A ROBUST METHOD DEVELOPED FOR SPECIES ANALYSIS DURING A TYPICAL HYDROMETALLURGICAL TEST WORK PROGRAMME FOR PRODUCTION OF BATTERY GRADE PHOSPHORIC ACID ‑ A MINTEK PACKAGE

By

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ABSTRACT

The current work evaluates the optimisation of an analytical method for the determination of fluoride and chloride impurities in a high phosphoric acid matrix. A typical battery grade acid is expected to contain meagre level of impurities to better enhance the capacity, voltage, specific energy, energy density, and thermal stability of lithium ion batteries, latter being the most crucial. Accurate determination of the species in the final product as well as streams generated throughout the three major phases of pre-treatment, solvent extraction and post-treatment is the only means to monitor the process effectiveness.

A robust inter-linked technique is required for preparation and analysis of various commodities and species during the process to meet the stringent impurity thresholds at each stage. These include determination of density, total suspended solids, P_2O_5, total organic carbon, critical base metals (arsenic, chromium, sulphur and boron), chloride and fluoride.

A precise determination of chloride and fluoride in the process is critical to ensure that the corrosiveness of the acid is minimised. The chloride and fluoride contents are expected not to exceed 20 and 10 ppm, respectively. These ions can be analysed using either ultraviolet-visible spectrophotometer (UV-Vis) or an ion chromatography. This paper therefore, details how analyses of such limited range were conducted, the development and optimization of the exclusion methods to suit the high phosphorus matrix of these samples. International certified reference material was used for validation purposes. The high phosphoric acid matrix resulted in challenges with both the UV-Vis and the Ion chromatography methods however, the ion chromatography exclusion method allowed for the determination of these ions at low concentrations. This comparative study showed good recoveries for both elements of interest (F^- and Cl^-) when using the ion chromatography exclusion method and the data obtained indicated good repeatability and reproducibility.

Keywords: Battery Grade Phosphoric Acid, Ion Chromatography, Exclusion, UV-Vis

INTRODUCTION

Phosphoric acid is a versatile industrial acid that finds numerous applications in the food and beverage industry. One of the primary uses of phosphoric acid, a colourless and odourless mineral acid, in the food industry is as a food additive and flavouring agent (1). It is commonly used in the production of carbonated soft drinks to provide a tangy taste and a slight acidic pH to balance the sweetness of the drink (2). Phosphoric acid also acts as a pH buffer in other food and beverage products such as jams, jellies, and sauces (3). The acidity of the acid helps to inhibit bacterial growth and prolong the shelf-life of the products (2).

Moreover, phosphoric acid is used in the food processing industry as a preservative and as a pH regulator. It is added to meat and poultry products to increase the water-holding capacity, resulting in juicier and more tender meat (3). Additionally, phosphoric acid is used in the production of cheese, yogurt, and other dairy products to lower the pH and create the ideal conditions for the growth of beneficial bacteria that contribute to the flavour and texture of the product (4).

Apart from these uses, phosphoric acid is also used in the food industry for its emulsifying and chelating properties (3). It is added to processed foods to stabilize emulsions, prevent separation of oil and water, and to enhance the texture of the food product. Phosphoric acid is also used as a chelating agent to remove minerals from food products, thereby preventing spoilage and rancidity (5).

Phosphoric acid is a critical component in the production of phosphatic fertilizers and industrial products due to its ability to react with phosphate rock and produce soluble forms of phosphate that are essential for plant growth (6). The acid is commonly used in the wet process of producing phosphoric acid, which involves the reaction of phosphate rock with sulphuric acid to produce phosphoric acid and gypsum as a by-product. The produced phosphoric acid is then neutralized with ammonia to form ammonium phosphate fertilizers such as mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP) (6).

In addition to its use in the production of fertilizers, phosphoric acid is also utilized in the production of various industrial products such as detergents (7), water treatment chemicals (8), metal surface treatment agents (9), and flame retardants (10). For instance, phosphoric acid is used as a rust inhibitor in the production of metal products by forming a protective layer on the metal surface. It is also used in the production of flame retardants due to its ability to release phosphorus that forms a protective layer on the surface of the material and prevents it from igniting (1).

Phosphoric acid has emerged as a key intermediate material in the production of lithium iron phosphate (LFP) for the battery material supply chain (11). The demand for LFP batteries has been increasing in recent years, driven by the growth of electric vehicles and the need for energy storage systems. Phosphoric acid is a vital component in the production of LFP cathode material, which is known for its long cycle life, stability, and safety. To meet the stringent purity requirements of the battery material supply chain, phosphoric acid used in LFP production must have ultra-high purity levels. Any impurities in the acid can have detrimental effects on the battery performance, resulting in reduced capacity, cycle life, and safety. Therefore, the production of ultra-high purity phosphoric acid is essential to meet the growing demand for LFP batteries (12).

