

Determination of Trace Anions in Concentrated Hydrogen Peroxide by Direct Injection Ion Chromatography with Conductivity Detection after Pt-Catalyzed On-Line Decomposition

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A method has been developed for the determination of trace anion impurities in concentrated hydrogen peroxide. The method involves on-line decomposition of hydrogen peroxide, ion chromatographic separation and subsequent suppressed-type conductivity detection. H_2O_2 is decomposed in Pt-catalyst filled Gore-Tex membrane tubing and the resulting aqueous solution containing analytes is introduced to the injection valve of an ion chromatograph for periodic determinations. The oxygen gas evolving within the membrane tubing escapes freely through the membrane wall causing no problem in ion chromatographic analysis. Decomposition efficiency is above 99.99% at a flow rate of 0.4 mL/min for a 30% hydrogen peroxide concentration. Analytes are quantitatively retained. The analysis results for several brands of commercial hydrogen peroxides are reported.

Introduction

Hydrogen peroxide has wide applications in various fields. It is used as a bleaching agent for fiber, cellulose and paper, as a deodorant in waste treatment, as an antiseptic or disinfectant for medical or packaging purposes, and as a wafer cleaning agent in the manufacturing process of semiconductors.^{1,2} Among these, semiconductor processing requires the highest standard of purity, typically the low or sub-ppb range for metals and sub-ppm for anions. And the purity requirements are becoming stricter as semiconductor technology advances.

For metal determination, hydrogen peroxide can be directly analyzed by graphite furnace atomic absorption spectroscopy (GFAAS)^{3,4} or inductively coupled plasma mass spectrometry (ICP-MS),⁵ the commonly employed techniques. However, hydrogen peroxide can not be injected to an ion chromatograph (IC)⁶ for anion determination because it may result in damage to the column packing materials.^{7,8} At present, the sample is either diluted or decomposed prior to injection into the IC system. The dilution method is simple, but it suffers from such sensitivity loss that low ppb level determination becomes impractical. Therefore, decomposition methods using platinum^{9,10} or UV radiation¹¹ are generally utilized for determination of trace anions. However, this pretreatment method is time-consuming and prone to contamination. Recently, a direct analysis method¹² was reported. In this method, hydrogen peroxide is injected into a concentrator column where analytes are concentrated while the matrix is removed by washing it with deionized water so that direct contact of the matrix with an analytical column is avoided. This method is straightforward and provides the advantage of preconcentration capability. To use this method, it needs a modification in its instrumental setup, requiring an additional pump and an injection valve. However, this might be inconvenient to the user who cannot afford an instrument for such a specified purpose. In

addition, it may require frequent replacement of the concentrator column. Durability of the concentrator column was not described in the article, but one can imagine that the column lifetime must be shorter than its normal use because the packed resin for an AG11 concentrator column is the same as that for an AS11 analytical column.

Herein, we introduce an alternative method for the direct analysis of concentrated hydrogen peroxide. In this method, H_2O_2 is pumped directly into the injection valve via an online H_2O_2 decomposer consisting of hydrophobic membrane tubing filled with Pt-catalyst where H_2O_2 decomposes into water and oxygen gas. The gas is eliminated through the membrane wall, while the aqueous eluate containing the analyte flows into the valve of the ion chromatograph. The decomposer is simple to fabricate and use with no additional equipment needed to assemble it. It can be simply connected to the sample injection valve. There is virtually no analysis time delay in using it. Construction details and analytical performances of the H_2O_2 decomposer, and the analytical results of various types of hydrogen peroxide are given.

