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Determinations of trace anions in hydrogen peroxide

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Abstract

Hydrogen peroxide plays an important role in the semiconductor industry and needs to be analyzed for anionic impurities. In the past, the sample was pretreated with Pt to avoid reactions of H_2O_2 with the resin material of the respective anion exchanger. However, this pretreatment with Pt is time-consuming, may cause contaminations and leads to degradation of stabilizers because of the heat generated during the treatment. An ion chromatographic technique has been developed allowing the direct injection of the sample. Within this paper chromatograms of different types of H_2O_2 were analyzed, the observed method detection limits and the reproducibility of this method are shown.

1. Introduction

Hydrogen peroxide is a chemical having a variety of uses. One of its common applications is the use as a reactant in the synthesis of inorganic and organic peroxides, such as perborates, percarbonates and peroxoacetic acid. Furthermore, H_2O_2 is used during the formation of softening compounds in polymers by the epoxidation of oils, fatty acids and for the technical production of diphenols and hydrazine [1]. It is used for bleaching of cellulose, paper, natural and synthetic fibres, and a variety of other materials, e.g. oils, waxes, starch, sulfuric acid, feathers, furs, sponges, etc. In the treatment of waste water, hydrogen peroxide plays an important role in the removal of cyanide, phenols and sulfur compounds. It can also be used for the desodoration of waste water and sludges by oxidation of H_2S. It can be applied as an antiseptic for medical purposes, for the disinfection of surfaces, and for the sterilisation of food packaging [2].

Since hydrogen peroxide is one of the most important chemicals for etching and cleaning processes in the semiconductor industry, the interest in an automated determination technique is increasing [3]. Since ionic impurities may cause defects and malfunction of the final micro chips, H_2O_2 has to be analyzed for ions. Due to the special purity requirements (e.g. anion concentrations in the low μg/l range) it is necessary to eliminate sources for contamination during the sample preparation and the subsequent analytical determination. For hydrogen peroxide samples, it is known that repeated injections of solutions containing higher concentrations of H_2O_2 than 3% can irreversibly degrade the analytical anion exchanger column used for ion chromatographic determinations [4,5]. The high eluent pH (>10) seems to support the oxidation reactions of hydrogen peroxide with the resin due to the formation of the peroxohydroxide anion (HO_2^-) [2,6].

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The most commonly applied sample preparation for H_2O_2 solutions is treatment with metals such as Pt to decompose hydrogen peroxide catalytically to H_2O and O_2 [7]. This pretreatment, however, is time-consuming, may cause contaminations and leads to the degradation of stabilizers because of the heat generated during the treatment.

We have developed an ion chromatographic (IC) technique allowing the direct injection of hydrogen peroxide samples. This technique includes an on-line matrix elimination and an enrichment step followed by an analytical separation. Due to the commonly used industrial formation process of hydrogen peroxide (autoxidation of anthrahydrochinone, extraction with organic solvents, distillation, etc.) mono- and divalent organic acids are present in the final product [7]. Therefore, a gradient elution is appropriate for the separation of the inorganic ions from these organic acids.

This paper presents the analysis of different types of H_2O_2, the observed method detection limits (MDLs) and the reproducibility.

2. Experimental

2.1. Apparatus

All experiments were carried out with a DX-300 IC system (Dionex, Sunnyvale, CA, USA) consisting of a quaternary gradient pump (AGP), a chromatographic module and a conductivity detector. Eluents were degassed by purging them with helium using the eluent degas module. The DX-300 system was modified as shown in Fig. 1. An additional inert double stack four-way slider valve (5000 p.s.i.; 1 p.s.i. = 6894.76 Pa) was placed between a rotary injection valve (Rheodyne 9126) and the analytical column. Both valves were controlled by controls 5 and 6 on the AGP. Separations were performed on an IonPac AS11 anion exchanger. The respective guard column (IonPac AG11) was used as a concentrator column. Conductivity detection was carried out using an anion self-regenerating suppressor (ASRS-1) in the recycle mode. To remove anionic contaminants from the eluent an anion trap column (ATC-1, Dionex)

