

Comparison of two Cryptand separator columns for the determination of trace chloride in semiconductor-grade nitric acid

L.E. Vanatta^{a,*}, A. Woodruff^b, D.E. Coleman^c

^a *Air Liquide - Balazs™ Analytical Services, Box 650311, MS 301, Dallas, TX 75265, USA*

^b *Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94085, USA*

^c *Alcoa Technical Center, MST-C, 100 Technical Drive, Alcoa Center, PA 15069, USA*

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Abstract

Improved ion-chromatographic approaches for measuring trace chloride in nitric acid are presented. Two columns, the IonPac Cryptand A1 and a higher-capacity Cryptand prototype, were tested and compared. Also, the use of a Continuously Regenerated Anion Trap Column (CR-ATC) was evaluated for its ability to purify electrolytically generated eluent. Nitric acid (70%) was used as the test matrix and chloride was used as the test analyte; prior to injection, the nitric acid was diluted to 0.7% for the A1 column and to 2.8% for the prototype column. Chloride could be quantified in only 20 min on either column; detection limits computed for 70% HNO₃ (at 95% confidence, $\alpha = \beta = 2.5\%$) were 1.8 and 1.5 ppm for the A1 and prototype columns, respectively. Results also showed that the CR-ATC was necessary for obtaining acceptable acid blanks.

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1. Introduction

In the determination of trace anions in semiconductor-grade chemicals, one of the most challenging types of compounds is strong mineral acids. In concentrated form, the overwhelming concentration of the acid's anion typically precludes the use of ion chromatography; ion-exclusion columns, which are used to remove large amounts of weak mineral acids [1] will not help with strong acids, since the latter are totally ionized. If the sample is first diluted to a chromatographically acceptable level, then the detection limit rises in proportion to the amount of the dilution. The only other viable alternative for concentrated strong acids has been to employ wet methods, which are laborious [2].

Kaiser et al. [3] made strides in addressing strong acids chromatographically, using a Dionex AS15 column and an Eluent Generator. They developed a method for chloride, sulfate and phosphate in 0.7% nitric acid; reported Method

Detection Limits were 41, 104 and 120 ppb (w/w), respectively. Although the method allowed for all three analytes to be determined in one injection, the procedure required 48 mM KOH for the analysis itself, followed by a 100-mM clean-up step and then reequilibration to 48 mM; total run time was about an hour.

Woodruff et al. [4] developed a variable-capacity, Cryptand-based column and used it to analyze 2% sulfuric acid; fluoride, acetate, formate and chloride ions were all well separated from the sulfate peak. Vanatta et al. [5] showed that this same column (known as the Dionex IonPac Cryptand A1) could be used to determine low-ppm levels of chloride and sulfate in semiconductor-grade etchants (i.e., mixtures of concentrated acids), if the mixture was first diluted 1:100. All three papers left unresolved the question of whether trace anionic contaminants in the eluent contributed to the peak areas of analytes detected in these types of acid samples. None of the previous publications achieves low-ppb detection limits (DLs) in "full-strength" strong acids.

The purpose of this paper is two-fold; i.e., to determine if: (1) residual anionic contamination in the eluent affects

* Corresponding author. Tel.: +1 972 995 7541; fax: +1 972 995 3204.
E-mail address: lynn.vanatta@airliquide.com (L.E. Vanatta).

analyte levels seen in acid samples and (2) a higher-capacity Cryptand column will provide lower DLs. The test analyte was chloride and the test matrix was 70% nitric acid.

A Dionex DX500, with an eluent generator, gradient pump and conductivity detector, was used for all work. Instrument control and data collection were carried out using Dionex PeakNet 5.1 software. Statistical analyses were performed using JMP 5.1 statistical software.

2. Experimental

2.1. Materials

A stock standard (1000 mg/L) of chloride was purchased from Spex (Metuchen, NJ, USA). For dilution of standards, deionized (DI) water (18 m Ω cm) was delivered by a point-of-use water-purification system (Ionics-Ahlfinger, Dallas, TX, USA). Nitric acid (70%) was obtained from Air Liquide America (Dallas, TX, USA).