Several methods have been developed to produce ultra-high purity phosphoric acid, including the solvent extraction method, the electrochemical method, and the ion exchange method. These methods involve the removal of impurities such as heavy metals, fluoride, and arsenic to ensure that the acid meets the purity standards required for LFP production.There are two primary flow sheeting methods used in industry for the production of phosphoric acid; the dry and the wet process (6, 13).

The wet-process phosphoric acid (WPA) usually contains impurities in combination with phosphoric acid. Some triggers to increased corrosiveness in technical phosphoric acids are fluorides, chlorides, and bromides. Care has to be taken while using phosphoric acids containing chlorides and at increased temperatures. The corrosion rate can increase more than 10-fold on a typical stainless steel grade when temperature slightly changes, even where only low amounts of chlorides are present in the acid, see Figure 1. High amounts of fluorides in combination with temperature increase may also have unpropitious effect on corrosive resistance, see Figure 2 (14).

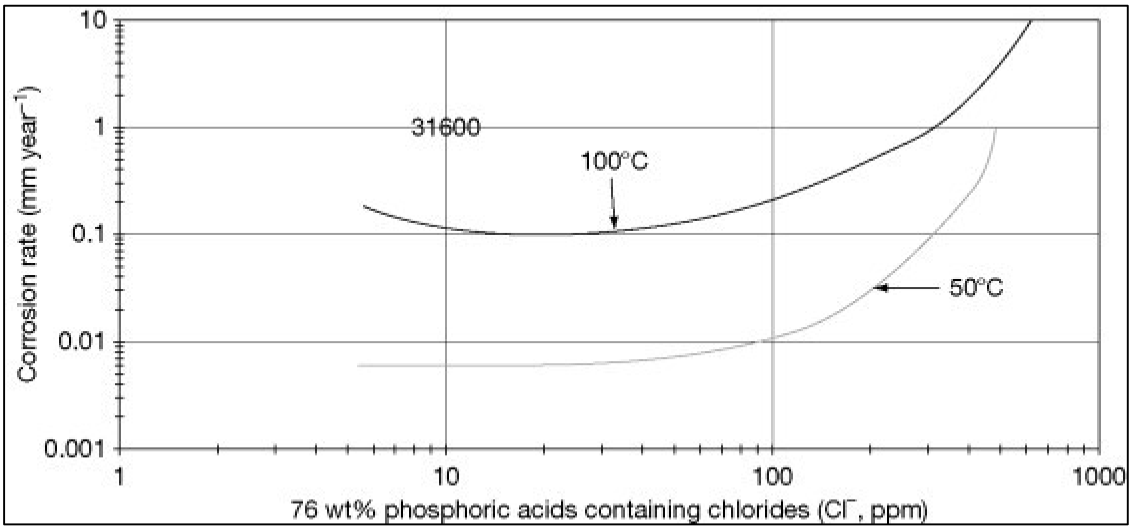


Figure 1: Corrosion rate for the stainless steel grade S31600 in phosphoric acid containing chloride (14)

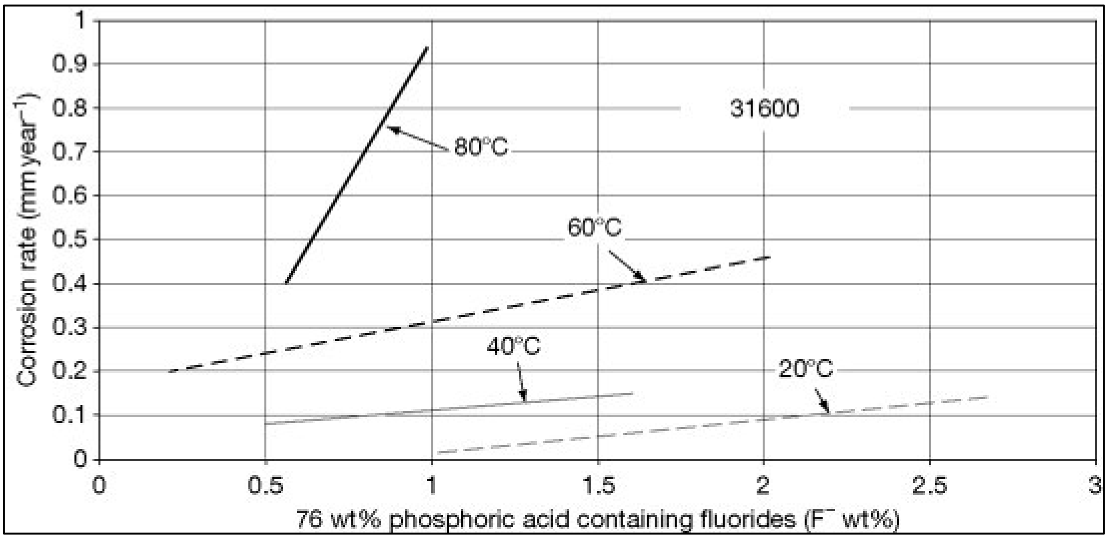


Figure 2: Corrosion rate for the stainless steel grade S31600 in phosphoric acid containing fluorides (14)

