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Journal of Chromatography A, 956 (2002) 121–128

JOURNAL OF  
CHROMATOGRAPHY A

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# Automated trace anion determinations in concentrated electronic grade phosphoric acid by ion chromatography

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## Abstract

Modifications have been made to the method of ion-exclusion pre-separation followed by ion exchange with conductivity detection for the determination of trace levels of chloride, sulfate and nitrate in concentrated phosphoric acid. Ion-exclusion separation and pre-concentration of impurity anions is performed using Dionex AS6-ICE and AS11-HC (4 mm) columns, respectively, with water eluent. Final separation is performed using Dionex AG11-HC and AS11-HC (2 mm) columns, KOH gradient elution, and suppressed conductivity detection. Improvements to the method include addition of an autosampler and eluent generator, and use of external standard calibration. These instrumental and procedural changes significantly improve the method's throughput, while the method's capability relative to phosphoric acid specifications is maintained, as verified through statistical evaluation of control sample analyses. Detection limits of 60, 680, and 40 ppb (w/w) are obtained vs. semiconductor-grade phosphoric acid specifications of 1000, 12 000, and 5000 ppb for chloride, sulfate, and nitrate, respectively. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Semiconductors; Phosphoric acid; Inorganic anions

## 1. Introduction

A recent application of ion chromatography (IC) in the semiconductor industry involves the determination of trace levels of anions in ultra-pure concentrated phosphoric acid [1,2]. Trace analysis by conventional ion chromatography in highly ionic matrices must deal with interference from the large concentration ratio of matrix to analyte ions. Trace analysis methods developed for IC often require a matrix elimination step prior to the final separation [1,3]. For phosphoric and other weakly ionized acids, an approach which uses ion exclusion chromatography as a pretreatment step for isolating contaminant anions with low  $pK_a$  values from the matrix acid has been developed [1]. The ability to directly pre-treat an 85% phosphoric acid sample, prior to

column switching for a final ion-exchange separation of chloride, sulfate and nitrate from phosphate, allows method detection limits of  $<100 \mu\text{g/l}$  in this highly ionic matrix.

Drawbacks to the currently recommended procedure [4] include manual injection of acid samples and use of specialized modules. The ion-exclusion pre-separation step, loading of a concentrator column, and final step-gradient elution of both the weakly retained analyte anions and the more strongly retained matrix anions result in chromatographic run times approaching 1 h. Additional requirements of monitoring blank chromatograms to ensure low detection limits and use of multiple standard addition quantitation severely limit the throughput of the method on a sample/day basis.

We have modified the existing procedure to in-

corporate use of a commercial autosampler for injection of concentrated phosphoric acid diluted 1:1 with deionized water. The valving in the chromatography compartment of the autosampler has been adapted to this column-switching method. These changes allow unattended chromatograph operation for higher sample throughput. The modified procedure also uses external standard calibration with matrix-matched standard and blank. By eliminating standard addition as recommended in the original method, a further increase in sample throughput is obtained. A final change to the method utilizes an eluent generator for simplification of instrumental operation and system stability.

These method modifications have proved successful as demonstrated by the chromatographic performance discussed here. Method detection limits, precision and accuracy using diluted samples are comparable to those in the original method and acceptable for the purpose of monitoring electronic-grade phosphoric acid purity. Results of system operation over 4 months give a realistic assessment of method performance.

## 2. Experimental

### 2.1. Chemicals

Electronic grade 85% phosphoric acid was obtained from Astaris LLC (St. Louis, MO, USA). Reagent-grade 85% phosphoric acid was obtained from J.T. Baker (Phillipsburg, NJ, USA). Inorganic Ventures (Lakewood, NJ, USA) supplied 1000  $\mu\text{g}/\text{ml}$  chloride, sulfate, and nitrate ion chromatography standards. Ca. 18 M $\Omega$  water for the IC system and sample and standard dilutions was supplied from a Millipore (Bedford, MA, USA) 4-Bowl Plus water purification system.