2.2. Apparatus and columns

Unless otherwise noted, all instrument modules and supplies were from Dionex Corp. (Sunnyvale, CA, USA). A DX 500 microbore ion chromatograph was used for all analyses. Two analytical columns were used: (A) an IonPac Cryptand A1 Analytical (150 mm \times 3 mm), along with a Cryptand G1 Guard (30 mm \times 3 mm) and (B) a prototype Cryptand analytical (250 mm \times 4 mm). Post-column eluent suppression was achieved using an Anion Self-Regenerating Suppressor (ASRS-Ultra or Ultra II) in the external-water mode; a 2-mm suppressor was used with column (A) and a 4-mm ASRS was employed with column (B). With all suppressors, constant equilibrium was maintained by allowing water to flow continuously through the regenerant chamber, even when the chromatograph was not in use [6]; flow rate (with ASRS current off) was approximately 15 mL/min. Suppressor current was 19 mA for column (A) and 75 mA for column (B).

The columns and suppressor were housed in an LC25 Chromatography Oven with rear-loading 10-port Rheodyne valve; oven temperature was 33 °C. 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 deionized water to an EluGen eluent-generator cartridge (EGC), which was controlled by a Reagent Free Controller (RFC-30). The RFC-30 also supplied current to the suppressor, as well as controlled a continuously regenerated anion trap column (CR-ATC); this latter device removed trace contaminants from electrolytically generated eluent [7]. During the evaluation of contamination in the eluent, an IonPac ATC (2 mm) was sometimes used to clean the manually prepared eluent. Eluent concentration was 15 mM at 0.50 mL/min for the 3-mm separator, and 30 mM at 1.0 mL/min for the 4-mm column. A 7.5- μ L 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. Detection was via a CD20 Conductivity Detector at an output range of 10 μ S.

Instrument control and data collection were accomplished using a personal computer and PeakNet 5.1 software. JMP 5.1 software (SAS Institute, Cary, NC, USA) was used to carry out statistical calculations.

2.3. Preparation of standards

All solutions were prepared in new high-density polyethylene (HDPE) narrow-mouth bottles (125-mL capacity) (Nalge Nunc, Rochester, NY, USA). Vinyl gloves (Oak Technical, Stow, OH, USA) were worn at all times when handling standards and samples. Transfer pipets (Fisher Scientific, Pittsburgh, PA, USA) were used to deliver small volumes of liquids.

For the calibration studies, six chloride standards were prepared: a blank; 10, 25, 50, 75 and 100 ppb (w/w). These solutions were in 0.7% HNO₃ for the Cryptand A1 column and in 2.8% HNO₃ for the prototype separator. This set of standards was run in quintuplicate and all analyses were made on the same day. Solutions were randomized within each replicate. Peak areas (PAs) were used to measure the chromatograph's response to each anion.

All masses (for standards preparation) were determined using a Sartorius MC1 analytical balance (Sartorius Corp., 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.

3. Results and discussion

3.1. Initial considerations

To accomplish both goals of this research, it was decided to keep the plumbing design and chromatographic methods as simple as possible, thereby eliminating unnecessary work and reducing the risk of instrumental and/or chemical complications. Thus, one analyte and one matrix (chloride and 70% nitric acid) were chosen for the testing. These selections were made because prior research [5] showed that chloride was easily separated from nitrate. In addition, semiconductor-grade HNO₃ was easily obtainable and chloride is a contaminant of great concern in the electronics industry.

To keep the chromatographic method uncomplicated, an isocratic KOH program was used on each type of Cryptand column. The selected concentrations were based on preliminary work, which indicated that these strengths (see Section 2.2) were good choices for separating chloride and nitrate on the respective separators. Temperature had been shown previously to have minimal influence on the separation, so 33 °C was used since it had been used in the former work [5].