Ion chromatography (IC) is a widely used method for determining F and Cl levels in WPA (15, 16). IC has high sensitivity and selectivity, making it suitable for detecting very low levels of F and Cl in complex matrices. The technique separates and quantifies ions in a sample using ion-exchange resins and conductivity detection. IC is also relatively easy to use and requires minimal sample preparation, making it a popular choice for routine analysis of F and Cl in WPA.

Inductively coupled plasma mass spectrometry (ICP-MS) is another powerful analytical method for determining trace elements in complex matrices such as WPA (17). ICP-MS has high sensitivity, selectivity, and multi-element capability, making it suitable for analysing a wide range of elements, including F and Cl. The technique ionizes the sample using high-temperature plasma and measures the resulting ions using a mass spectrometer. ICP-MS also allows for the determination of isotopic ratios, which can provide additional information about the origin and fate of the elements in the sample (18).

The matrix effect of phosphoric acid can however be detrimental to ICP methods. The high concentration of phosphate ions in phosphoric acid can interfere with the determination of trace elements by ICP-MS by reducing ionization efficiency, producing polyatomic interferences, and increasing background noise. These effects can result in inaccurate and imprecise measurements of trace elements in phosphoric acid (19).

To overcome the matrix effect in ICP-MS analysis of phosphoric acid, several sample preparation techniques have been developed, including dilution, ion exchange, and sample digestion (20, 21). Dilution of the sample with a matrix-matched solution can reduce the concentration of interfering matrix elements, improving the accuracy and precision of the analysis. Ion exchange can remove interfering matrix elements selectively, allowing for more accurate and precise measurements of trace elements. Sample digestion can break down the matrix to release the target elements for analysis, but this technique requires more complex and time-consuming sample preparation (21).

The determination of trace anions by Ion Chromatography in phosphoric acid is nevertheless hindered by a large excess of phosphate ion. Diluting the concentrated sample overcomes the problem of a large concentration of the interfering matrix ions, but lacks the required sensitivity for the contaminant ions of interest. Therefore, trace inorganic anions need to be separated from the high concentration of phosphate prior to an ion-exchange separation (22).

It is worth noting that the concentration of phosphoric acid after the last defluorination and dechlorination stages is typically very high, often greater than 50% by weight (1). This is because the final purification steps involve the removal of impurities using carbon columns and/or ion exchange resins. These steps are designed to remove any remaining impurities, including fluoride and chloride ions, and to concentrate the phosphoric acid. The concentration of phosphoric acid before the final purification steps may vary depending on the efficiency of previous purification steps and the initial concentration of impurities. However, it is generally expected that the concentration will be lower before these steps and higher after them (10).

This report describes the theory, set up, and analytical procedure for the determination of fluoride and chloride at trace levels in 62% (w/w) phosphoric acid. An ion-exclusion column is used to separate the analyte ions from an excess of phosphate matrix ions. A selected fraction from the ion-exclusion separation is “cut” and sent to an anion-exchange concentrator column. The concentrated ions are then eluted onto a column set, on which the anions of interest are separated and detected by suppressed conductivity.

EXPERIMENTAL

This method addresses the challenge of determining trace concentrations of contaminant ions such as fluoride and chloride in a matrix composed of a high concentration of phosphate ion. This is accomplished in two steps: an ion-exclusion (ICE) pre-separation followed by injection of a portion of the ICE separation to an ion chromatographic (IC) separation. The ion-exclusion mechanism separates ionized species from non-ionized or weakly ionized species. This occurs because of a negatively charged hydration shell on the stationary phase surface called the Donnan membrane.
The strong acid ions, such as chloride and fluoride, are excluded and elute first and the weakly ionized phosphate matrix ions (concentrate) are retained and elute later.

Equipment

- Thermo Scientific™ Dionex™ ICS-5000+ HPIC™ Ion Chromatography system consisting of:
    1. Gradient Pump, microbore configuration
    2. Conductivity Detector with a temperature controlled conductivity cell
    3. Enclosure with 2 Rheodyne® valves, PEEK™, rear loading
- Thermo Scientific™ Dionex™ Dionex RP-1 single piston pump
- Pressurizable Reservoir Chamber
- 1 Air pressure gauge, 0–171 kPa (0–25 psi) (for external water)
- Green PEEK tubing, diameter of 0.75 mm, to connect columns and make a 200 µl sample loop
- Thermo Scientific™ Dionex™ PeakNet™ Chromatography Workstation

The main operating parameters and/or conditions are presented in Table 1.