Experimental Section

Materials, Standards and Samples. Platinum wire (99.99+%, 0.127 mm diam., Aldrich, Milwaukee, WI, USA), platinum on activated carbon (1% Pt, 30-150 mesh, Aldrich), nichrome wire (0.4 mm diam., Jukwoo Metal, Japan), glass beads (250-300 μm , Sigma), and silicagel (230-400 mesh, Merck, Rahway, NJ, USA) were used as purchased. Platinum was coated on glass beads and silicagel by soaking them in 1,000 ppm platinum solution, filtering the solution, and subsequent heating of the filtered residue in a furnace at 600 °C overnight. Platinum was electroplated on nichrome wire by applying electrical current (3.4 V DC, 0.03 Amp.) through the wire in 100 ppm Pt solution (0.1 N HCl) for three hours. Microporous Teflon membrane, Gore-Tex (1-2 μm pore size, 70% porosity, 1.8 mm i.d., 0.5 mm

thick, Berghof Inc., CA, USA) was used for H₂O₂ decomposer fabrication. Sodium carbonate (99.7%, A.C.S reagent grade, Aldrich) and Sodium bicarbonate (99.5%, A.C.S reagent grade, Aldrich) were used in eluent preparation for the IC analysis. A potassium permanganate solution for the titration of H₂O₂ was prepared using reagent grade KMnO₄ (Wako Chemical Co., Japan) and was subsequently standardized by using sodium oxalate standard. Deionized water from a Milli-Q water purification system was used for both standard and solution preparations. Anion working standard solutions were prepared weekly by serial dilutions of 1,000 ppm stock standards (Wako Chemical Co., Japan). All other chemicals not described were of analytical or equivalent grade.

The H₂O₂ samples, three electronic grades and three reagent grades, were obtained from different commercial suppliers. All samples were assayed to be 32-35%. The reagent grade H₂O₂ may have contained stabilizers but further information was unavailable.

H₂O₂ Decomposer Fabrication. The decomposer was fabricated by packing various types of platinum catalyst in microporous Teflon membrane tubing (Gore-Tex, pore size 1-2 μm, porosity 70%, 1.8 mm i.d., Berghof, CA, USA). An on-line decomposer for H₂O₂ was made by filling Pt-catalyst in a piece of Gore-Tex tubing and then closing off both ends with porous polypropylene frit discs (35 μm pore size, Belart Plastic Co., USA). Both sides of the Gore-Tex tubing were extended using silicone tubing (0.51 mm i.d. 1.53 mm o.d.), with the aid of teflon tape. Finally, the tubing was jacketed in a glass tube (6 mm i.d.) through which pure water flowed. This coolant jacket prevented sample solution from being contaminated from air and from overheating. Due to the hydrophobic nature of Gore-Tex tubing, the oxygen produced escaped freely through the membrane wall while the ionic analytes remained in aqueous solution. A schematic diagram of the decomposer is illustrated in Figure 1.

System Configuration. Instrumental arrangements for an online decomposition and an ion chromatography system are shown in Figure 2. The arrangement is a typical system for suppressed cation chromatography. A peristaltic pump is connected to an online H₂O₂ decomposer which is in turn connected to the six-way injection valve of the ion chromatograph. The peristaltic pump (Miniplus 3, Gilson, Middleton, WI, USA) is connected to two bottles, one for the sample and the other for the deionized water coolant. Flow rate for sample and coolant are 0.3 mL/min and 3.6 mL/min,

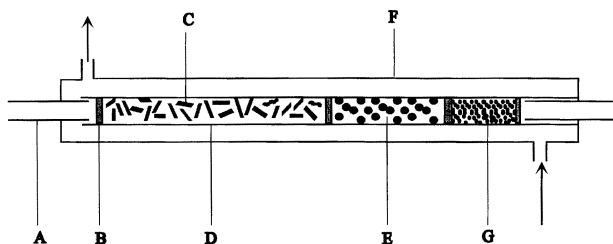


Figure 1. Construction of the online H₂O₂ Decomposer: A, Silicon tubing; B, Polypropylene frit; C, Pt-wire cut; D, Gore-Tex tubing; E, Pt-wire cut; F, Glass tubing; G, Pt-coated silicagel.