The grafting process and the Cryptand used in the prototype were exactly the same as were used in the smaller separator. The base resin in both was the same (i.e., a macroporous resin with pore sizes around 100 angstroms and 55% crosslink). The only difference between the two packings was the bead size, which was 6.5 μ in the prototype versus 5.0 μ in the A1 column. This change was made to keep the column pressures sufficiently low in the larger separator. The difference in capacities was due simply to increased volume and were 73 and 229 μ equivalents/column for the smaller and larger designs, respectively.

3.2. Eluent-contamination issue

Since the size of the blank (in this research, the unspiked acid at the appropriate dilution for each separator column) is critical to any calibration study, the eluent-contamination issue was addressed first. The Cryptand A1 (150 mm \times 3 mm) was used for this investigation. Since the 50% NaOH concentrate typically used to make eluent “manually” is quite dirty, a 50 mM solution was prepared and pumped through the column for several days. To allow for maximum contamination of the Cryptand resin, no trap column was installed.

At the end of this period, the column was switched over to manually prepared 15 mM KOH eluent and allowed to equilibrate thoroughly. Four injections of 0.7% HNO₃ were made and the areas of the chloride peaks measured; values ranged from 23,600 to 25,000 units. Subsequently, the instrument was reconfigured to deliver 15 mM KOH that was generated and cleaned electrolytically. One injection of deionized water was made while the instrument stabilized. Four more injections of the same acid solution were chromatographed. The first injection had a chloride peak area of 13,800, significantly less than before. Peak areas continued to fall; the value for the fourth injection was 2900. Six more injections were made the following day; areas ranged from 3300 at the start of the day to 2100 at the end of the day.

To confirm the need for efficient eluent cleaning, the system was once more replumbed for manually prepared eluent; this time, a chemically regenerated ATC was included right after the pump. Two deionized-water blanks were run during instrument stabilization, followed by four injections of the 0.7% HNO₃. Chloride peak areas once more were high (30,000–33,000), even with the ATC in place. Thus, at least some of any anionic contaminants in the eluent will stick to the analytical column’s resin. While water-based samples and standards do not dislodge these anions from the stationary phase, acid concentrations at least as high as 0.7% HNO₃

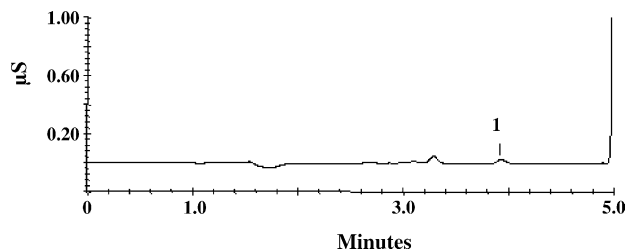


Fig. 1. Chromatogram of unspiked 0.7% nitric acid on the smaller (i.e., Cryptand A1) column. Peak 1 is chloride; large peak at approximately 5 min is nitrate. See Section 3.3.1 for experimental details.

will cause problems. Therefore, the cleanest eluent available is needed for this type of analysis.

3.3. Calibration studies and detection-limit calculations

3.3.1. Cryptand A1 (150 mm \times 3 mm)

The first calibration experiments were performed using the smaller (150 mm \times 3 mm) analytical column (see Section 2.3 for details on standards preparation and on the calibration design). A representative chromatogram of 0.7% nitric acid is shown in Fig. 1. Statistical analysis of the calibration data showed that a linear model with weighted-least-squares (WLS) fitting was needed [8]. Weights were calculated by first computing the standard deviation of the responses at each concentration. These standard deviations were fitted with a straight line, using ordinary-least-squares (OLS) fitting. The equation for this line was used to determine the weights; at each concentration, the formula was the reciprocal square of the equation, divided by the mean of all the reciprocal squares. Hubaux-Vos detection limits [9] were calculated and were found to be 18 ppb at 95% confidence ($\alpha = \beta = 2.5\%$).

