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Reproducible digestion method for ion-chromatographic analysis of anions in 30% hydrogen peroxide

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Abstract

Semiconductor-grade hydrogen peroxide (30%) is analyzed for anion contamination to be certain the levels of each analyte do not exceed 30 ppb (w/w). This paper presents a reproducible, platinum-decomposition approach that uses ion chromatography to quantify the various analytes (fluoride, chloride, sulfate, bromide, nitrate, and phosphate). Important to the success of the method are: (1) use of disposable HDPE bottles for the digestion, (2) immersion of the bottles in a water bath, (3) careful re-mixing of the digesting peroxide after two (of six total) hours, and (4) careful clean-up and sample-handling procedures (to avoid contamination). Except for fluoride and nitrate, all analytes exhibited recoveries from 89.6 to 98.3%, with ± prediction intervals (at the 95% confidence level) from 1.5 to 3.0 ppb. Fluoride's recovery was low (74.9%), but reproducible (± prediction interval at 95% confidence=2.0 ppb). Nitrate recovery was 99.1%, but noisy (± prediction interval at 95% confidence=8.7 ppb); this imprecision was thought to be due to contamination from atmospheric nitrite. A Dionex DX 500 microbore ion chromatograph with AS15 column and 1-ml sample loop were used for all determinations; detection was by conductivity. Statistical analyses were performed using JMP software.

Keywords: Statistical analysis; Platinum digestion; Calibration curves; Detection limit; Hydrogen peroxide; Inorganic anions

1. Introduction

Semiconductor-grade hydrogen peroxide (30%, w/w) has been monitored for years to be sure the concentrations of various anions are below certain levels; current specifications are for a maximum of 30 ppb (w/w) of each species [1]. Ion chromatography has been used routinely for these determinations. However, care must be taken to protect the separator columns from the peroxide, since complex matrices will degrade the resins [2]. An often-used approach has been to decompose the H_2O_2 with platinum before injecting the resulting solution into the instrument. Nevertheless, the procedure often is not very reproducible [3] and only appears once in the literature [4]. This publication by Carpio et al. is limited in its relevance here, since the work involved cation analysis by capillary electrophoresis. Furthermore, a rigorous spiking/reproducibility study was not conducted. Recently, researchers [5–9] have reported on-line matrix-elimination techniques that make pre-digestion unnecessary. These methods have disadvantages that are unacceptable to some laboratories. In one case [5], the apparatus required is not available commercially; in the other procedures, a concentrator column must be replaced often because of peroxide-induced deterioration. In addition, extra chromatographic hardware is needed, requiring the dedication of an instrument to this

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method. Hence, there still is a need for a reliable, well-documented decomposition method for anions in peroxide.

This paper addresses this gap in the literature. The goals of the research are: (1) to develop a reproducible Pt-digestion procedure for use in anion analysis of H_2O_2 and (2) to conduct statistically sound calibration and recovery studies. The anions that were investigated were fluoride, chloride, sulfate, bromide, nitrate, and phosphate.

2. Experimental

2.1. Materials

Sodium hydroxide (50%, w/w, with ≤0.10% sodium carbonate) from Fisher Scientific (Pittsburgh, PA, USA) was used to make the concentrated (200 m*M*) eluent solution. Stock standards (1000 ppm, w/w, each) of fluoride, chloride, bromide, nitrate, sulfate, and phosphate were purchased from Alltech Associates (Deerfield, IL, USA). For eluent preparation and dilution of standards, deionized (DI) water (18 MΩ cm) was delivered by a point-of-use water-purification system (Ionics-Ahlfinger, Dallas, TX, USA). Hydrogen peroxide (30%) was obtained from Air Liquide America (Dallas, TX, USA).

Water for eluents was sparged with helium before use. Subsequently, the DI water (for diluting the eluent concentrate) and the NaOH reservoirs were kept under pressure with helium throughout their life.

Peroxide test strips (range of 0–25 ppm) from EM Science (Gibbstown, NJ, USA) were used when checks of H_2O_2 levels were desired.

2.2. Apparatus and columns

Unless otherwise noted, all instrument modules and supplies were from Dionex (Sunnyvale, CA, USA). A DX 500 microbore ion chromatograph was used for all analyses. Analytical columns were an IonPac AG15 Guard (50 mm×2 mm) with AS15 Analytical (250 mm×2 mm). All tubing in the chromatography paths was PEEK (polyether ether ketone) [0.005 in. (0.125 mm) I.D.].

A GP40 Gradient Pump was used to deliver eluent to the system. The initial concentration was 10 m*M* NaOH; at 6.0 min, the concentration was stepped to 40 m*M*. Chromatographic run time was 27 min. Eluent flow-rate was 0.40 ml/min. A 1-ml sample loop was loaded via an AS40 Automated Sampler, using PolyVials (5 ml) and plain caps. Before use, all vials were rinsed 20 times with DI water from the tap; each rinsing consisted of filling the vial completely and then pouring out the water.

