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Capillary electrophoresis methods for the trace cation analysis of semiconductor grades of hydrogen peroxide☆

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ABSTRACT

Method development and applications of capillary electrophoresis to the analysis of cations in highest purity grades of hydrogen peroxide which are used for semiconductor processing are discussed. Indirect UV detection in conjunction with electromigration sampling provides a sufficient sensitivity for measurements of low ppb (v/v) levels of contaminants. In contrast to hydrostatic sample introduction, the range of signal *vs.* concentration proportionality is limited with electromigration sampling. However, meaningful calibration plots can be obtained over the range of 1 to 35 ppb. Examples of electropherograms are presented for two different samples of semiconductor grade hydrogen peroxide. Also given are estimates of detection limits for cations found in analyzed samples.

INTRODUCTION

Purity requirements for semiconductor processing have increased to a level, typically the low or sub-ppb range, where only the most sensitive analytical tools available can be utilized. Inductively coupled plasma mass spectrometry (ICP-MS), graphite furnace atomic absorption spectroscopy (GFAAS), and ion chromatography (IC) are currently the most frequently employed methods. Unfortunately, the monitoring of hydrogen peroxide and other process chemicals under manufacturing conditions is frequently impossible by the current methods. Safety, clean room requirements and cost effectiveness are among the most important impediments to utilization of, for example, ICP-MS directly in the manufacturing environment.

Optimized capillary electrophoresis (CE) methodology for ion analysis [1] is emerging as an alternative to ICP-MS and GFAAS for trace metal analysis. With CE, frequent monitoring of multiple ions appears to be more feasible, even under the conditions encountered in semiconductor manufacturing.

Hydrogen peroxide was chosen for our study because it is utilized widely in critical wafer processing steps [2]. It also has a history of metallic contamination problems. Many of the contaminants can be traced to the measures which are used for stabilization of hydrogen peroxide against decomposition. Additionally, the presence of high levels of organic contami-

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nants have been detected by total organic carbon (TOC) measurements, as well as by IC and HPLC procedures [3]. According to recent results by one of the authors [4], even the newly introduced stabilizer-free grades of hydrogen peroxide contain a large number of carboxylic impurities. Based on that observation, our study focused entirely on the evaluation of the usefulness of CE for the analyses of unstabilized samples of hydrogen peroxide.

EXPERIMENTAL

Instrumentation

All assays of hydrogen peroxide samples as well as of standard solutions were carried out with the Quanta 4000 capillary electropherograph (Waters). A positive power supply was utilized for all analyses of cations reported here. Data were analyzed with the help of Waters Millennium Data Station. The rate for data sampling was at 20 Hz. The capillary of standard dimensions (60 × 52 cm, 75 μm I.D.) was also from Waters. Indirect UV detection was carried out at 185 nm in all separations. Polypropylene vials (4 ml) from Sun Brokers (Wilmington, NC, USA) were used for both sample and carrier electrolyte solutions. Electromigrative sampling of cations was performed for 30 s at 10 kV. Additional and more specific separation and sampling conditions are given in figure captions.

Chemicals

Only deionized, 18.2 MΩ water generated by the Milli-Q Laboratory Water Purification System (Millipore, Bedford, MA, USA) was used in all experiments. The UV Cat 1 [5] carrier electrolytes were prepared following the previously described procedures. The UV Cat 2 carrier electrolyte was made up by dissolving 11.5 mg of UV Cat 2 (Waters) and 36.6 mg of 2-hydroxy-2,4,6-cycloheptatrienone, which is known as tropolone (Aldrich, Milwaukee, WI, USA), in 50 ml Milli-Q water. The resulting electrolyte solution of pH 4.25 was filtered and degassed prior to use. Whereas the UV Cat 2 electrolyte gave better results after a preconditioning of fused-silica capillary with 10% KOH, the UV Cat 1 electrolyte was employed without any preconditioning of capillaries. Ultrex grade 30% hydrogen peroxide was from Baker (Phillipsburg, NJ, USA). The unstabilized, semiconductor grade, 30% hydrogen peroxide was purchased from two different suppliers.