3.3.2. Cryptand prototype, 250 mm \times 4 mm

The same calibration design and ordering of standards was used with this larger column. However, because of the higher capacity, a 2.8% concentration of HNO₃ could be injected onto the column. A typical chromatogram of 2.8% nitric acid is shown in Fig. 2. Calibration diagnostics showed a straight line with OLS fitting was appropriate. The Hubaux-Vos (H-V) detection limit (95% confidence, $\alpha = \beta = 2.5\%$) was 58 ppb.

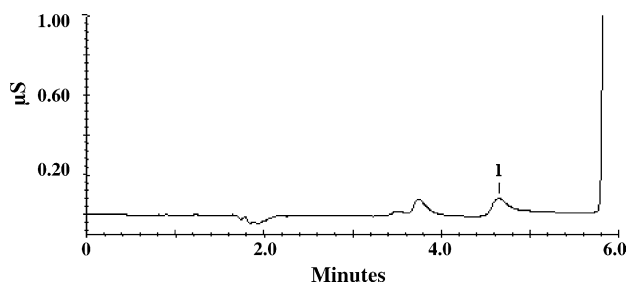


Fig. 2. Chromatogram of unspiked 2.8% nitric acid on the larger (i.e., Cryptand prototype) column. Peak 1 is chloride; large peak at approximately 6 min is nitrate. See Section 3.3.2 for experimental details.

3.4. Evaluation of detection-limit results

While the detection limits in Section 3.3 clearly differ by a factor of approximately three, a statistical comparison was desired. To determine if the two DLs exhibited a statistically significant difference, an *F*-test was used. H-V DLs are based on the formula for the prediction interval associated with the regression process. For two identical calibration studies, the only thing that differs in the equation is the root mean square error (R.M.S.E.). The square of R.M.S.E. is a variance, two of which are comparable via the *F*-test. The R.M.S.E.s in this case were 416 and 951 for the smaller and larger columns, respectively. At both the 99% and the 95% confidence levels, the test shows that the two values are statistically different.

To obtain the DLs for the original, 70% acid, the dilution factors must be applied. The resulting limits are 1.8 and 1.5 ppm for the smaller and larger columns, respectively. The statistically significant difference applies to these “converted” DLs; hence, the goal of an improved (albeit fairly small) detection limit has been achieved via the prototype separator. Also, 1.5 ppm remains well above the 50 ppb desired by the semiconductor industry.

3.5. Method for chloride in 0.7% HNO₃

An additional finding was made during this research; using the smaller column, low-ppb levels of chloride can be determined in 0.7% nitric acid in about 20 min. This run time is a significant improvement over the one hour required in the Kaiser method, which quantifies chloride, sulfate and phosphate in this matrix. In addition, for chloride, the Cryptand A1's DL of 18 ppb is in the same range as is the Kaiser limit of 41 ppb. The raw data from the latter study are not available; hence, it is not possible to determine if there is a statistically significant difference between these two DLs.

4. Conclusions

The two stated goals of this research were achieved. First, it was determined that in the analysis of acidic samples, anionic contamination in the eluent can increase the response for analytes. Second, it was found that a higher-capacity Cryptand prototype column can lower detection limits slightly.

Additionally, a shorter procedure was found for quantifying chloride in 0.7% HNO₃. The calibration curve for this method is based on matrix-matched chloride standards. If chloride is found to be in the blank (a typical result), then the calibration curve must be adjusted statistically to yield unbiased results for actual samples. This procedure is accomplished by subtracting the mean peak area of the blanks (in the calibration design) from the *y*-intercept value in the

calibration equation. This “net” formula is used to predict sample concentrations.

5. Nomenclature

Mathematical symbols used

- α average probability of false positives.
 β average probability of false negatives.

Terms and abbreviations used

- CR-ATC continuously regenerated anion trap column.
 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.
 Prediction interval a range of values defined by a pair of limits that bracket the uncertainty in one future measurement.
 RFC reagent free controller.
 R.M.S.E. root mean square error. The square of the root of the mean squared error from a fit (typically, error is taken to be the residual).
 WLS weighted least squares. Ordinary least squares, except the responses are numerically weighted to reflect non-uniform levels of variation in the responses.

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