per liter.

Results of formaldehyde analysis in rainwater by the proposed method and HPLC in combination with DNPH-derivatization are given in Table 2.

HMSA is unstable at pH > 9. By adding 0.01 N NaOH to the carrier stream, HMSA decomposes in sulfite and formaldehyde. The spectrophotometric reagent is added in a phosphate buffer pH 4, so the reaction between 4-PDS and sulfite is faster than the competitive HMSA recombination. This was confirmed by comparative analysis of 1 mg/l and 4 mg/l sulfite standards (bypassing the Pt reactor) and HMSA standards.

The calibration is linear up to 5 mg/l, the detection limit is 50 µg HMSA per liter.

Rainwater, mist and dew were sampled at the ECN located near the coast of the North Sea in the Netherlands. Analysis shows that a large fraction of S(IV) in these samples is present as HMSA. Some results are given in Table 3. Levels of HMSA are in the same order

**Table 2** Analysis of formaldehyde in rainwater by the proposed method and by HPLC in combination with DNPH derivatization (February 1987)

<i>Sample no.</i>	<i>4-PDS CH<sub>2</sub>O (µg/l)</i>	<i>HPLC CH<sub>2</sub>O<sup>a</sup> (µg/l)</i>
1	270	240
2	60	55
3	70	65
4	70	70
5	80	70
6	150	155
7	90	105
8	80	75
9	120	125
10	80	75
11	170	135
12	120	105

<sup>a</sup>Eluent: 65% methanol/35% 0.01 M HCl. Loop: 100 µl. Column: RP-18 (4.2 × 100 mm). UV detection: 360 nm.

**Table 3** HMSA and sulfite analysis of rainwater, mist and dew by the proposed method (January–February 1987)

<i>Sample</i>	<i>pH</i>	<i>Sulfite (mg/l)</i>	<i>HMSA (mg/l)</i>
dew 1	4.82	0.3	0.2
dew 2	4.56	0.4	0.1
dew 3	4.38	0.3	0.1
mist 1	2.93	3.6	5.0
mist 2	2.90	1.5	4.4
mist 3	2.94	1.7	3.7
mist 4	2.80	1.6	4.9
rain 1	5.45	0.2	1.8
rain 2	3.76	1.1	1.0
rain 3	3.65	0.6	0.5
rain 4	3.57	0.7	0.5
rain 5	3.62	0.5	0.4



of magnitude as reported by Munger *et al.*<sup>5</sup> The proposed method will be applied in further research to evaluate the role of HMSA in atmospheric chemistry.

## CONCLUSION

A flow injection set-up was constructed, which allows the determination of  $\text{H}_2\text{O}_2$ , sulfite, formaldehyde and hydroxymethanesulfonic acid. Amperometric  $\text{H}_2\text{O}_2$  detection offers the possibility of a simple, robust field instrument. 4-PDS proved to be a very versatile reagent. Based on the 4-PDS/sulfite reaction selective and sensitive determinations were developed for sulfite, formaldehyde and hydroxymethanesulfonic acid. Substantial concentrations of the latter compound were observed in precipitation, fog and dew in The Netherlands.

## Acknowledgement

Appreciated contributions were made by M. Geusebroek and A. van Wensveen-Louter.

## References

1. S. A. Penkett, B. M. R. Jones, K. A. Brice and A. E. J. Eggleton, *Atmos. Environ.* **13**, 123 (1979a).
2. L. R. Martin and D. E. Damschen, *Atmos. Environ.* **15**, 1615 (1981).
3. T. J. Kelly, P. H. Daum and S. E. Schwartz, *J. Geophys. Res.* **90**, 7861 (1985).
4. J. W. Munger, D. J. Jacob and M. R. Hoffman, *J. of Atmospheric Chemistry* **1**, 335 (1984).
5. J. W. Munger, C. Tiller and M. R. Hoffman, *Science* **231**, 247 (1986).
6. G. L. Kok, S. N. Gitlin and A. L. Lazrus, *J. of Geophysical Research* **91**, D2, 2801 (1986).
7. G. L. Kok, *Atmos. Environ.* **14**, 656 (1980).
8. D. Klockow and P. Jacob, in: *Chemistry of Multiphase Atmospheric Systems* (W. Jaeschke and V. Mohner, eds.) (Springer-Verlag, Berlin, 1984).
9. P. Van Zoonen, C. Gooyer, N. H. Velthorst, R. W. Frei and G. Gubitz, *Anal. Chem.* **57**, 2071 (1985).
10. A. L. Lazrus, G. L. Kok, S. N. Giltin, J. A. Lind and S. E. McLaren, *Anal. Chem.* **57**, 917 (1985).
11. G. Masuch, A. Kettrup, R. K. A. M. Mallant and J. Slanina, *Intern. J. Environ. Anal. Chem.* **27**, 183 (1986).

12. P. K. Dasgupta and H. Hwang, *Anal. Chem.* **57**, 1009 (1985).
13. P. W. West and G. G. Gaeke, *Anal. Chem.* **28**, 1816 (1956).
14. P. K. Dasgupta, K. De Cesare and J. C. Ullrey, *Anal. Chem.* **52**, 1912 (1980).
15. M. Lindgren, A. Cedergren and J. Lindberg, *Anal. Chim. Acta* **141**, 279 (1982).
16. M. A. Bhatt and V. K. Gupta, *Analist* **198**, 374 (1983).
17. S. J. Kniseley and L. Troop, *Anal. Chem.* **38**, 1246 (1966).
18. R. E. Humphrey, M. H. Ward and W. Hinze, *Anal. Chem.* **42**, 698 (1970).
19. T. Nash, *J. Biochem.* **55**, 416 (1953).
20. R. V. Smith and P. W. Erhardt, *Anal. Chem.* **47**, 2462 (1975).
21. E. B. Rietz, *Anal. Lett.* **13**(A12), 1073 (1980).
22. International Standard ISO 2227: Formaldehyde solutions for industrial use—  
Determination of formaldehyde content, ref. no. ISO 2227-1972.
23. G. L. Kok, K. Thompson, A. L. Lazrus and S. E. McLaren, *Anal. Chem.* **58**, 1192 (1986).