All standard solutions were prepared from analytical grade salts (Aldrich) rather than by dilution of 1000 ppm (v/v) AAS standard concentrates. AAS standards were not used since they are generally acidic solutions, and it was desired to avoid introducing any species, particularly protons, which could affect the metal complexing equilibria and which are not present in the samples being analyzed. Moreover, protons in the sample can give rise to an unwanted peak.

Catalytic decomposition of hydrogen peroxide

An aliquot of 30% hydrogen peroxide was placed into a precleaned (24 h in 0.1 *M* nitric acid, 24 h in 18.2 MΩ water) and prechecked PMP (polymethylpentene) beaker (blank electropherograms of cations in a volume of deionized after 30 min residence in a precleaned beaker). The PMP beakers were obtained from VWR Scientific (Westwood, MA, USA). After immersion of precleaned platinum gauze (Aldrich, 525 mg + 25 × 25 mm), the sample began to boil vigorously as the decomposition progressed. The completeness of peroxide destruction was verified by titrations, carried out after addition of iodide, using thiosulfate as volumetric solution and starch as indicator. The reduction of peroxide was usually complete after *ca.* 2 min.

RESULTS AND DISCUSSION

Selection of carrier electrolytes

Two carrier electrolytes were evaluated for application to hydrogen peroxide samples. The separation and detection results with these electrolytes had been reported previously for aqueous samples. The UV Cat 1 electrolyte [5] makes possible separations of up to 28 different cations. The UV Cat 1 electrolyte includes 4-methyl-2-benzylamine which serves as the chromophore to make indirect UV detection possible and HIBA (α-hydroxyisobutyric acid) for metal complexation. The range of cations that can be separated by the UV Cat 2 electrolyte is narrower and is

limited to the following analytes: potassium, barium, strontium, calcium, sodium, magnesium, manganese, zinc and nickel [6]. The reported detection limits in aqueous standards are in the range of 18 to 388 ppb [5] and 31 to 267 ppt [6] by hydrostatic and electromigration sampling, respectively. The UV Cat 2 electrolyte consists of a proprietary organic basic cation which absorbs strongly in the UV and tropolone to serve as the chelating agent.

The comparison of cation separations with the two different carrier electrolytes is shown in Fig. 1A and B. Hydrogen peroxide in both samples was destroyed prior to the analysis using the catalytic procedure described earlier. Previously, the UV Cat 2 electrolyte was shown to yield 2.5 to 5 times higher sensitivity relative to that observed for the same cations and by similar sampling procedure in the UV Cat 1 electrolyte [6]. Improved sensitivity between the two electrolytes is recognizable also in Fig. 1 for the peaks belonging to calcium, magnesium and manganese. The enhancement in sensitivity of the UV Cat 2 electrolyte relative to the UV Cat 1 electrolyte is probably attributable to the differences in the metal complexing properties that exists been tropolone and HIBA; however, a detailed explanation for the differences in sensitivity is beyond the scope of this paper. The peaks belonging to sodium and potassium, on the other hand, show comparable peak areas by both methods. The authors attribute this to their inability to control trace levels of sodium and ammonium under the experimental conditions chosen for this report. Ammonium comigrates with potassium in both electrolytes but a separation of ammonium and potassium can be achieved by inclusion of a suitable crown ether in the electrolyte [7]. Higher levels of inadvertent contamination of the sample analyzed with the UV Cat 1 electrolyte is assumed to be a possible explanation for comparable peak areas obtained for potassium/ammonium and sodium peaks.