Post-column eluent suppression was achieved using an Anion Self-Regenerating Suppressor (ASRS-Ultra, 2 mm) in the external-water mode. To maintain constant equilibrium [10], water was allowed to flow continuously through the regenerant chamber, even when the chromatograph was not in use. Flow-rate (with ASRS current off) was approximately 15 ml/min. Detection was via a CD20 Conductivity Detector at an output range of 10 μS.

Instrument control and data collection were accomplished using a personal computer and PeakNet software. JMP software (SAS Institute, Cary, NC, USA) was used to carry out statistical calculations.

2.3. Standards preparation

All standards were prepared in new high-density polyethylene (HDPE) narrow-mouth bottles (Nalge Nunc, Rochester, NY, USA). Either 125- or 250-ml containers were used, depending on the volume requirements of the solution. Vinyl gloves (Oak Technical, Stow, OH, USA) were worn throughout the standard-preparation process.

A mixed standard (100 ml) containing 10 ppm of each of the six desired analytes was prepared from the various 1000-ppm stock standards. Two types of intermediate solutions (250 ml; each preparation was 100 ppb in each analyte) were made from the 10-ppm solution. The diluent was DI water for the first type of solution and 30% hydrogen peroxide for the second type. The concentrations of the water-based working solutions were 12, 15, 18, 21, 24, 29, 35, 41, and 47 ppb. The levels of the peroxide-based spikes were 10, 12.5, 15, 17.5, 20, 25, 30, 35, and 40 ppb; these preparations were used for the platinum-digestion work. Lower concentrations were prepared with the latter matrix, since the digestion process drives off 15% of the mass through loss of oxygen. A standard-preparation blank was also prepared for

each type of matrix; i.e., several grams of pure matrix were poured out and brought up to final mass with additional matrix.

To avoid contamination, deliveries of 10-ppm and 100-ppb solutions were accomplished by pouring. These masses were recorded accurately; the final mass was then adjusted to give the desired concentration. Final amounts of diluents were delivered by polyethylene transfer pipets (from Fisher) that were thoroughly rinsed out with and dedicated to the particular matrix (i.e., either DI water or H_2O_2). New transfer pipets were used to deliver the various 1000-ppm solutions.

All masses (for standards preparation and for digestion work) were determined using a Sartorius BP301S analytical balance (Sartorius, Edgewood, NY, USA) and were recorded to four decimal places. This balance was located in a fume hood suitable for acids. Dilution errors in the daily working standards were estimated by conducting a Monte Carlo simulation. This exercise was based on the upper bound (0.0001 g) on the magnitude of weighing error for the balance. In the simulation, weighing errors were randomly drawn from a Normal distribution with mean equal to zero and standard deviation equal to the upper bound. The distribution of these relative concentration errors was found never to exceed 0.1% relative error, which was considered negligible.

All standards were prepared fresh each day they were to be used. Each day, preparations and analyses were performed in random order. Peak areas (PAs) were used to measure the chromatograph's response to each anion.

2.4. Digestion protocol

2.4.1. Materials

Vinyl gloves were worn throughout all steps of this process. Digestions were carried out in new 125-ml HDPE narrow-mouth bottles. Platinum gauze (25 mm×25 mm, 45 mesh, woven from 0.198-mm-diameter wire, 99.9% on metals basis) was obtained from Alfa Aesar (Ward Hill, MA, USA). The Pt pieces were shipped flat and, as such, would not fit through the mouth of a narrow-mouth bottle. Therefore, each piece was bent over in half while the metal was still in its plastic wrap. A wide-mouth 125-ml HDPE bottle was dedicated to the rinsing and storing of each piece of Pt. To prepare the metal for initial use, each piece was soaked in its container for approximately 2 weeks. Every day or so, the water was changed by emptying and filling the container approximately four times before filling for the final time. Before the pieces were used the first time, they were soaked overnight in 20 ml of DI water. These solutions were tested for anions the next day; all levels were negligible.

Polypropylene forceps (Nalge Nunc) were used to handle the Pt gauze, with a specific pair being dedicated to a specific piece of metal. When not in use, each pair of forceps (blades only) was stored in a 125-ml HDPE narrow-mouth bottle that was filled completely with DI water.

Cooling baths were established in 64-oz. HDPE containers (VWR International, So. Plainfield, NJ, USA; 1 oz.=28.35 g). Square holes (1 in. sq.) were cut in the center of each lid. Each container was filled with DI water to within 25 mm of the top. The initial bath temperature was 21 °C.