### 2.2. Instrumentation

All instrumentation is manufactured by Dionex (Sunnyvale, CA, USA) and configured as a DX500 microbore system using the following modules: AS50 autosampler and chromatography compartment with 10 ml sample vials, GP50 pump with microbore heads, EG40 eluent generator with KOH cartridge,

and ED40 electrochemical detector operated in the conductivity mode. Eluent suppression is provided by an ASRS-ULTRA operated in the recycle mode and connected to the 'B' control plug of the AS50 chromatography compartment. The ion-exclusion separation is driven by an external GPM-I pump controlled from one of the AS50 relays. A 50 $\times$ 2 mm AG11-HC guard column and 250 $\times$ 2 mm AS11-HC separation column are used for the final separation. A 250 $\times$ 9 mm ICE-AS6 column is used for the ion-exclusion separation followed by a 50 $\times$ 4 mm AG11-HC column used to concentrate anions prior to injection into the ion-exchange system. A 50 $\times$ 4 mm AG10 column is used as a trap between the GPM-I pump and injection valve.

Connections to the AS50 chromatography compartment valves are made as described in Fig. 1. The 200  $\mu\text{l}$  sample loop is fabricated as described in Ref. [4]. A 250  $\mu\text{l}$  'loop volume' is specified in the AS50 plumbing configuration which results in a total sample loop flush volume of 1 ml. The injection valve is used to introduce the 43% phosphoric acid sample onto the ion-exclusion column, while the column-switching valve is used to collect ion-exclusion effluent onto the AG11-HC 4 mm concentrator

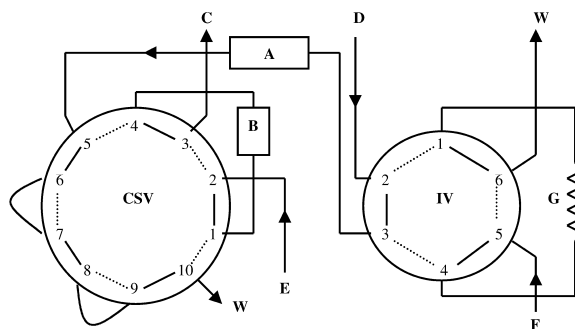


Fig. 1. Plumbing schematic for column switching valve (CSV) and injection valve (IV) in AS50 chromatography compartment. A=AS6-ICE column, B=AG11-HC (4 mm) column, C=to AG11-HC/AS11-HC separator columns, ASRS and detector, D=from auxiliary pump, E=from GP50 pump, F=sample line from AS50 autosampler, G=200  $\mu\text{l}$  loop, W=waste. Flow paths: for CSV, solid lines='B' position and dotted lines='A' position; for IV, solid lines='LOAD' position and dotted lines='INJECT' position. Polyether ether ketone (PEEK) tubing inner diameter for inter-valve connections=0.25 mm, except 0.75 mm for AS6-ICE connections and 200  $\mu\text{l}$  sample loop (44 cm long). See Ref. [4] for details.

column, and to throw this column in-line with the IC separation system. All instrument operations, data collection, and analyses are performed using Dionex PeakNet 5.1 software.

### 2.3. Methods

All vials and plastic beakers are soaked in 18 M $\Omega$  water overnight prior to use. A 5 g sample of phosphoric acid is weighed directly into a disposable 15 ml polypropylene beaker (Fisher Scientific, Pittsburgh, PA, USA) to which is added an equal mass of deionized water. A Mettler (Hightstown, NJ, USA) AT200 four-place electronic balance is used for all weighings. Samples are mixed by pouring between beaker and sample vial several times.

Details of the PeakNet 5.1 method operations and events are given in Table 1. The system is run with an 8 min ion-exclusion pre-separation time and a 4 min collection time on the concentrator column. The AS50 valves are programmed to initial positions of injection valve=LOAD and column switching valve (CSV)='B'. At 0.0 min, the injection valve is switched to INJECT to introduce sample to the ion-exclusion system. At 8.0 min, the CSV switches

to 'A' to begin collecting analytes on the 4 mm AG11-HC concentrator column. The CSV is switched back to the 'B' position at 12.0 min to introduce the concentrator column into the ion-exchange system and begin final analyte separations.

Pump, detector, autosampler, and eluent generator timed events, including the KOH gradient profile, are given in Table 1. No pressure coils are needed between the EG40 and columns to maintain the back pressure at approximately 2100 p.s.i. (1 p.s.i.=6894.76 Pa). Data collection from the ED40 is begun at 12.0 min, the effective sample injection time. The GPM-I pump for the ion-exclusion system is operated at 0.5 ml/min (450 p.s.i.) with deionized water.