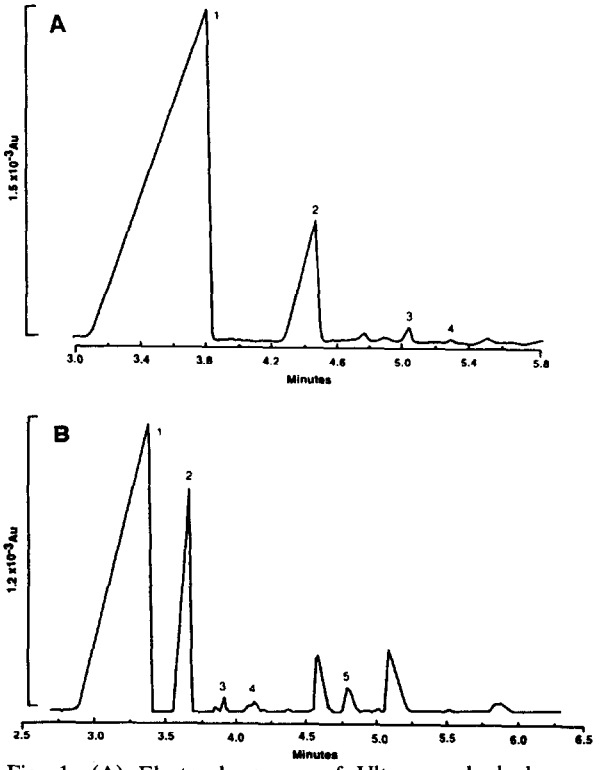

Fig. 1. (A) Electropherogram of Ultrex grade hydrogen peroxide, after catalytic decomposition, using 5 m*M* UV Cat 1–6.5 m*M* HIBA (pH 4.4). Fused-silica capillary dimensions 60 × 52 cm, 75 μm I.D.; separation voltage +20 kV; sampling for 30 s at 10 kV; indirect UV detection at 185 nm. (B) Electropherogram of identical sample and identical conditions used for Fig. 1A except the electrolyte was 1.2 m*M* UV Cat 2–3.0 m*M* tropolone. Peaks: 1 = potassium/ammonium, 2 = calcium, 3 = sodium, 4 = manganese (A) or magnesium (B), 5 = manganese.

We did not attempt to quantitate the impurities in the laboratory grade hydrogen peroxide. Yet, by comparison with subsequent separations in this report, it is clear that the levels of analytes shown in Fig. 1A and B are in the range of 0.1 to 1 ppm. These concentrations are at least an order of magnitude higher than those investigated in our calibration study (see the *Calibration Plots* paragraph below) and also much higher than the concentrations usually encountered in any semiconductor grade hydrogen peroxide. The additional, unknown peaks in Fig. 1A and B are attributable to the sample and not the carrier electrolyte.

Sample preparation

Hydrogen peroxide matrix can interfere with capillary electrophoretic analysis due to its redox (E_o = +0.8 V, [8]), complexing (log K_{FeL} *ca.* 9.3, [9]) and weakly acidic (p*K* *ca.* 11.6, [10]) properties.

Separations of cations with the help of the UV

Cat 1 carrier electrolyte are not possible in the 30% hydrogen peroxide. The quality of separation is strongly affected by excessive peak broadening and baseline noise. The highest analyzable concentration of hydrogen peroxide with the UV Cat 1 electrolyte is *ca.* 3%. This observation makes it preferable to employ catalytic reduction as a sample preparation for this method in order to avoid loss of sensitivity by dilution.

In contrast, the UV Cat 2 electrolyte can be used for analysis of cations even at 30% hydrogen peroxide. Neither a dilution nor catalytic reduction of peroxide matrix is required for separations with that electrolyte. An example of a direct cation analysis of concentrated hydrogen peroxide sample is shown in Fig. 2. The ability of UV Cat 2 electrolyte to separate cations without any interference from hydrogen peroxide is probably due to a more constant complexing behavior of tropolonate ligand contained in that electrolyte. Complexing ligands are used in CE electrolytes to increase selectivity. Due to the very close values of electrophoretic mobilities of most cations, CE separations would otherwise be difficult or impossible [1,5]. Whereas the complexing ability of most ligands (including α-hydroxyisobutyric acid in the UV Cat 1 electrolyte), decreases with increasing acidity, the values of stability constants of the tropolonate complexes are to a large degree independent of pH [8]. Based on this and on the quality of the separation shown in Fig. 2, UV Cat 2 appears to be the electrolyte of choice for the analysis of cations in concentrated hydrogen peroxide samples.