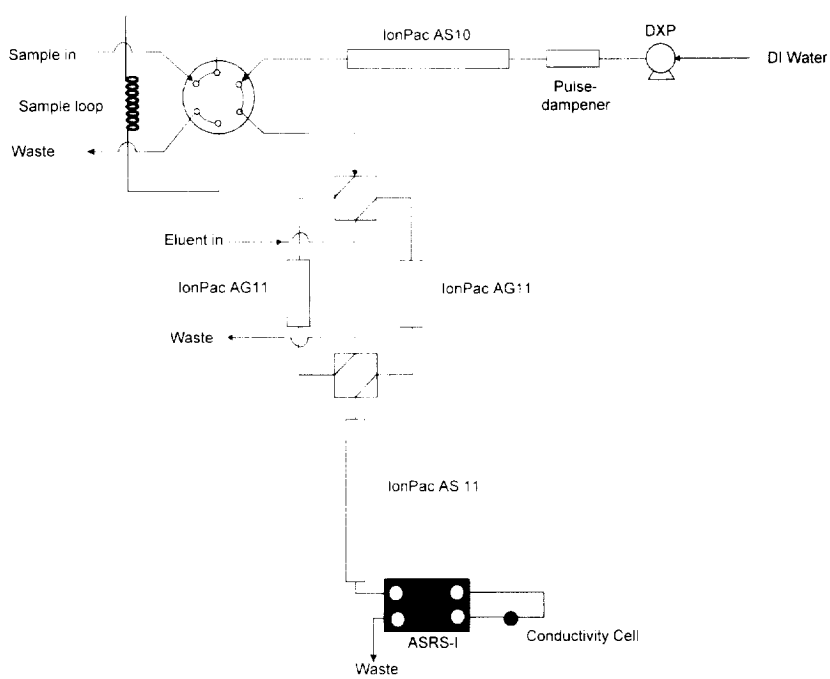

Fig. 1. Schematic flow diagram of the IC system used for the determination of anions in hydrogen peroxide. For experimental details see Table 1. DI = Deionized.

was placed in line with the gradient pump and the concentrator column. An external pump (DXP, Dionex) was used for sample delivery to the concentrator column via the injection valve, and for the subsequent rinsing step with water. The DXP flow-rate was set to 1.5 ml/min. In order to remove anionic traces from the water used, an additional column (IonPac AS10) was placed between the DXP and the metal free injection device. Instrument control, data collection and processing were performed with a chromatographic data system (AI-450, Dionex).

2.2. Reagents

Deionized water (18 MΩ cm resistivity at 25°C, used for eluent preparation) was obtained from a water-purification system (Seral, Ransbach-Baumbach, Germany). Sodium hydroxide (50%) was purchased from Baker (Gross Gerau, Germany).

Diluted working standards of all anions under investigation were prepared freshly from 1000 mg/l stock solutions. All stock solutions were stored in polyethylene containers, the working standards were prepared in polypropylene flasks.

2.3. System preparation

After installation of the IC system all parts including DXP and IonPac AS10 column were rinsed with 200 m*M* NaOH for about 12 h. During this cleaning procedure, the valves 5 and 6 were switched periodically ON and OFF to remove contaminants from interior valve parts. After this rinsing procedure, the DXP and the IonPac AS10 were flushed with deionized water for about 1 h. Before starting the analytical examinations, the "system blank" was tested by running the method (Table 1) without flushing the injection loop. Since metals are known to induce the decomposition of hydrogen peroxide, it is necessary to reconfigure the injector by using a rotor seal, which is normally used for the

Table 1
Ion chromatographic conditions

Columns	Dionex IonPac AG11 / AS11
Trap columns	ATC-1
	IonPac AS10
Eluents	E1: 50 m*M* NaOH
	E2: deionized water
	E3: 200 m*M* NaOH

AGP Program (linear gradient)