2.4.2. Procedure

To allow for determination of the ''before'' and ''after'' masses of peroxide, accurate masses were recorded at each stage of the digestion process. Also, contamination-control measures (e.g., wearing vinyl gloves, rinsing containers and implements as needed) were observed throughout. The basic outline of the digestion procedure is given in the following paragraphs. Interested readers are invited to contact the corresponding author for complete details.

To digest a spiked peroxide, approximately 20 g of the solution was poured into a new 125-ml HDPE bottle. A piece of Pt was transferred into the bottle using forceps. Immediately thereafter, the cap was screwed on loosely, and the capped neck was inserted through the hole in the water-bath lid. The bottle was then placed into the bath and the bath lid was snapped into place. This configuration provided maximum contact between the reaction bottle and the water, and allowed this exothermic reaction to proceed in a controlled fashion. Oxygen that was driven off escaped through the loosened bottle cap.

During the initial stages of the decomposition, bubbling caused droplets to be deposited on the walls of the bottle and on the inside of the cap. When tested during preliminary work, these drops were

found to contain high levels of undigested peroxide. To return this material to contact with the Pt, the following procedure was implemented. The reaction was allowed to proceed for 2 h, after which time each bottle was removed from the bath and the cap secured. The bottle was shaken gently to remix the liquid. When all liquid was seen to be in the bottom of the bottle, the cap was loosened and the assembly returned to the water bath for another 4 h. (This 6-h digestion reduced the peroxide level to between ca. 50 and 200 ppm.) At the end of 6 h, the digestion solution was analyzed on the ion chromatograph.

3. Results and discussion

3.1. Initial calibration studies

Before any peroxide analyses were performed, a statistically designed calibration study was conducted, using the water-based standards. These experiments provided: (1) the appropriate model for the calibration curve, (2) the detection limit (DL), and (3) the ± prediction interval (± p.i.). These data were used to evaluate subsequent results. This suite of standards was tested on each of eight separate days, thereby providing 80 data points for each anion. A representative chromatogram of the 29-ppb water-based standard is shown in Fig. 1.

Prior to beginning the calibrations, models were proposed for each anion's curve. Straight lines were postulated for all anions except fluoride; past experience suggested that a quadratic fit would be appropriate for this analyte. After all standards had been analyzed, the proposed models were tested, using calibration diagnostics discussed in previous papers [11,12]. Statistical analysis of the peak-area data first involved examining the responses for trends. For each concentration, the PAs were plotted versus day. A straight line was plotted through the points using ordinary least squares (OLS) and the *P*-value for the slope determined. A significant slope (i.e., $P<0.01$) indicated the presence of a time trend. For sulfate, bromide, nitrate, and phosphate, significant downward trends were observed for five to seven concentrations. Over the course of the calibration study, the percent changes in peak areas were in the 5–10% range. These trends indicated that frequent recalibration might be necessary, depending on the behavior of subsequent check standards. The impact of these declines on the calibration curves themselves were found to be minimal, as shown below.

For these initial calibration data, the regression results are summarized in Table 1. A straight line

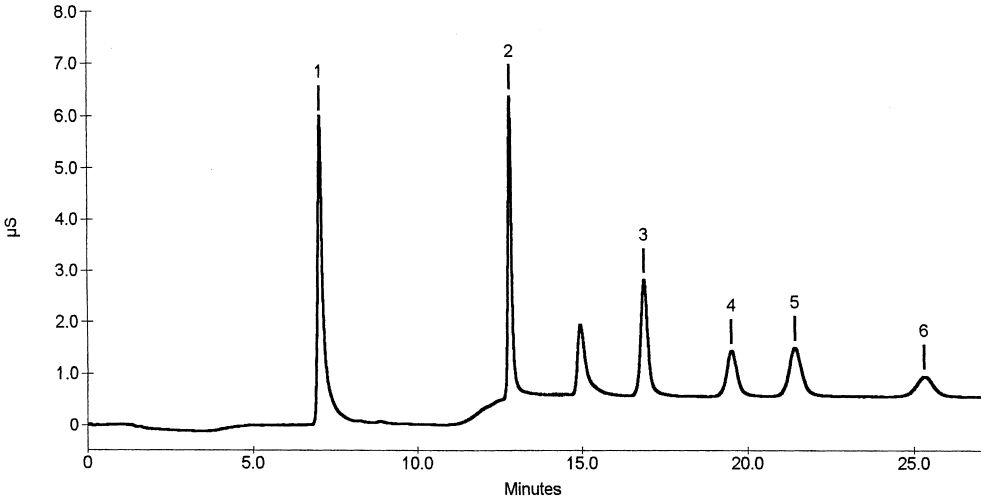

Fig. 1. Example chromatogram of a 29-ppb water-based standard on the AS15 column. Peak identities: (1) fluoride, (2) chloride, (3) sulfate, (4) bromide, (5) nitrate, and (6) phosphate.