Table 1: Operating Conditions

Parameter	Conditions
Ion Exclusion	
Analytical Column	Dionex IonPac ICE-AS6, 9 x 250mm
Trap Column	Dionex IonPac AG10, 4 mm
Eluent	Deionized water from Millipore system, 18.2 MΩ·cm
Flow Rate	0.50 ml/min
Ion Chromatography	
Analytical Column	Dionex IonPac AS11-HC, 2 mm
Guard Column	Dionex IonPac AG11-HC, 2 mm
Concentrator Column	Dionex IonPac AG11-HC, 4 mm
Eluent	20 mM NaOH, step to 200 mM NaOH
Flow Rate	0.38 ml/min
Sample Volume	200 µl
Detection	Suppressed conductivity, Dionex Anion Self-Regenerating Suppressor (ASRS), AutoSuppression external water mode
Suppressor Current Setting	300 mA
Expected System Backpressure	16.5 MPa (2400 psi) (with concentrator column in line)
Expected Background Conductivity	2–3 µS

Reagents and standards

Deionized water from Millipore system, 18.2 MΩ·cm resistance, Sodium hydroxide, 50% (w/w) aqueous solution (Fisher Scientific) and Thermo Scientific™ Dionex™ Chloride and Fluoride 1000 mg/l.

The concentrated phosphoric acid sample is loaded via a pressurized reservoir into the 200 µl sample loop at a flow rate of 0.5 ml/min. This technique ensures that a representative sample of the concentrated phosphoric acid sample is loaded into the sample loop. It is important to pass at least 4 loop volumes through the sample loop to ensure reproducible sampling. The concentrated phosphoric acid sample is then delivered with the high-purity water carrier stream to the Dionex IonPac ICE-AS6. A Dionex IonPac AG10 is placed after the Dionex RP-1 pump to act as an anion trap column for the deionized water, illustrated in Figure 3.

The first portion of the ICE separation is sent to waste and disposed of properly, then the concentrator column is placed in-line with the ICE column and the portion eluted later is captured on the concentrator column. After some time, the 4-mm Dionex IonPac AG11-HC concentrator column is placed in-line with the 2 mm Dionex IonPac AS11-HC analytical column set and the concentrated ions (fluoride and chloride) are separated.

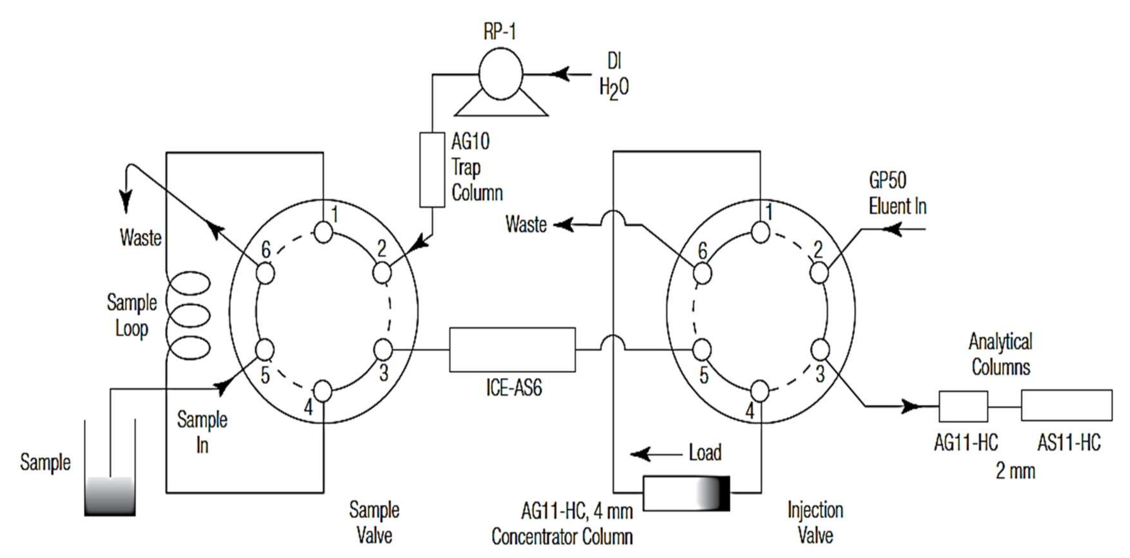


Figure 3: A schematic illustration the operation of the chromatography hardware

The IC separation utilizes the Dionex IonPac AS11-HC column with an isocratic eluent of 20 mM NaOH. The attractive feature of this separation is that phosphate elutes last. During the IC separation, the pressurized vessel is filling the sample loop for the next analysis. The deionized water rinses the Dionex IonPac ICE-AS6 column and associated tubing to ensure there is no contamination from the previous sample. After the phosphate has eluted from the column, the eluent concentration is stepped from 20 to 200 mM NaOH for 5 minutes. This ensures that the column is rinsed of residual phosphate. The method returns the system to equilibrate at 20 mM NaOH for the next injection.