Time (min)	Curve	E1 (%)	E2 (%)	E3 (%)	5 INJ	6 AUX
0.0 start rinsing step	5			100	0	0
2.0 end rinsing step	5			100	0	0
2.1 start equilibration	5	3	97		0	0
10.5 end equilibration	5	3	97		1	0
12.1 start sampling	5	3	97		1	1
15	5	3	97		1	1
28	5	80	20		1	1
30	5	80	20		1	1

Eluent flow-rate	1 ml/min
Detection	Dionex CDM-3 conductivity detector
Suppressor	ASRS-1 (auto-recycle mode; range 3)
Sample injection volume	750 μl
DXP Flow-rate	1.5 ml/min

automation with autosamplers, to avoid metallic injection needles (Fig. 1).

2.4. System operation

The chromatographic conditions are listed in Table 1. After the rinsing and equilibrating step the DXP was started to deliver water with a flow-rate of 1.5 ml/min. At 10.5 min the injection valve was switched on, while valve 6 was kept off. Concurrently, the DI water flushed the sample loop and passed through the IonPac AG11 column. At this point, the dissolved anions were retained, while the hydrogen peroxide was eluted off the concentrator column to the waste. At 12.1 min, the IonPac AG11 concentrator was switched in-line with the IonPac AS11 (valve 6 ON) at which point the retained anions were eluted to the analytical column. At the same time, the DXP was stopped.

2.5. Samples

The samples were obtained from different suppliers. Sample B was not stabilized, whereas phosphate and pyrophosphate were added to the samples W1 and W2 to prevent catalytic decomposition of H_2O_2 by formation of phosphate or pyrophosphate complexes. However, sample F was stabilized with an unidentified compound. The chemical properties are shown in Table 2. These samples represent a collection of the different types of commercially available hydrogen peroxide.

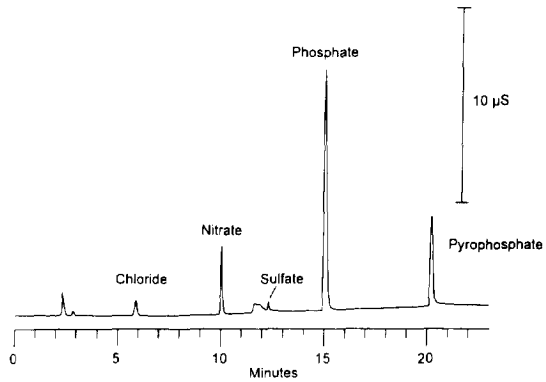

Fig. 2. Standard separation of five anions using the chromatographic conditions mentioned in Table 1. Sample concentrations: chloride (10 µg/l), nitrate (100 µg/l), sulfate (5 µg/l), phosphate (1 mg/l), pyrophosphate (500 µg/l).

3. Results and discussion

As hydrogen peroxide is one of the most important chemicals in the semiconductor industry, it must be analyzed for low concentrations of anionic impurities. Therefore, a new sample preparation technique, combining a matrix elimination and a concentrating step, was developed.

To ensure the applicability of the described method for both stabilized and non-stabilized H_2O_2, a guard column was used as the concentrator. A combination of both an IonPac AG11 as a concentrator column and an IonPac AS11 analytical column allows simplified gradient work [8] due to their common selectivity.

Fig. 2 shows that the ions of interest elute within 20 min. For hydrogen peroxide containing

Table 2
Chemical properties of the H_2O_2 samples investigated

Sample	Supplier	Content of H_2O_2 (%)	Stabilizer	Used for
B	A	35	None	Semiconductor purposes, "electronic grade"
W1	B	60	Phosphate, pyrophosphate	Oxidation reactions, "reagent grade"
W2	B	60	Phosphate, pyrophosphate	Oxidation reactions, "reagent grade"
F	Fluka	30	?	Oxidation reactions, "reagent grade"