Table 1
Results of calibration-study evaluation for AS15

Anion	Model[a]	R^2_{adj}	DL (ppb)[b]	± p.i. (ppb) at 29 ppb[c]
Fluoride	Straight line	0.9979	**2.2**	1.0
Chloride	Straight line[d]	0.9989	**1.9**	0.9
Sulfate	Quadratic[d]	0.9995	**0.4**	0.2
Bromide	Straight line[d]	0.9958	**2.1**	1.1
Nitrate	Straight line[d]	0.9958	**1.2**	0.5
Phosphate	Straight line[d]	0.9924	**1.0**	0.4

[a] See Section 3.1 for discussion of model choices.
[b] DL, detection limit, calculated by the method of Hubaux and Vos (see Refs. [11,12]); $\alpha=\beta=0.025$; Detection limits that are below the lowest standard of 10 ppb have been emboldened.
[c] ± p.i. at 29 ppb = ± prediction limit at 29 ppb; $\alpha=\beta=0.025$.
[d] Weighted least squares (WLS) required for this analyte.

was the appropriate model for all analytes except sulfate; in this last case, the residual pattern and a formal lack-of-fit test both indicated that a quadratic was needed. In all cases except fluoride, the standard deviation of the response increased with concentration. Thus, the fitting technique of weighted least squares (WLS) was required in these instances. All ± prediction intervals (≤1.1 ppb at 29 ppb) and Hubaux–Vos detection limits (≤2.2 ppb) were considered acceptable. (Note: Throughout the paper, all statistical intervals and detection limits are reported at the 95% confidence level.) These results also indicate that the peak-area trends discussed above were not practically important (in terms of their absolute magnitude), even though they were statistically significant.

3.2. Digestion studies

3.2.1. Protocol

The protocol for the digestion study was as follows. A sufficient quantity of 30% peroxide was obtained for use throughout the project. On each day of the study, the working standards (including the blank) were prepared in both DI-water and hydrogen-peroxide matrices (see Section 2.3 for details), and the latter solutions were digested (see Section 2.4 for details). The analysis schedule was as follows. The instrument was activated and equilibrated by analyzing two samples of DI water, followed by two 30-ppb standards in water. Then the 10 water-based standards were tested, followed by the 10 digested peroxide spikes. The final analyses were two injections of the same 30-ppb standard tested at the beginning (i.e., after the two initial DI waters).

After analysis, the predicted concentrations were calculated, using the calibration curves developed from the initial calibrations (see Section 3.1). The water-based standards served as checks of the initial calibration curves. After being corrected for reaction-induced mass changes, the peroxide data were evaluated for precision and bias.

3.2.2. Data evaluation

3.2.2.1. Statistical considerations

To evaluate the reproducibility of the digestion process, a regression-based approach was used [13]. For all digestions and ''check'' standards, the predicted concentrations were obtained using the initial calibration curves. Digestion results were corrected for mass changes and for any positive blanks. These net concentrations were each plotted versus the true concentration, and a straight-line regression (with OLS fitting) performed. (This curve should be used to correct analyte concentrations in samples. As always, extrapolation should be avoided, if possible; here, the range should be restricted to between 10 and 40 ppb.)

3.2.2.2. Chromatographic observations

A representative chromatogram of a spiked peroxide is shown in Fig. 2. The plot is complicated (especially at the front end) because of the presence of organic acids. To ensure reliable results, extreme care was taken to integrate each peak the same way in all chromatograms.

Over the course of the study, the retention times (t_R) moved in slightly (0.8 min for phosphate, the latest peak). Apparently something in the digested samples caused a reduction in the capacity of the column. However, the peak areas did not suffer as a result, so the shift was not practically important.

3.2.2.3. Statistical results

As with the initial calibration results, the PA data first were inspected for trends. This analysis was performed on the water-based standards only; digestion-induced mass changes rendered this process meaningless for the peroxide samples. Fluoride and