Calibration

Four calibration standards (Table 2) at low concentration levels, similar range to the expected concentrations in the samples were prepared by diluting the working standard.

Table 2: Calibration Standards

Anion	Evaluation Type	Level 1	Level 2	Level 3	Level 4
Fluoride, mg/l	Area	0.78125	3.125	12.50	50.00
Chloride, mg/l	Area	0.78125	3.125	12.50	50.00

RESULTS AND DISCUSSIONS

A representative blank is presented in Figure 4. It was found that after concentrated phosphoric acid had been in the sample loop pathway, several cycles of deionized water were required to completely rinse away the high concentration of phosphate matrix ions. A blank was established by running ten replicates and obtaining reproducible results. These levels, which were quantified based on a calibration curve for these ions in deionized water, were found to be below the concentrations expected for high-purity grade concentrated phosphoric acid. A small amount of phosphate was detected in the blank, as carryover from previous injections. However, this is not expected to significantly impact sample analysis.

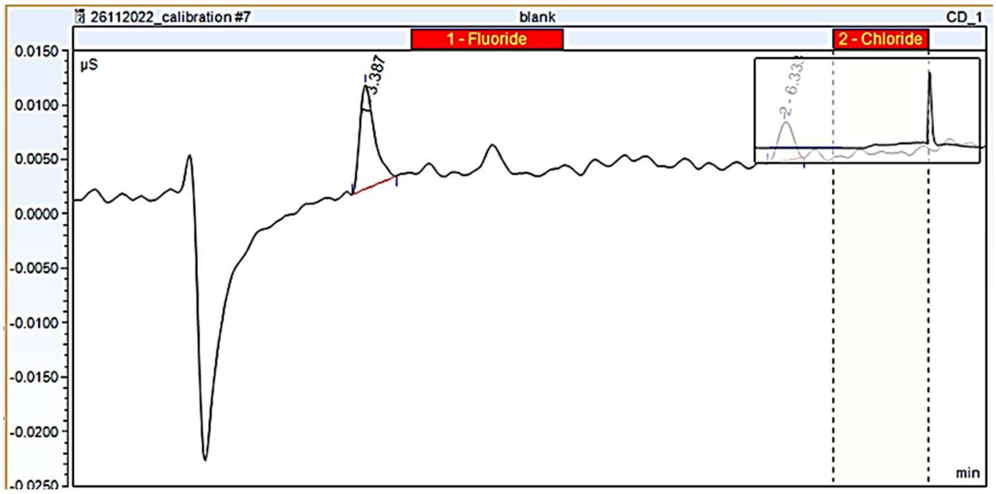
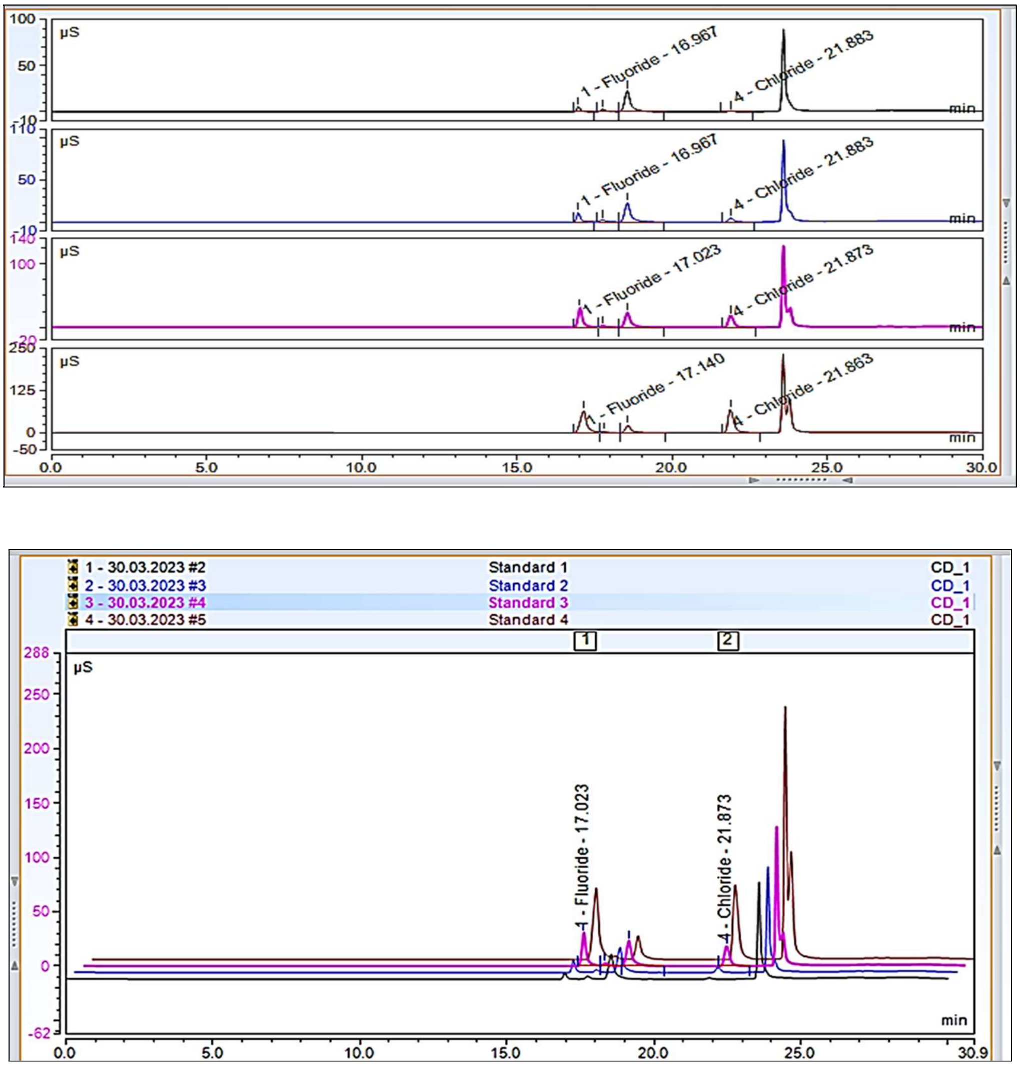