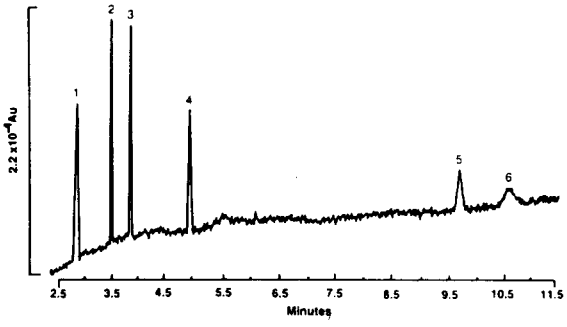

Fig. 2. Electropherogram of semiconductor grade 30% hydrogen peroxide spiked with 15 ppb of cations using same CE conditions as in Fig. 1B. Peak identification: 1 = potassium; 2 = calcium; 3 = sodium; 4 = manganese; 5 = nickel; 6 = zinc.

Calibration plots

Electromigration is a preferred mode of sample introduction from hydrogen peroxide samples. Due to the relatively low degree of dissociation, even at highest concentrations, hydrogen peroxide samples exhibit a lower conductivity than any of the carrier electrolytes under discussion. The preconcentration effect caused by electrostacking [1] can thus be expected not only for the catalytically reduced, but for concentrated hydrogen peroxide samples as well.

Feasibility of quantitation was evaluated by calibration plots for the concentration range of cations between 1 and approximately 35 ppb. Working conditions were such that it was not possible to prepare samples below 1 ppb without the danger of environmental contamination. It was found that above these levels (*i.e.* at 50–100 ppb and higher), slopes of calibration curves obtained by electromigration decreased almost to zero, making any quantitation difficult. These effects were observed with and without catalytic destruction of peroxide and can not thus be attributed to sample matrix. Linearity of electromigration sampling was investigated by one of the authors and conditions for reliable quantitation with that sampling mode were outlined in a recent report [11].

Fig. 3 shows representative calibration results for some of the cations analyzed directly in undecomposed 30% peroxide with the help of the UV Cat 2 electrolyte. Table I summarizes the linear regression results which cover the range of 1 to approximately 35 ppb. The slopes are given for both ppb and micromolar units. The former unit is in common use in the semiconductor industry, while the latter is of greater utility in making comparisons of CE behavior. Regarding the regression coefficients, we note that the value of the regression slope for sodium (2624) is approximately one half of that for all divalent cations in the same plot (Ca 4359, Mn 5393, Ni 4977 and Zn 5120). This shows the expected better sensitivity for divalent cations [12] on one hand and the compensating effect of sampling recoveries on peak areas on the other

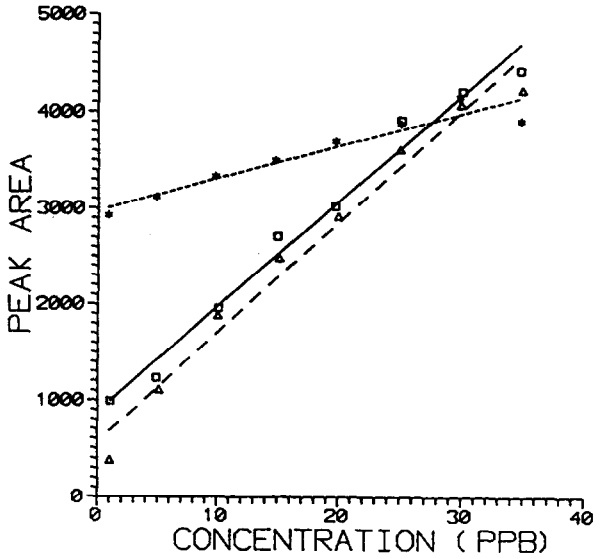

Fig. 3. Representative calibration plots shown for selected cations obtained using UV Cat 2 procedure. * = Potassium; △ = sodium; □ = calcium.