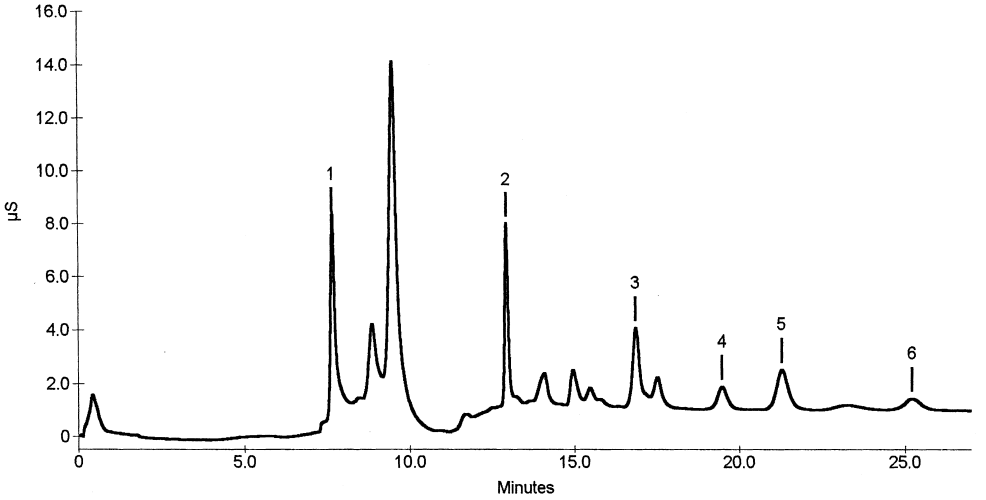

Fig. 2. Example chromatogram of a 30-ppb peroxide-based standard on the AS15 column. Peak identities: (1) fluoride, (2) chloride, (3) sulfate, (4) bromide, (5) nitrate, and (6) phosphate. Plot is from Day 1 of the digestion study.

chloride each had three concentrations with significant slopes. Percent changes again were in the 5–10% range, except for an 18.8% change for the 18-ppb Cl^-. Nitrate had one significant slope, with a change of 6.4%.

Subsequent regression analyses of the data showed that these trends were not practically important. Table 2 summarizes the results. Proportional recoveries (i.e., slopes) were all above 0.93. Intercepts showed an offset of less than 0.5 ppb for all analytes; the ± confidence interval included zero for all ions except bromide, but that lower limit was only 0.01 ppb away from zero. The ± prediction intervals for all curves were ≤2.0 ppb. All of these data were considered acceptable.

For the digestions, the proportional recoveries varied (Table 3). The lowest value was 0.749 for fluoride; however, the ± prediction interval for the overall equation was a respectable 2.0 ppb. All such intervals were an acceptable 3.0 ppb or less, except for nitrate; this last value was 8.7 ppb. All intercepts were negative, and (except for sulfate and phosphate) the ± confidence interval did not include zero. Thus, for fluoride, chloride, bromide, and nitrate, a constant-loss component existed for the digestion process. There is an alternative explanation, which cannot be evaluated with these data: that the straight-line models do not hold between zero and the lowest spike concentration (10 ppb). For each analyte, the inclusion of a small curvature component in the

Table 2
Recoveries from digestion study: water-based standards (see Section 3.2.2 for details)

Analyte	Slope	Intercept	± p.i. (ppb) at 29 ppb[a]
Fluoride	0.997	0.386	1.8
Chloride	0.976	0.097	1.7
Sulfate	0.935	−0.139	0.9
Bromide	0.935	0.403	1.4
Nitrate	0.941	0.014	1.1
Phosphate	0.942	−0.214	2.0

[a] ± p.i. at 29 ppb = ± prediction limit at 29 ppb; $\alpha=\beta=0.025$.

Table 3
Recoveries from digestion study: digested peroxides (see Section 3.2.2 for details)

Analyte	Slope	Intercept	± p.i. (ppb) at 30 ppb[a]
Fluoride	0.749	−0.730	2.0
Chloride	0.930	−1.717	1.5
Sulfate	0.925	−0.081	1.6
Bromide	0.896	−1.294	2.3
Nitrate	0.991	−2.473	8.7
Phosphate	0.983	−0.654	3.0

[a] ± p.i. at 30 ppb = ± prediction limit at 30 ppb; $\alpha=\beta=0.025$.

model (e.g., quadratic or exponential) could possibly allow each intercept to be statistically indistinguishable from zero.

The scatter plot for nitrate is shown in Fig. 3 and has been coded by day. As can be seen from this figure, there is some segregation by day (e.g., all of the ''O'' markers fall below the regression line, while all of the ''Y'' markers fall above that line). A probable explanation for this occurrence is that nitrite, which typically is present in the laboratory atmosphere, was absorbed into the peroxide during the digestion process. In such an oxidative environment, this analyte will be converted immediately to nitrate, thereby raising the recoveries by random amounts. Daily fluctuations of the atmospheric nitrite levels would account for the observed by-day patterns. Thus, the noise in these data probably could be reduced by controlling the laboratory atmosphere during digestion; such an undertaking was outside the scope of this project.

3.2.3. Follow-up studies

Following the conclusion of the digestion study, a brief, preliminary investigation was conducted into the cause of the retention-time reduction. A previous paper [9] postulated that the loss of capacity probably was caused by either: (1) destruction of the resin by residual peroxide or (2) adherence of peroxide contaminants (e.g., organic matter) to the exchange sites. To test the first explanation, 10 peroxide samples were digested for a period of 30 h. This process reduced the peroxide level to between 2 and 10 ppm. Analysis of these digestions on the ion chromatograph caused t_R-values to decrease for the last four peaks (Fig. 4a).