### 2.4. Quantitation

As per Ref. [4], sample peak areas are corrected for trace levels of chloride, sulfate and nitrate arising from the ion-exclusion eluent (water) and other system components. Blank areas are obtained by averaging peak areas from duplicate injections of water before and a single injection after sample analyses. External standard calibration is performed by injection of reagent-grade phosphoric acid alone

Table 1  
PeakNet 5.1 method operations

Module/settings	Timed events				
<i>GP50 gradient pump</i>	<i>Time [min]</i>	<i>Flow [ml/min]</i>			
Pressure limits (p.s.i.): high=3000, low=200	Init	0.38			
	0.0	0.38			
<i>EG40 eluent generator</i>	<i>Time [min]</i>	<i>Eluent concentration [mM]</i>			
Offset volume=100 $\mu$ l	0.0	20			
	30.4	20			
	30.5	100			
	40.4	100			
	40.5	20			
	45.0	20			
<i>ED50 electrochemical detector</i>	<i>Time [min]</i>	<i>Range [<math>\mu</math>S]</i>	<i>Collect</i>		
Data collection time=33.0 min	Init	30	–		
Scale=40 $\mu$ S, –1 $\mu$ S	0.0	30	–		
Mode=conductivity	12.0	30	Begin		
Rate=5 Hz					
<i>AS50 autosampler</i>	<i>Time [min]</i>	<i>Valve</i>	<i>CSV</i>	<i>TTLs</i>	<i>Relays</i>
Cycle time=0	Init	Load	B	0 0	1 0
Sample needle height=2 mm	0.0	Inject	B	0 0	1 0
	8.0	–	A	0 0	1 0
	12.0	–	B	0 0	1 0

and spiked with analytes. A stock mixed standard containing 60  $\mu\text{g/ml}$   $\text{Cl}^-$ , 300  $\mu\text{g/ml}$   $\text{SO}_4^{2-}$ , and 45  $\mu\text{g/ml}$   $\text{NO}_3^-$  is prepared from 1000  $\mu\text{g/ml}$  commercial standards. To approximately 0.6 ml of this stock is added 50 g reagent acid and 49.4 g deionized water to prepare the working standard containing 360, 1800, and 270 ppb (w/w)  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  as injected, or 720, 3600 and 540 ppb  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  based on 85% acid. Since final solution densities are  $1.273 \pm 0.003$  g/ml for both standards and samples containing 42.2–42.8%  $\text{H}_3\text{PO}_4$ , standards can be prepared on a mass basis. Response factors (rf) for each anion in (peak area)/ppb are calculated from the acid blank-corrected standard areas divided by the concentrations injected (or on an 85% acid basis). Sample concentrations are then calculated from water blank corrected sample areas divided by rf.

### 3. Results and discussion

#### 3.1. System operation

Operation of the ion chromatography system as described above for trace analysis of anions in phosphoric acid has proved reliable over the course of several months. The only complication seen using an AS50 autosampler for direct injection of 43% phosphoric acid has been de-lamination of the PTFE coating on the syringe needle. This has caused no apparent problems, since 316 stainless steel is resistant to corrosion by 85% phosphoric acid at room temperature [5].

Consistently low system blanks are important for good quantitative results. We have found that maintaining a flow of 0.3–0.5 ml/min water through the ion-exclusion system when not analyzing samples is helpful in producing low blank areas. Typical blank and standard chromatograms are shown in Fig. 2. Note that the areas for a deionized water blank and for the J.T. Baker reagent acid blank are comparable, with sulfate being the only peak present in either blank at an appreciable level vs. the standard. Since reagent acid and water blanks are equivalent, a matrix-matched external standard method was employed in this work for quantitation.