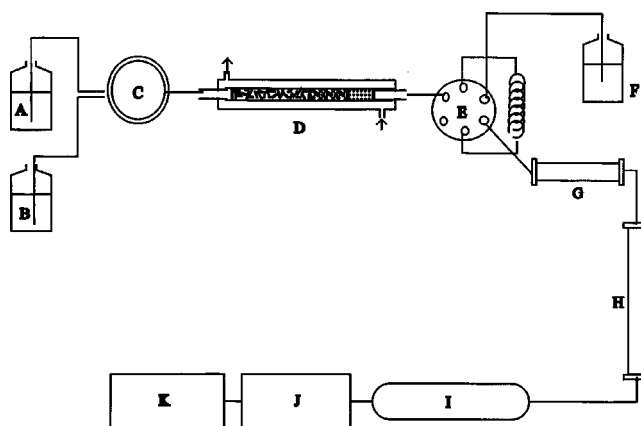


Figure 2. Instrumental configuration for the online decomposition for H₂O₂ and ion chromatography system: A, sample bottle; B, deionized water; C, peristaltic pump; D, H₂O₂ decomposer; E, six-way injection valve; F, carbonate buffer eluent; G, guard column; H, analytical column; I, anion suppressor; J, conductivity detector; K, recorder.

respectively. The ion chromatograph used was a basic suppressed IC instrument Altech model 325 pump, Altech model 350 conductivity detector (Altech Associates Inc., Deerfield, IL, USA), and anion auto regeneration suppressor (ASRS, Dionex, Sunnyvale, CA, USA). The chromatographic conditions were 3.5 mM Na₂CO₃ and 1.0 mM NaHCO₃ of eluent at a flow rate of 1.2 mL/min. Both a Dionex AG14 (50×4 mm) guard column and AS14 (250×4 mm) separator column were used for ion separation. Conductivity output was set at 1 μS/cm full scale and monitored with either a chromatography data system (Chromate™, Interface Engineering Co., Seoul, Korea) or a strip chart recorder.

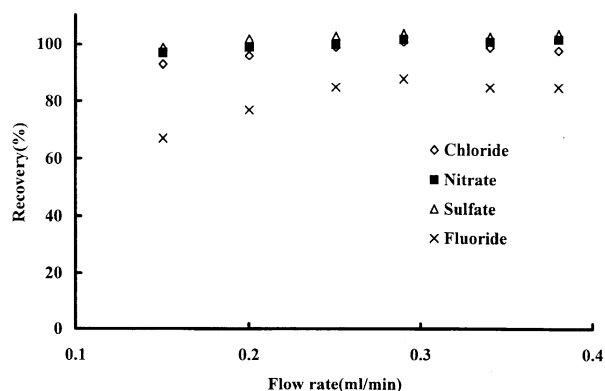
Results and Discussion

H₂O₂ Decomposition. In designing and fabricating an online decomposer, efficiency, speed and cleanliness are the most important parameters to be considered. H₂O₂ should be decomposed to a level so that no deterioration of the ion chromatography column occurs. This level should be variable depending on the type and manufacturer of the column. According to our experience, 0.01% H₂O₂ solution can be injected for a few weeks without loss in column efficiency (Dionex AS4A-SC and AS14). To reach this level from concentrated H₂O₂ (30-35%), the efficiency of the decomposer needs to be better than 99.95%. In addition, it is highly desirable to have a decomposer in which decomposition proceeds fast enough so the sample analysis time is not delayed. In the event of a slow decomposition reaction, the sample injection rate must be controlled to ensure decomposition efficiency and this may limit the sample analysis speed. Lastly, there should be no sample contamination during decomposition. Bearing the above criteria in mind, six types of decomposer were constructed and tested for their individual performances. The test results are summarized in Table 1. Initially, 26 cm long Gore-Tex tubing containing