hand. If hydrostatic sampling were used, slowly migrating zinc ions would yield a larger area than, for example, the same amount of manganese ions. In electromigration, however, this effect is compensated for by a lower sampling recovery of less mobile ions, such as zinc, relative to that of more mobile ions, such as manganese. This also means that an approximate quantitation for multiple peaks is feasible after a calibration with just one standard. Because of the discussed compensation of increasing areas by decreasing recoveries, such "universal calibration" is probably possible only with electromigrative sampling. Of note in Fig. 3 is the regression line for the potassium peak. This can be explained by a large contamination of blank peroxide standard by either potassium or ammonium (see the discussion of the K/NH_4 peak in one of the preceding paragraphs). The nonzero intercepts reveal that the purest available semiconductor hydrogen peroxide which was selected for this work contained calcium, sodium, manganese, nickel, and potassium, but nondetectable levels of zinc.

TABLE I

LINEAR REGRESSION SUMMARY FOR CALIBRATION CURVES

Cation	Slope[a]		Intercept	R^2 [b]
	m_1	m_2		
Potassium	1310	33.5	2958	0.921
Calcium	4359	108.8	870	0.980
Sodium	2624	114.1	564	0.977
Manganese	5393	98.2	442	0.966
Nickel	4977	84.8	569	0.997
Zinc	5120	78.3	−33	0.960

[a] m_1 slope for micromolar concentration, m_2 slope for ppb concentration.
[b] Correlation coefficient.

Analysis of samples

The two electropherograms in Fig. 4A and B illustrate the ability of the discussed technique to detect a group of cationic impurities even in the highest purity samples of hydrogen peroxide. Concentrated peroxide samples can be analyzed directly without the catalytic decomposition step usually employed prior to the CE analysis of anions. The detection limits at 2 × the signal-to-noise ratio are summarized in Table II. The detection limit for potassium is not reported, since, as discussed previously, potassium comigrates with ammonium under the conditions of analysis.

Copper was found to be an exception. The most reproducible results for this cation were obtained using the peroxide decomposition step and the UV Cat 1 electrolyte. Using this procedure, a detection limit of 1.3 ppb was established.

The ability to analyze directly the undiluted hydrogen peroxide samples is essential for the reliable determination of alkali and alkaline earth cations. If sample handling is reduced to a minimum, the possibility of sample contamination by these analytes is also minimized. In actual practice, it is necessary to work in a clean room environment or under prefiltered laminar flow conditions to keep the environmental contamination to an absolute minimum. Moreover, an accurate quantitation of all the detected cations in the semiconductor grades of hydrogen peroxide, which was not pursued in this particular study due to the inability to control airborne contamination, would require the use of