Although previous work [4] inferred that phos-

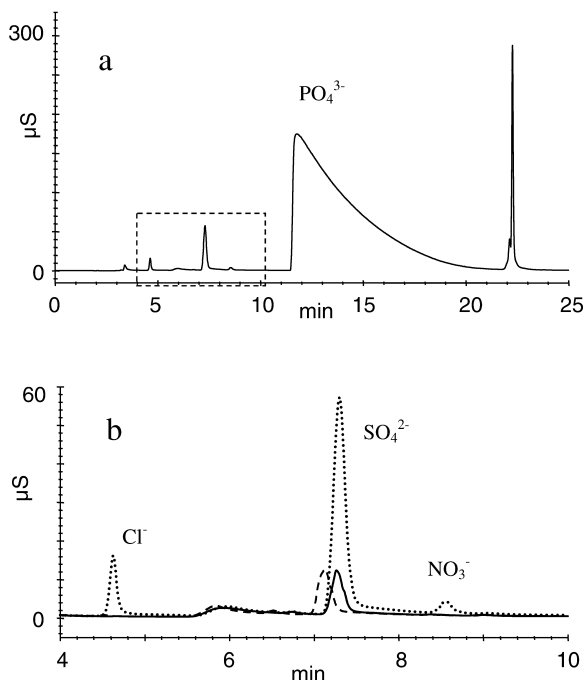


Fig. 2. (a) Typical separation of trace anion standard in phosphoric acid with trace impurity area highlighted by dashed box. Peak at 22 min is suspected to be pyrophosphate. (b) Trace impurity area showing comparison of deionized water and Baker reagent acid injections vs. standard containing 360 ppb  $\text{Cl}^-$ , 1800 ppb  $\text{SO}_4^{2-}$ , and 270 ppb  $\text{NO}_3^-$  after dilution. Solid line=water blank, dashed line=Baker reagent 85% acid blank, dotted line=standard.

phoric acid samples more dilute than 85% cannot be successfully pre-treated by ion-exclusion, we found that the elution of the phosphate peak begins at 10 min when 43% acid is injected, similar to that reported for 85% acid. With the diversion of ion-exclusion effluent to the concentrator column set at 8–12 min, the 4 min accumulation of background impurities on the concentrator column minimized water blank areas and improved detection limits (the major contribution to blank peak areas is from impurities in the deionized water used as the ion-exclusion eluent, and leaching from the ion-exclusion column).

#### 3.2. Detection limits

Method detection limits were evaluated based on the ability to detect peak areas greater than those seen in water blank injections. Blank peak area

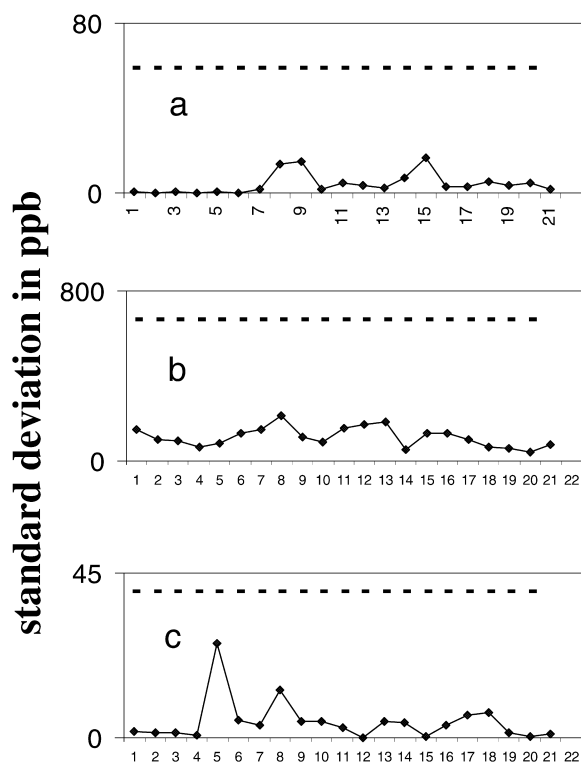


Fig. 3. Plot of within-day standard deviations in ppb for water blanks ( $n=3$ ) run on 21 days vs. overall  $3\sigma$  from all 62 blank injections for (a)  $\text{Cl}^-$ , (b)  $\text{SO}_4^{2-}$ , and (c)  $\text{NO}_3^-$ . (—♦—)=within-day  $1\sigma$ ; (---)=overall  $3\sigma$ .