Table 1. Decomposition Efficiencies for Various Types of H₂O₂ Decomposer

Decomposer description	Flow rate		Decomposition Efficiency (%)	
	Packing Material	Flow rate		
5% Platinum on Activated Carbon (100-200 mesh)		30	0.2	> 99.9
Twisted Platinum Wire (0.25 mm diam.)		26	0.50	34.6
Platinum on Glass Beads (100-200 mesh)		30	0.20	26.4
Platinum Wire-Cut (0.25 mm diam. 2-3 mm length)		5	0.4	99.3
Platinum Plated Nichrome Wire-Cut (0.25 mm diam. 2-3 mm length)		30	0.4	99.9
Platinum Wire-Cuts & Platinum on Silica-gel (0.25 mm diam., 0.125 mm diam., 2-3 mm length, 230-400 mesh)		5 + 2 + 1	0.40	>99.99

coiled platinum wire and 30 cm long tubing packed with Pt-coated glass beads were constructed but both gave less than 50% decomposition efficiencies at 0.50 and 0.20 mL/min flow rates, respectively. Upon raising the temperature of the decomposer to 40 °C, the efficiency increased by up to only 50%, but this was far below the target value. From this experiment, it became evident that a more effective catalyst was required. Thus we constructed a decomposer made of 5% Pt on activated carbon (100-200 mesh). This decomposer gave near complete decomposition efficiency (>99.9%). However, we immediately realized that use of this decomposer was not practical for two reasons. Firstly, at a reasonably fast flow rate, H₂O₂ decomposition proceeded so vigorously in the first 2-3 cm parts of the tubing that leakage of the sample solution through the membrane, caused by explosive generation of oxygen gas, was unavoidable. Secondly, the packing material was too impure to be used for trace analysis. In order to avoid an explosive reaction, we fabricated two decomposers with Pt wire-cut (0.25 diam., 2-3 mm length) and with Pt plated nichrome wire-cut (0.125 mm diam., 2-3 mm length). The former gave 99.3% efficiency while the latter >99.99%. The nichrome wire-cut decomposer was acceptable with respect to decomposition efficiency. However, we faced with several obstacles in applying it to a real sample analysis. H₂O₂ decomposition efficiency gradually degraded, presumably due to the oxidative dissolution of nichrome and therefore frequent replacement of the packing material was needed. This problem can be solved by using the same size Pt wire-cut (which was unavailable at that time). However, because of the membrane's large size and surface area, it was not only difficult to keep the blank low, but it required a lengthy sample washing time. Evidently, this problem may be resolved by reducing the membrane size and this can be done by serial packing of three Pt-catalysts of varying activity; from low to high. The last decomposer was constructed by serial packing of 5 cm long with 0.25 mm diam. Pt wire-cut (2-3 mm long), 1 cm long with 0.125 mm diam. Pt wire-cut (1-2 mm long) and 2 cm long with Pt coated silicagel (230-400 mesh). This decomposer was only 8 cm long, but highly efficient (>99.99%) and less prone to contamination. By jacketing the membrane tubing with deionized water-flowing glass tubing, it was possible to keep contamination from ambient air to below the detection limits and it minimized water loss from the sample solution. Without water cooling, water loss

**Figure 3.** Effects of sample flow rate on the analyte recovery.

through the membrane wall due to excessive heat generation from the H₂O₂ decomposition reaction becomes significant, causing a deterioration of precision. The efficiency of decomposition of this decomposer was invariable to a sample flow rate of up to 0.4 mL/min.

Analyte Recoveries. The effects of the sample injection flow rate on the analyte recoveries were determined by analyzing standards spiked with H₂O₂. Standard additions were made to the purest electronic grade H₂O₂ to make a final concentration of 0.5 ppm chloride. The results are depicted in Figure 3, showing near quantitative recoveries except for fluoride, of which recoveries were non-quantitative, especially at low and high flow rates. The different behavior of fluoride from that of other ions may be explained by its high volatility. Since Gore-Tex membrane is gas permeable, any species transformable to a volatile neutral species can escape through the membrane. Therefore, the weaker and the more volatile the conjugate acid, the higher the loss of an anion. Careful examination of other ions in Figure 3 reveals that the recoveries are in the increasing order of chloride, nitrate and sulphate and this can be explained by way of the same reasoning. The recoveries of the analytes are increasing with the flow rate to reach the maxima at a flow of 0.29 mL/min, and then decreasing slightly. This can be interpreted on the basis of ion residence time in the membrane and by the scrubbing effect of oxygen gas. These two effects work the other way and as a result, there may be a maximum recovery.