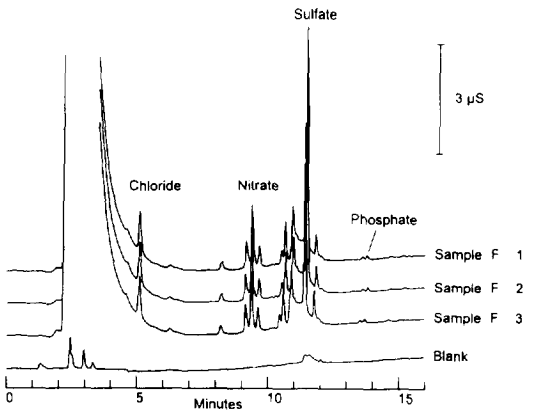

Fig. 3. Determination of anions in 30% H_2O_2 ("reagent" grade). For quantitative details see Table 3 (sample F).

no pyrophosphate, separation time can be reduced to 15 min.

Fig. 3 shows a summary of chromatograms, obtained by multiple injections of sample F. Using the described chromatographic conditions, it is possible to separate chloride from the predominant peak in the beginning of the chromatogram. Due to the NaOH eluent, phosphate elutes as a trivalent anion at about 13.5 min. A blank chromatogram is included in this figure to demonstrate the good baseline performance. The small peaks, which can be seen in the blank chromatogram can be attributed to compounds that are not totally removed from the deionized water. Short-chain organic acids such as formic and acetic acid elute between 2 and 4 min. The little hump at 11.5 min can be assigned to carbonate. These peaks do not interfere with the ions of interest. The upper three chromatograms represent typical chromatographic results for sample F. The respective amounts for the inorganic ions are summarized in Table 3. Close to the retention time of sulfate various unknown peaks are detected. Due to their retention, these peaks can probably be assigned to the group of divalent organic acids, or to organic acids with a stronger adsorptive behaviour towards the resin of the analytical column.

Fig. 4 shows the analysis of the electronic-grade sample B. Here, much lower amounts of anions (Table 3) are present with a different content of organic acids. In contrast to sample F, where two peaks elute close to nitrate, no

Table 3
Concentrations and standard deviations (S.D.) observed for the anions in the investigated hydrogen peroxide samples

Sample	Concentration				
	Chloride	Nitrate	Sulfate	Phosphate	Pyrophosphate
W1	422 µg/l	21.5 mg/l	0.74 mg/l	172 mg/l	32.9 mg/l
S.D.	29 µg/l	0.34 mg/l	0.03 mg/L	3.7 mg/l	0.6 mg/l
W2	4.42 mg/l	115 mg/l	3.04 mg/l	32.9 mg/l	97.9 mg/l
S.D.	0.5 mg/l	4 mg/l	1.1 mg/l	1.7 mg/l	3.8 mg/l
F	13.67 µg/l	44.3 µg/l	97.2 µg/l	9.79 µg/l	–
S.D.	0.12 µg/l	1.54 µg/l	2.09 µg/l	0.13 µg/l	–
B	2.47 µg/l	1.44 µg/l	< 3.4 µg/l	–	–
S.D.	0.12 µg/l	0.20 µg/l	0.62 µg/l	–	–

All values are averages of three replicates.

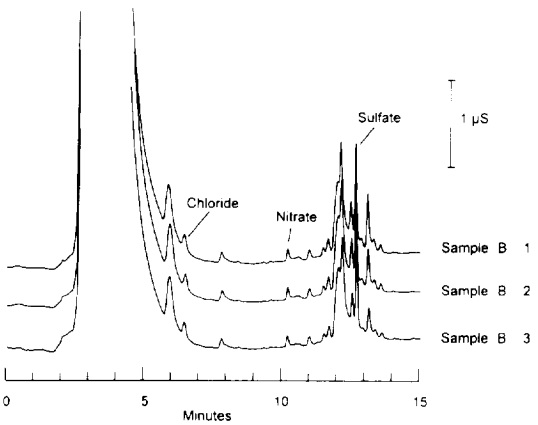

Fig. 4. Anion analysis in electronic grade H_2O_2 (35%). The observed concentrations and standard deviations are summarized in Table 3 (sample B).