averages and standard deviations were determined for 62 injections performed on 21 different days, and a summary of the data is shown in Fig. 3 and reported in Table 2. Detection limits are defined in this paper as concentrations corresponding to peak areas that exceed the blank value plus three standard deviations. Pooled within-day standard deviation values of  $\sim 6$  ppb for Cl and  $\text{NO}_3^-$  and  $\sim 120$  ppb for  $\text{SO}_4^{2-}$  are excellent vs. current electronic-grade acid

upper specifications of 1–12 ppm (w/w) for these anions. However, calculating a daily blank precision from only three injections produces a poor estimate of method detection limits and significant day-to-day variation in standard deviations are seen, as shown in Fig. 3. A more rugged estimate of method detection limits given in Table 2 is based on the overall standard deviation from all 62 injections and a 99.7% ( $3\sigma$ ) confidence interval. These stringent detection limits remain quite acceptable for electronic-grade acid analysis, although they fall above the values quoted for the manual method with neat 85% acid injection (0.15 ppb for  $\text{Cl}^-$ , 31 ppb for  $\text{SO}_4^{2-}$ , and 2.5 ppb for  $\text{NO}_3^-$ ). It is likely that previous detection limit estimates were obtained in a relatively short time frame. The 4 months used in this work incorporate more day-to-day variation and may contribute to the increase in detection limits. It also is important to note that identical  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  detection limits are obtained using either water blank or high purity acid blank injections, since the predominant blank peak magnitude and variation is due to the ion-exclusion system blank. Chloride detection limits from acid blanks are approximately twice that from water blanks, but the latter are reported here for consistent comparison with Ref. [4]. In either case, the limits are sufficiently low for semiconductor-grade acid analysis.

### 3.3. Precision and accuracy

The original IC method for trace analysis in concentrated phosphoric acid recommended the use of single or multiple standard addition for quantitation [4]. The availability of reagent-grade  $\text{H}_3\text{PO}_4$  with low levels of trace anions as a matrix allows use of external standard calibrations. A comparison of

Table 2  
Method detection limits ( $3\sigma$ ) and SEMI specifications

	$\text{Cl}^-$ (ppb, w/w)	$\text{SO}_4^{2-}$ (ppb, w/w)	$\text{NO}_3^-$ (ppb, w/w)
Based on pooled within-day standard deviation of blanks ( $df=41$ )	20	360	20
Based on overall blank standard deviation ( $df=61$ )	60	680	40
SEMI specifications [6]	1000	12 000	5000

the two methods' performance can be found from analysis of a control sample.

A control sample was prepared by spiking reagent grade acid to levels one-half that of the external standard, or 360, 1800, and 270 ppb  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , respectively, based on 85% acid. Since the external standard was also a spike of the reagent acid, both external standard and standard addition calculations can be applied to analyses of control

samples vs. standard. Results from 23 control sample analyses run on 16 different days over the course of 4 months are given in Fig. 4 and summarized in Table 3. In our implementation of the method, the precision exhibited by the external standard quantitation is found to be superior to that seen for single standard addition quantitation. This improvement is not unexpected since the external standard technique relies on interpolation between the origin and peak