Figure 4: Representative Blank

To verify proper quantification of analytes in the phosphoric acid matrix, fluoride and chloride standards with increasing concentrations were analysed. Chromatograms for the analysis of standards in 60% (w/w) phosphoric acid is shown in Figure 5. The large phosphate matrix (peak 5) is well separated from the anions of interest. Any residual phosphate left in the column was eluted with the high eluent concentration.



1 - 30.03.2023 #2	Standard 1	CD_1
2 - 30.03.2023 #3	Standard 2	CD_1
3 - 30.03.2023 #4	Standard 3	CD_1
4 - 30.03.2023 #5	Standard 4	CD_1

Figure 5: Calibration Standards

To assess method reproducibility, retention time precision was calculated from standards and samples spiked with known quantities of the anions injections. The retention time was reproducible for all injections with an average of 17.087 and 22.053 minutes for fluoride and chloride respectively.

Calibration curves are presented in Figures 6 and 7. Fluoride and chloride yielded coefficients of determination (r^2) values 0.9986 and 0.9999 respectively.

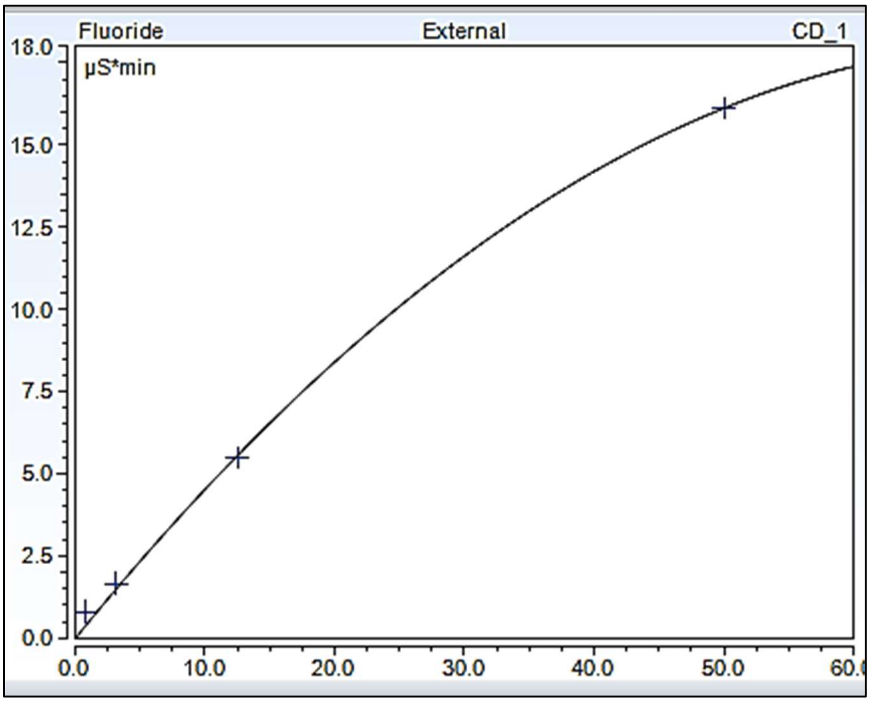


Figure 6: Fluoride Calibration Curve

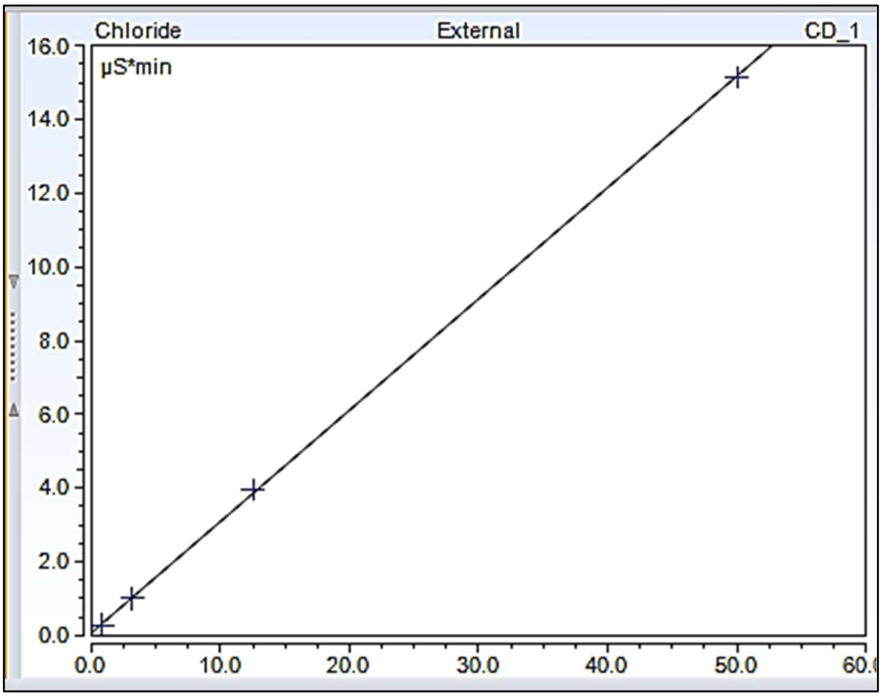


Figure 7: Chloride Calibration Curve

Method detection limits (MDLs) were calculated using the standard deviation of ten replicate injections multiplied by the Student's *t*-value for the 99.5% confidence level. MDLs for fluoride and chloride are in the low µg/l range. The calculated MDLs for this method are well below the maximum limit of impurity guidelines for phosphoric acid established by semiconductor equipment and materials international (SEMI) for the purest grade of phosphoric acid, as shown in Table 3.

Table 3: Method detection limits for trace anions in phosphoric acid

Anion	*MDL (µg/l)
Fluoride	1.10
Chloride	0.40

*Method Detection Limit = (SD) x (ts)99.5% where (ts) is for a single-sided Student's *t*-test distribution for n = 10.

To determine method precision, a sample of a battery grade 62% phosphoric acid was analysed by this method. A chromatogram is shown in Figure 8. The large phosphate matrix (peak 5) is well separated from the anions of interest.