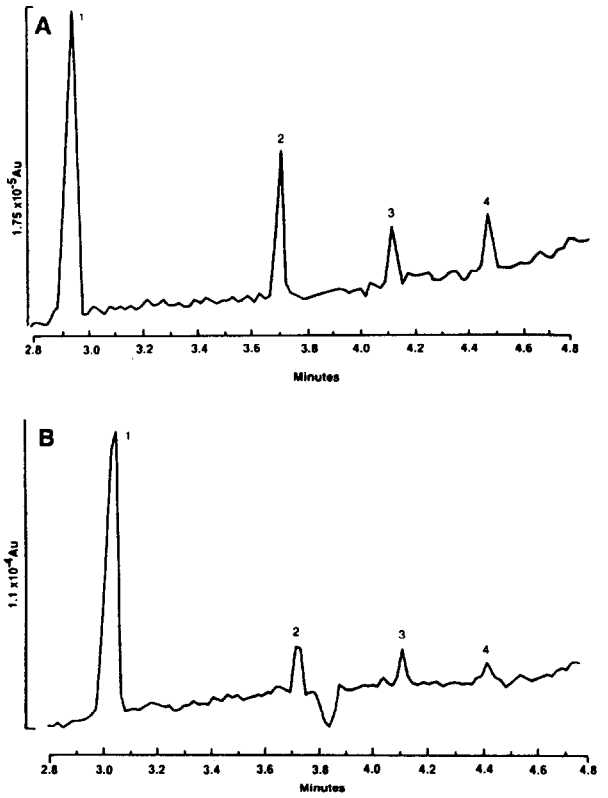

Fig. 4. (A) Electropherogram of source A semiconductor grade hydrogen peroxide (30% undecomposed, unstabilized) obtained using UV Cat 2 procedure listed in Fig. 1B. Detected species: 1 = potassium/ammonium; 2 = calcium; 3 = sodium; 4 = magnesium. (B) Electropherogram of source B semiconductor grade hydrogen peroxide obtained using same conditions as Fig. 4A. Detected species: 1 = potassium/ammonium; 2 = calcium; 3 = sodium; 4 = magnesium.

standard additions or the use of the calibration curve determined with a grade of hydrogen peroxide having lower trace metal contaminant levels that was available for this study. For example, using the standard additions approach, the Ca level for sample B was determined to be 6.2 ppb and Na was found to be 3.8 ppb.

The group IA cations have to be monitored and controlled carefully during semiconductor processing due to the deleterious effects of these ions upon semiconductor device properties, which can be attributed to the high diffusional mobility of these cations. From the alkaline earths, calcium is found most frequently in hydrogen peroxide samples of otherwise highest purity and the levels of that cation have to be also followed closely. Because of its lower cost and less extensive time requirements, the discussed method offers itself as an interesting alternative to GFAAS, which is exclusively utilized for IA and IIA cations at the present time [4].

TABLE II

LIMITS OF DETECTION IN 30% HYDROGEN PEROXIDE ANALYZED DIRECTLY WITH UV CAT2–TROPOLONE

Cation	Detection limit (ppb)
Potassium	–
Barium	2.8
Strontium	1.8
Calcium	0.7
Sodium	0.7
Magnesium	0.5
Manganese	1.3
Lithium	0.6
Nickel	3.3
Zinc	3.0

It is reasonable to assume that this CE approach can be further optimized to reduce the detection limits to the ppt levels which has already been achieved for water [6]. This study has illustrated the importance of the carrier electrolyte. There is a remaining need to not only enhance sensitivity but also to increase the number of metal ions which can be simultaneously determined. In fact, purity specifications for semiconductor processing chemicals continue to become more demanding. Soon the maximum allowable concentration of each metal ion will be 1 ppb, and an upper limit of 0.1 ppb is projected for the near future. Therefore, this work illustrates the enormous potential of CE for quality control testing of ultrapure chemicals.

REFERENCES

1 P. Jandik, W.R. Jones, A. Weston and P.R. Brown, *LC·GC*, 9 (1991) 634.
2 W. Kern, *Semicond. Int.*, 7 (1984) 94.
3 S. Sato *et al.*, *Technical Papers on Ultra Clean Technology*, Vol. 2, May 1988.

4 R. Carpio, J. Baylis, A. Diebold, R. Mariscal, T. Pinkston, D. Powell and E. Rosenfeld, in D.N. Schmidt (Editor), *Proceedings of the Symposium on Contamination Control and Defect Reduction in Semiconductor Manufacturing I*, Vol. 92-21, The Electrochemical Society, Pennington, NJ, 1992.
5 A. Weston, P.R. Brown, P. Jandik, W.R. Jones and A.L. Heckenberg, *J. Chromatogr.*, 593 (1992) 289.
6 A. Weston, P.R. Brown, P. Jandik and A.L. Heckenberg, *Anal. Chem.*, in press.
8 R.C. Weast (Editor), *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 74th ed., 1993, pp. 8–24.
9 J. Evans, N. Uri and E.P. George, *Trans. Faraday Soc.*, 45 (1949) 230.
10 A.E. Martell, Texas A&M University, personal communication.
11 P. Jandik, M. Fuchs and W.R. Jones, *Electrophoresis*, submitted for publication.
12 E.S. Yeung, *Acc. Chem. Res.*, 22 (1989) 125.