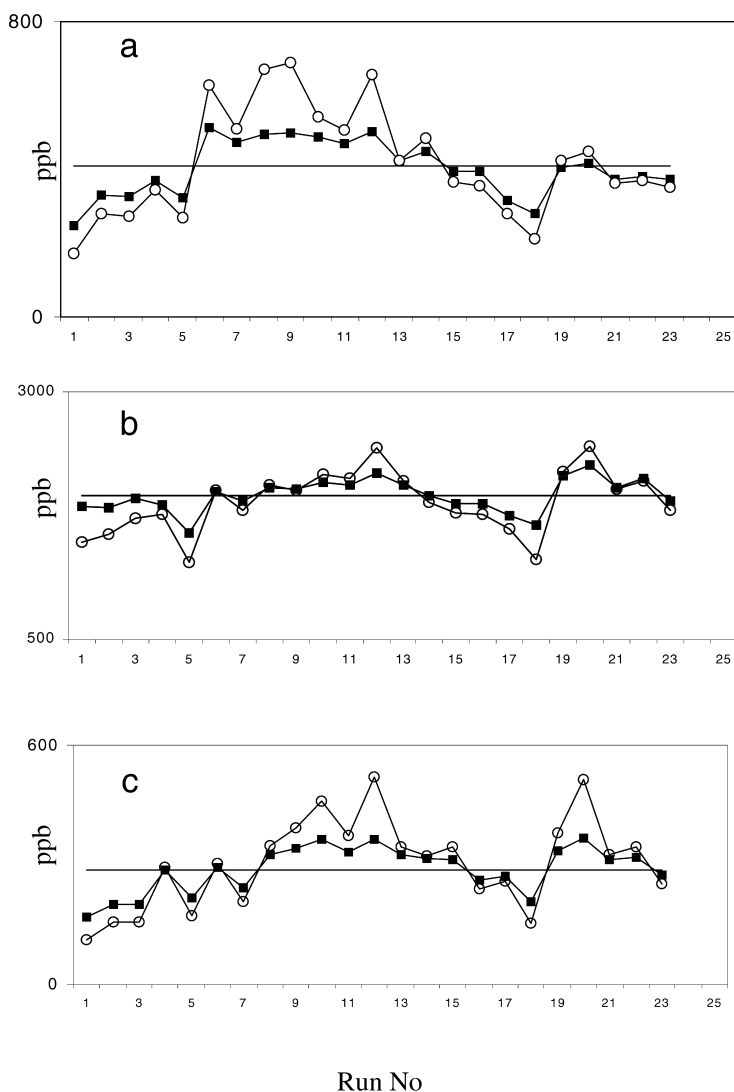


Fig. 4. Run charts for (a)  $\text{Cl}^-$ , (b)  $\text{SO}_4^{2-}$ , and (c)  $\text{NO}_3^-$  analyses for a control sample containing 360 ppb  $\text{Cl}^-$ , 1800 ppb  $\text{SO}_4^{2-}$ , and 270 ppb  $\text{NO}_3^-$  using external standard (solid points) and standard addition (open circles) for quantitation.

Table 3  
Precision from control sample analysis

	Level±SD (RSD) [ppb]		
	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>
This method (n=23)			
external standard	409±70 (17%)	1950±166 (9%)	288±58 (20%)
Ref. [4] <sup>a</sup> (n=7)	20±1.2 (6%)	433±24 (6%)	9.5±2 (21%)

<sup>a</sup> Reported values converted to ppb (μg/kg) using density=1.684 kg/l.

Table 4  
Accuracy from known control sample analysis and actual sample spike recoveries

	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>
<i>Control sample analysis</i>			
Known [ppb]	374	1870	280
Found [ppb] (n=23)	409	1950	288
<i>Spike recoveries (n=12)</i>			
Spike range [ppb]	330–1060	1650–5300	250–800
Spike recoveries [%]	92±8	94±8	93±13

areas of the standard, while standard addition employs extrapolation from the standard and sample back to the *x*-intercept.

Table 4 shows that acceptable accuracies are seen vs. known values for the control sample. In addition, accuracies derived from spike recoveries of standard additions to actual samples show comparable values to those published for the original method. Finally, the accuracy of SO<sub>4</sub><sup>2-</sup> results obtained using this method have been verified by independent inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses as shown in Table 5.

Table 5  
Accuracy for SO<sub>4</sub><sup>2-</sup> by comparison with ICP-AES results<sup>a</sup>

Sample	ppb (w/w) found	
	IC	ICP-AES [7]
A	4900	4620
B	4470	4550
C	4980	4720
D	2700	2770
E	1070	1140
F	6870	6790
G	4450	4560

<sup>a</sup> Total S from ICP-AES converted to SO<sub>4</sub><sup>2-</sup>

## 4. Conclusions

The modified method for phosphoric acid analysis using a 1:1 dilution with an autosampler and external standard calibration shows acceptable performance for trace analyses at and below the specification levels for electronic-grade phosphoric acid. Some apparent degradation in detection limits and method precision is seen vs. reported results for neat 85% acid injections, as would be expected due to reduced peak areas for diluted samples. While it is possible that the AS50 autosampler could be used for neat 85% acid injections, it has been shown that analysis of diluted samples can be accomplished without any serious degradation of either method or hardware performance. Use of an eluent generator along with the autosampler brings a higher level of automation to this analysis, allowing a 20-fold increase in laboratory productivity (one sample/day in an 8 h shift for the manual method vs. ~20 samples/day for overnight automated analysis).

## Acknowledgements

The author would like to thank Dr. Robert V. Brill of Astaris LLC, St. Louis, MO, USA for helpful discussion of detection limit determination strategies, and Dr. L. Alan Shaver of Astaris LLC, Lawrence, KS, USA for sulfur analysis of samples using ICP-AES.

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