Subsequently, an aliquot of 30% peroxide was diluted to 10 ppm. Ten replicates of this solution were analyzed as above. As can be seen from Fig. 4b, there was virtually no decrease in retention times, except for a small change for phosphate.

These preliminary data suggest that the problem is not due to the trace amounts of peroxide in the solutions. Instead, the shift seems to be caused by contaminants (possibly organic) in the peroxide. These species may be adhering to the exchange sites, thereby decreasing the capacity of the column. A

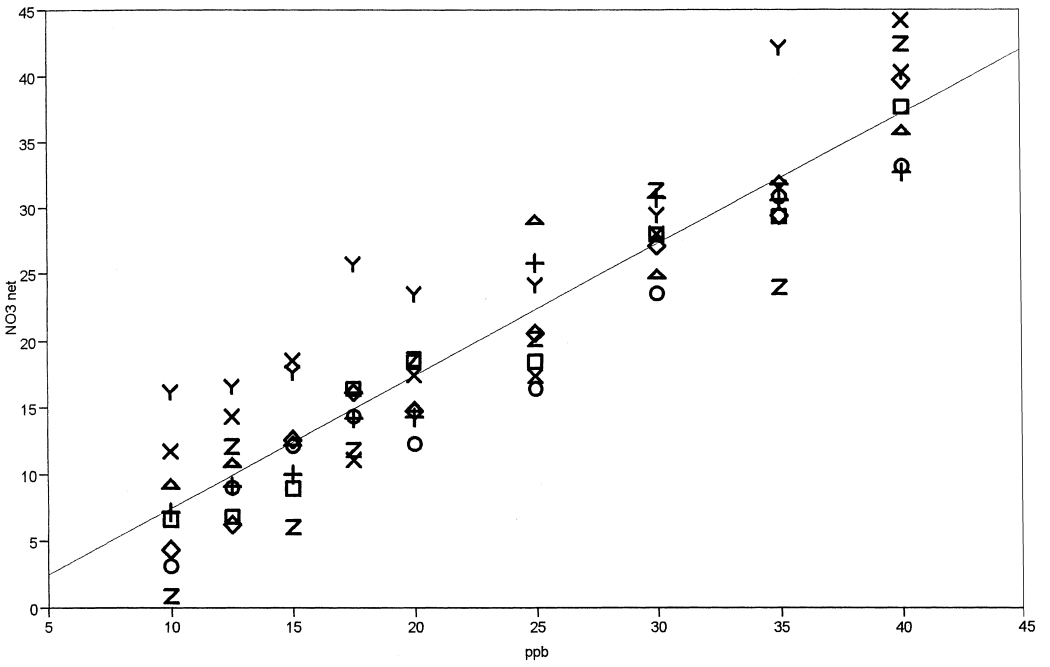

Fig. 3. For nitrate in digested peroxide, scatter plot for the straight-line regression of predicted ppb versus true ppb. See Sec. 3.2.2.3 for details.