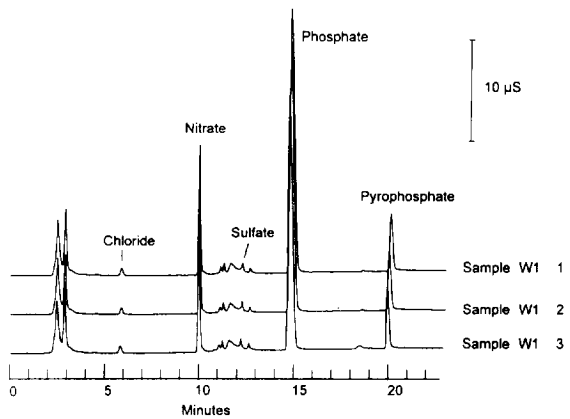

Fig. 5. Replicate chromatograms for the determination of anions in stabilized 60% hydrogen peroxide. For experimental conditions see Table 1. The sample was diluted with freshly prepared deionized water (1:50). The contents for the determined anions are summarized in Table 3 (sample W1).

significant signals are observed in this sample within this time frame. Despite the lower content of ionic contaminants in sample B, the composition of organic acids seems to be more complicated than in sample F. A significant difference between these samples can be found in the retention region around sulfate. While sample F harbors only four major peaks within this region, the chromatograms (Fig. 4) for the electronic-grade H_2O_2 show at least nine different compounds eluting close to sulfate. Both experiments show that sulfate is resolved from these impurities, allowing a reproducible quantitation (Table 3).

For the analysis of sample W1 a dilution of the original sample with deionized water was necessary to prevent an overloading of the concentrator column due to the higher concentrations of all ions of interest (Table 3). Fig. 5 shows chromatograms obtained by replicate injections of this sample, demonstrating the repeatability of this technique. Due to the resulting lower concentrations of the expected organic acids eluting in front of chloride, at least two peaks were obtained within the time frame of 2 to 4 min.

To shorten the overall analysis time, as shown in Fig. 6, a step gradient allows the determination of the major components within 12 min, in comparison to about 21 min with a linear gradient (Fig. 5) [9]. Sample W2 is hydrogen peroxide stabilized with a different content of phosphate and pyrophosphate (Table 3) compared to sample W1. To avoid overloading of the concentrator column with the ions of interest it was necessary to dilute sample W2 with deionized water, too.

All chromatograms of the examined samples

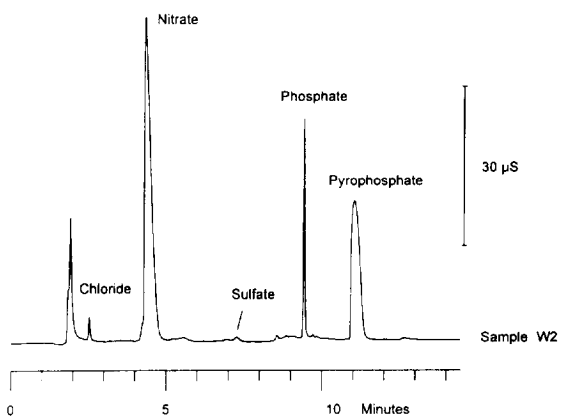

Fig. 6. Anion determination in stabilized 60% hydrogen peroxide (sample W2) using a step gradient [9]. Sample loop: 250 µl; gradient: 10 m*M* NaOH for 6 min, then change to 44 m*M* NaOH. Further experimental details see Table 1. The sample was diluted with freshly prepared water (1:10). Concentrations and standard deviations are summarized in Table 3.

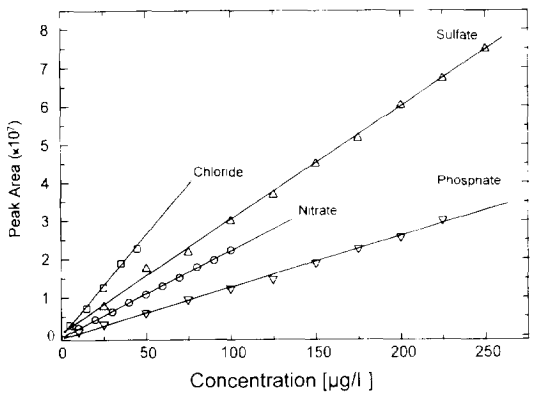

Fig. 7. Calibration curves for the determined trace anions in hydrogen peroxide.