The above argument is supported by the effects of the solution's pH on the analytes' recoveries. As shown in Figure

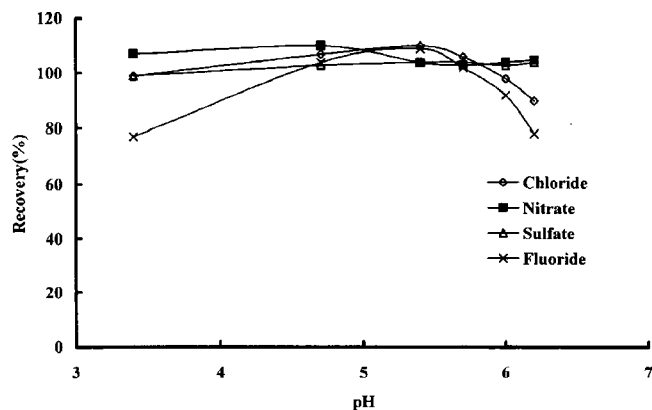


Figure 4. Effects of pH on the analyte recovery.

Table 2. Standard Additions and Recoveries of Trace Anions in 30% Hydrogen Peroxide

Analyte	Added	Found ($\mu\text{g/l}$)	Recovery* (n = 5)
Chloride	10.0	9.0	89.9 ± 5.8
	100	92.4	92.4 ± 3.1
	500	504.5	100.9 ± 1.5
Nitrate	10	98.4	98.4 ± 6.4
	100	103.0	103.0 ± 2.6
	500	509.0	101.8 ± 0.6
Sulfate	20.0	20.0	100.0 ± 6.4
	200	201.4	100.7 ± 2.3
	1,000	1040	104.0 ± 0.8

*Five replicate determinations

4, analyte loss decreased considerably upon the increase of the solution's pH. At high pH, dissociation equilibrium of a weak acid favors ionized forms. Recovery drops at high pH is an artifact of ion chromatography due to peak broadening by the hydroxide ion and this effect is more pronounced for early eluting ions such as chloride.

Precisions, Detection Limits and Calibrations. The precisions of the method evaluated by ten replicate analyses of electronic grade H₂O₂ spiked with standards showed RSDs of 5.8%, 6.4% and 6.5% RSD for 10 $\mu\text{g/l}$ chloride, 10 $\mu\text{g/l}$ nitrate and 20 $\mu\text{g/l}$ sulphate, respectively and of 0.85%, 0.48% and 0.64% for 500 $\mu\text{g/l}$ chloride, 500 $\mu\text{g/l}$ nitrate and 1,000 $\mu\text{g/l}$ sulphate, respectively. From the low concentration precision data, the detection limits defined by three times the standard deviations were calculated to be 1.8, 1.9

and 3.9 $\mu\text{g/l}$ for chloride, nitrate and sulphate, respectively. The calibration curves obtained by the analysis of standard spiked H₂O₂ over a range of 10-1,000 $\mu\text{g/l}$ were slightly concave due to the nonlinear response of anions in weakly acidic eluent. Correlation coefficients for linear fitting were in the order of 0.99. Therefore, the use of quadratic fitting or linear fitting over a narrow concentration range is recommended to minimize errors.

Accuracy and Interferences. Due to the lack of certified H₂O₂ standards for trace anions, the accuracy of the method was evaluated indirectly by two separate methods. The first method was based on the analyses of the samples spiked with known standards. As shown in Table 3, analyte recoveries are quantitative except for chloride at low concentrations. The second method involved parallel analyses of several samples by two different methods and then comparing the results. Three electronic grades from one company and three reagent grades from three different companies were analyzed by this method. Two samples of each grade were analyzed by the conventional batch decomposition method. The results by both methods are in very close agreement (Table 3).