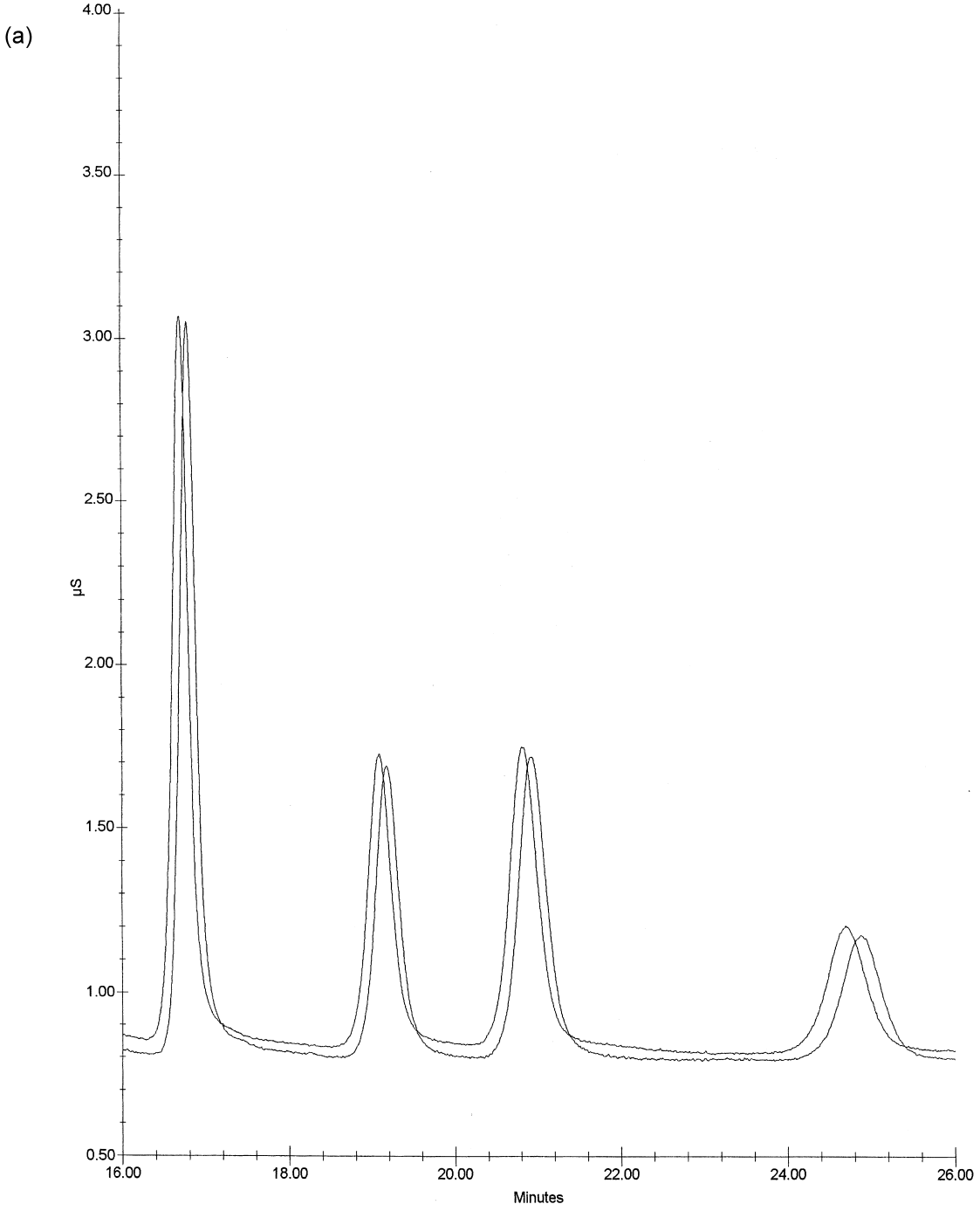

Fig. 4. Comparison of standards analyzed immediately before and immediately after: (a) 10 digested peroxides (final H_2O_2 concentration was ≤10 ppm) were chromatographed and (b) 10 diluted peroxides (to 10 ppm) were chromatographed. In each graph, the tracing with the shorter t_R is the ''immediately after'' standard. See Sec. 3.2.3 for details.