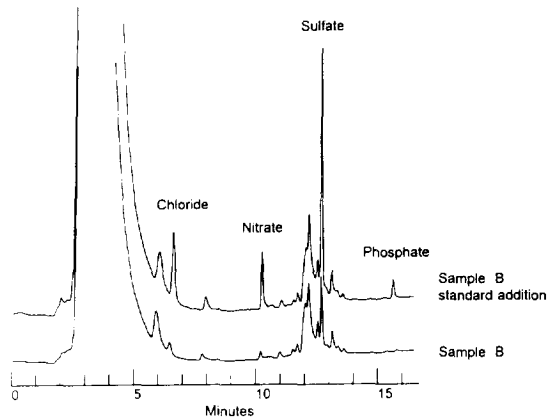

Fig. 8. Standard addition of anions to sample B. Bottom: original sample; top: sample B after spiking with 20 µg/l of chloride, nitrate, sulfate and phosphate.

show a predominant peak during the first minutes of the separation. The identification of the compounds responsible for this peak was carried out using capillary electrophoresis. Using a buffer solution consisting of 5 m*M* potassium hydrogenphthalate with 3.25 m*M* NaOH, and 1.6 m*M* triethanolamine with 0.75 m*M* hexamethonium hydroxide, adjusted to pH 6.3 with HCl (1 *M*), it is possible to detect acetate and formate via indirect UV detection at 250 nm. The voltage applied for the separation was 15 kV and was kept constant during the run. The chosen capillary had an inner diameter of 50 µm and a length of 50 cm. Gravity injection was used for 10 s at an altitude of 100 mm. Preliminary investigations indicate concentrations of about 33 mg/l acetate and 4 mg/l formate in sample B, and 27 mg/l acetate and 4 mg/l formate in sample F.

Sample W1 was also investigated but due to the high concentrations of nitrate, phosphate and pyrophosphate, no peaks were detected, even after a dilution of the sample.

The quantification for the ions of interest was carried out using external standard calibration utilizing mixed standard solutions with at least five different calibration levels (Fig. 7). The results are listed in Table 4. As can be seen, most of the linear calibration plots result in *r* values around 0.999. For concentrations lower than 5 µg/l the relative standard deviations (R.S.D.s) increased (Table 3), therefore standard addition should be used to more accurately determine the respective anions (Fig. 8).

The detection limits —based on three times

Table 4
Calibration parameters for anion determinations in hydrogen peroxide

Ion	Range (µg/l)	Linear correlation coefficient	Within-run precision (µg/l), $n = 3$[a]	MDL (µg/l)	R.S.D. (retention time)[a]
Chloride	5–45	>0.998	0.47	1.5	0.2
Nitrate	10–100	>0.999	0.14	0.4	0.1
Sulfate	25–250	>0.999	1.14	3.4	0.2
Phosphate	10–225	>0.999	0.82	2.5	0.1

[a]For the lowest calibration level.

standard deviation of the lowest respective standard— are between 0.4 to 3.4 μg/l (Table 4).

4. Conclusions

An improved method for the determination of trace anions in concentrated hydrogen peroxide solutions has been developed. This method involves elimination of the hydrogen peroxide matrix while the anions of interest are concentrated. The retained anions (chloride, nitrate, sulfate, phosphate and pyrophosphate) can be eluted using a sodium hydroxide gradient, and can be determined in low μg/l concentration ranges using suppressed conductivity detection, without further sample pretreatment. Due to the matrix-elimination step, it is possible to inject hydrogen peroxide solutions up to an H_2O_2 content of 35% directly, without damaging the anion exchange column. The detection limits for most anions are 0.4 to 3.4 μg/l.

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