H₂O₂ decomposition is accompanied by a sample mass and volume change, due to the loss of oxygen gas. In addition, the sample solution becomes heated due to the heat of reaction and as a result, the change in sample volume can be significant owing to water vapor loss through the membrane. The measurement was made by calculating the difference in volume of H₂O₂ before and after decomposition. Oxygen loss was measured to be 4.7% for 30% H₂O₂ and 7.8% for 35% H₂O₂. These are in agreement with the calculated values. Therefore, when variable contents of H₂O₂ are analyzed, volume correction is required for accurate determination. The volume change caused by heat loss becomes negligible when the decomposer is water-cooled. Concerns regarding a species change during Pt-catalyzed H₂O₂ decomposition have been mentioned in the earlier studies.¹² We tested for nitrate and sulphate, but no detectable variations were observed.

Sample Analysis. The results acquired by this method for three electronic (A, B, C) and three reagent (M, J, Y) grade hydrogen peroxides from various manufacturers are listed in Table 3. All values are the calculated averages of three replicate analyses. Typical ion chromatograms for sample A and M are shown in Figure 5. Analyte concentrations are gener-

Table 3. Comparisons of Analysis Results for Commercial Hydrogen Peroxide by This Method and by Ion Chromatography after Batch Decomposition unit: ppb

ID	sample grade	Chloride		Nitrate		Sulphate	
		this method	batch decomposition	this method	batch decomposition	this method	batch decomposition
A	electronic	7.6 ± 0.6	-	14.3 ± 0.4	-	14.4 ± 0.5	-
B	electronic	16.6 ± 1.3	14.8 ± 1.3	25.0 ± 1.3	27.0 ± 1.3	16 ± 12	160 ± 3
C	electronic	17.9 ± 0.2	18.0 ± 0.2	47.2 ± 0.5	48.3 ± 0.6	70.9 ± 0.8	66.1 ± 1.2
M	reagent	17.9 ± 1.3	16.5 ± 1.1	215 ± 17	223 ± 19	19.9 ± 0.9	20.6 ± 0.8
J	reagent	21.7 ± 0.7	-	11.2 ± 0.4	-	21.6 ± 1.2	-
Y	reagent	45.1 ± 1.5	40.3 ± 0.6	1130 ± 42	1140 ± 45	78.9 ± 3.1	75.3 ± 3.0

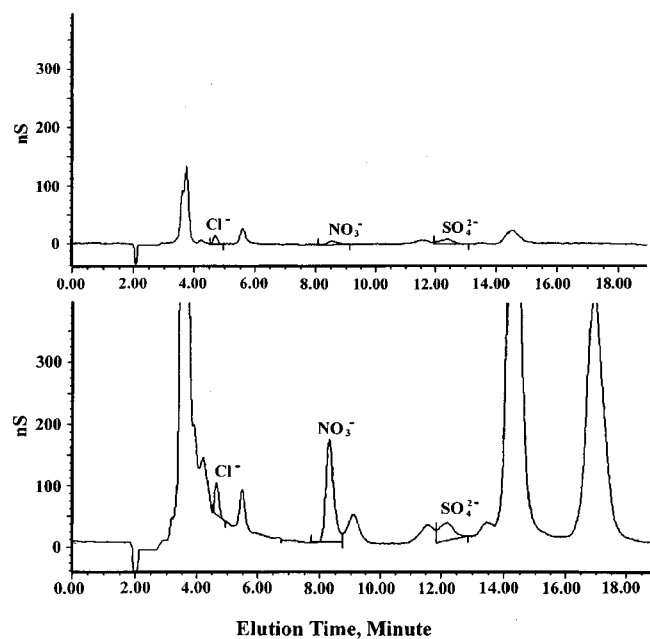


Figure 5. Typical ion chromatogram for H_2O_2 : (a) electronic grade sample A and (b) reagent grade sample M.

ally lower in electronic grades, especially nitrate. But, the real difference is evidently shown in the chromatograms; the one for reagent grade H_2O_2 has three distinctively large peaks. The first large peak seen after the water peak is likely from organic acid ions. The peaks at 14 and 17 minutes are suspected to be from two phosphate species, which are

known to be used as a stabilizer.

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