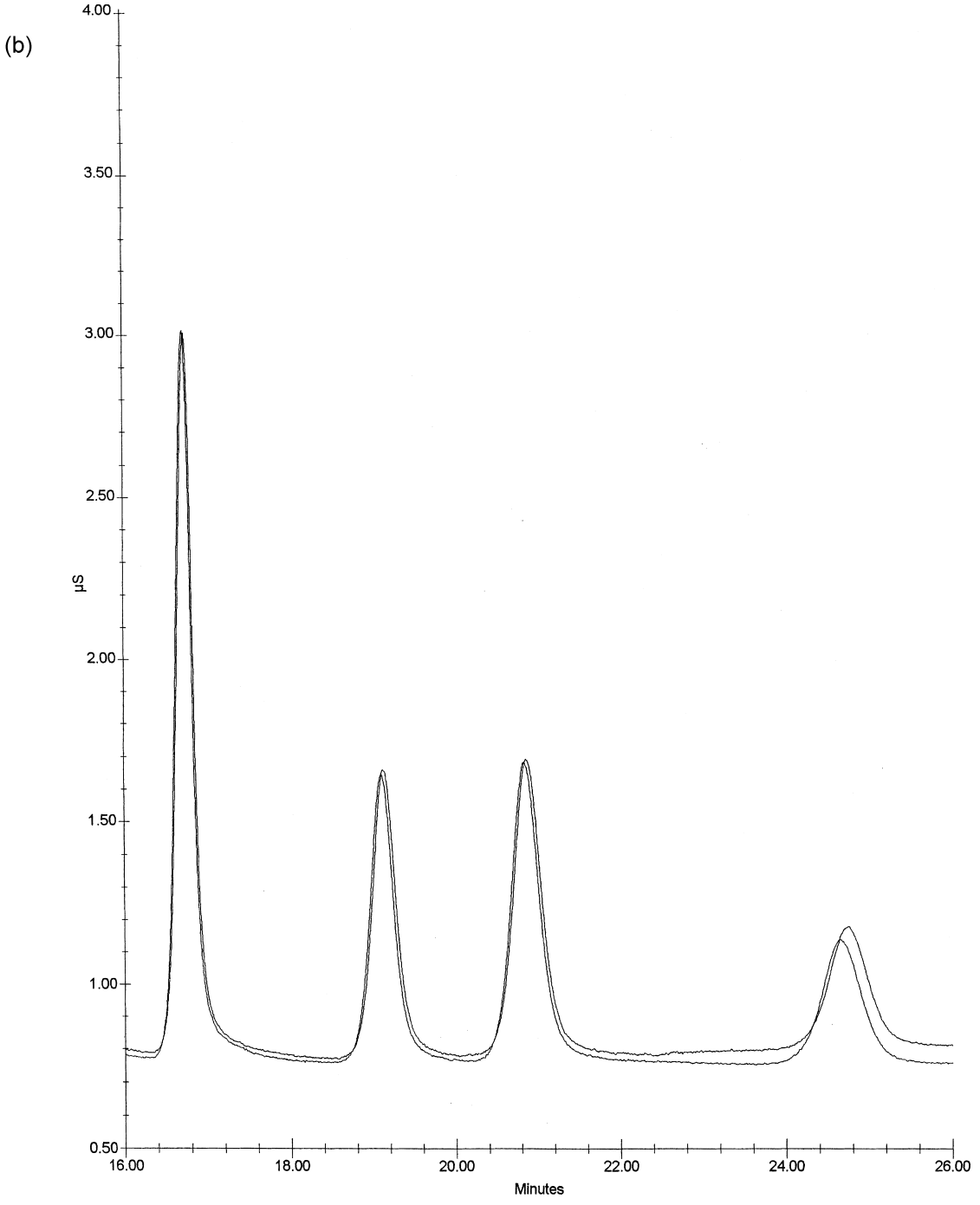

Fig. 4. (*continued*)

clean-up procedure might restore the column to its original condition, but this undertaking was beyond the scope of this project.

4. Conclusions

A reproducible digestion procedure has been developed for the ion-chromatographic determination of common anions in 30% hydrogen peroxide. The procedure is easy to perform and does not require elaborate equipment. The 6-h digestion step reduces the peroxide level to around 200 ppm or less.

The only analyte whose recovery curve had a poor ± prediction interval (8.7 ppb) was nitrate. This lack of precision probably was due to contamination from atmospheric nitrite in the laboratory during the digestion process; in H_2O_2, nitrite immediately is converted to nitrate. Therefore, extreme care should be taken if highly precise values are desired for NO_3^-.

Of the remaining five analytes, proportional recoveries were between 90 and 100% for all but bromide (89.6%) and fluoride (74.9%). Constant bias ranged from −0.081 to −1.717. However, ± prediction intervals were all acceptable (1.5–3.0 ppb). Thus, with these analytes, the recovery curves (slope and intercept) are acceptable statistically for correcting the predicted concentrations in actual samples.

This method has several advantages. Unlike on-line matrix-elimination procedures, this digestion protocol does not require the use of a concentrator column, which is slowly degraded by the peroxide; in addition, no water-rinse step is needed. Furthermore, the digested samples can be analyzed on any ion chromatograph that is configured to test low-ppb-level samples. This flexibility is advantageous to laboratories that test peroxide only occasionally. Second, except for the Pt gauze, only common laboratory supplies are needed for the digestion. While the Pt represents a substantial investment initially, the pieces can be rinsed easily and reused repeatedly.

At first glance, the 6-h digestion process seems prohibitively long. However, many samples can be processed simultaneously; the only limit is the number of Pt pieces available. Since the chromatographic runs require approximately 30 min, 12 samples can be prepared and analyzed in 12–13 h. An average of 1 h per sample is not uncommon for testing anions in difficult semiconductor matrices. Furthermore, the digestions run unattended, except for the remixing step after 2 h. Thus, this procedure is feasible for use in a routine semiconductor laboratory.

The procedure does suffer from one disadvantage: the gradual reduction in capacity of the separator column. However, this problem is common to all peroxide methods and may be due to contaminants (possibly organic) in the matrix itself. Nevertheless, the peak areas do not suffer as a result of this phenomenon. Thus, quantitation is not affected and the overall procedure is a reliable method for determining anion concentrations in 30% H_2O_2.

5. Nomenclature

Mathematical symbols used:

α,	average probability of false positives.
β	average probability of false negatives.
R^2_{adj}; R^2	''penalized'' for each independent variable used in the regression (R^2 measures the amount of total variation in the response ''explained'' by the dependent variable).

Terms and abbreviations used:

DL	detection limit. The concentration below which the analytical method cannot reliably detect a response.
OLS	ordinary least squares. A fitting technique that minimizes the sum of squares of the residuals.
p.i.	prediction interval. A pair of limits that bracket the uncertainty in one future measurement.
P-value	the probability value associated with a statistical test, representing the likelihood that a test statistic would assume or exceed a certain value, if the null hypothesis is true.
t_R	retention time (min). Statistically significant, causing a null hypothesis to be

rejected at some accepted confidence level.

WLS weighted least squares. Same methodology as OLS, except weights are incorporated to account for non-constant response variation.

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