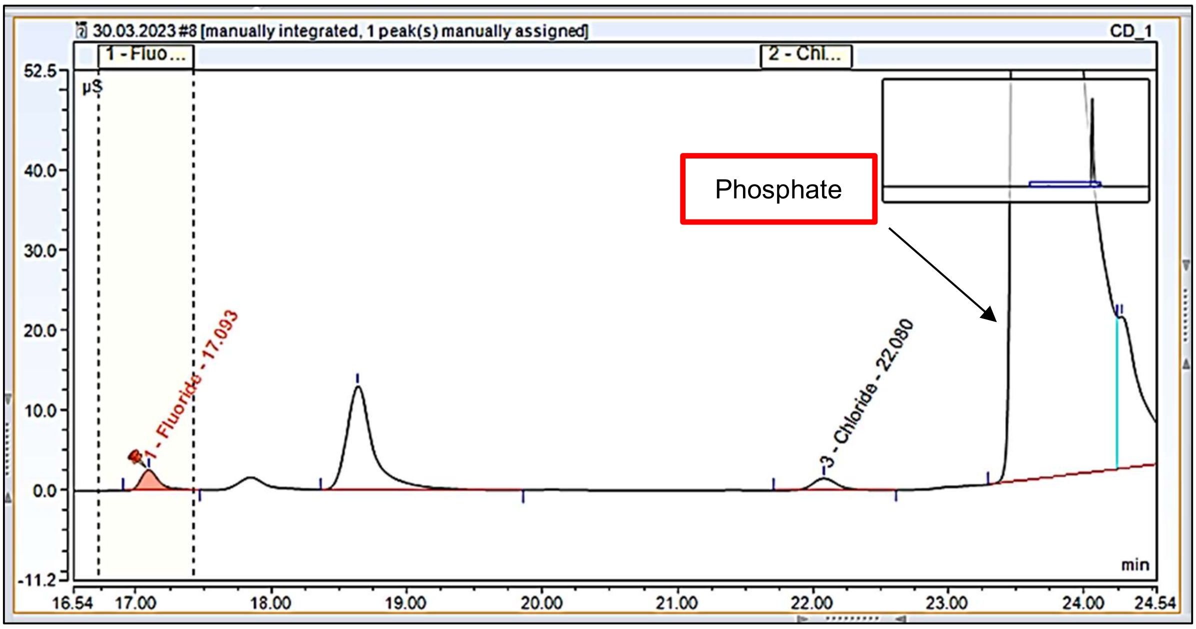


Figure 8: Determination of trace anions in high purity 62% phosphoric acid.

For six replicates, a relative standard deviation (RSD) of less than 5% was obtained for 87 µg/l fluoride and 150 µg/l chloride. Results are presented in Table 4. This sample was spiked with known concentrations and sent to be analysed by an external laboratory for verification purposes and results from the verification analysis are presented in Table 5.

Table 4: Determination of trace anions in battery grade 62% phosphoric acid

Anion	Fluoride	Chloride
Battery grade 62% phosphoric acid	**µg/l**	**µg/l**
	90	148
	85	148
	87	153
	88	151
	85	156
	84	145
+	86.5	150.2
STD Deviation	2.25	3.97
%RSD	2.61	2.64
Certified Value, mg/l	<1	<2

Table 5: Spike recovery of trace anions in battery grade 62% phosphoric acid

Anion	Spike, mg/l	Value obtained, mg/l	%Recovery	External lab. Value, mg/l
Fluoride	10	10.9	109	13.5
Chloride	10	9.0	90.0	9.1

CONCLUSIONS

The method development was a success, the study showed good recoveries for both elements of interest (F^- and Cl^-) using the ion chromatography exclusion method and the data obtained indicated good repeatability and reproducibility at low concentrations. The large phosphate matrix was well separated from the anions of interest. More international certified reference materials will be sourced and used for validation purposes.

ACKNOWLEDGMENTS

The authors would like to thank the staff and management of Mintek for provision of data to prepare this paper.

REFERENCES

1. Gilmour R. Phosphoric acid: purification, uses, technology, and economics: CRC Press; 2013.
2. Caballero B, Finglas P, Toldrá F. Encyclopedia of food and health: Academic Press; 2015.
3. Akoh CC. Food lipids: chemistry, nutrition, and biotechnology: CRC press; 2017.
4. Sodini I, Remeuf F, Haddad S, Corrieu G. The relative effect of milk base, starter, and process on yogurt texture: a review. Critical reviews in food science and nutrition. 2004;44(2):113-37.
5. Schorr M, Valdez B. Phosphoric acid industry: problems and solutions: BoD–Books on Demand; 2017.
6. Becker P. Phosphates and phosphoric acid: raw materials, technology, and economics of the wet process. revised and expanded: Marcel Dekker, Inc.; 1989.
7. Geeson MB, Cummins CC. Phosphoric acid as a precursor to chemicals traditionally synthesized from white phosphorus. Science. 2018;359(6382):1383-5.
8. De Boer MA, Wolzak L, Slootweg JC. Phosphorus: reserves, production, and applications. Phosphorus recovery and recycling. 2019:75-100.
9. Kadoma Y. Surface treatment agent for dental metals using a thiirane monomer and a phosphoric acid monomer. Dental materials journal. 2002;21(2):156-69.
10. Green J. A review of phosphorus-containing flame retardants. Journal of fire sciences. 1992;10(6):470-87.
11. Satyavani T, Kumar AS, Rao PS. Methods of synthesis and performance improvement of lithium iron phosphate for high rate Li-ion batteries: A review. Engineering Science and Technology, an International Journal. 2016;19(1):178-88.
12. Liu X, Gao Z, Cheng J, Gong J, Wang J. Research progress on preparation and purification of fluorine-containing chemicals in lithium-ion batteries. Chinese Journal of Chemical Engineering. 2022;41:73-84.
13. Schorr M, Lin I. Wet process phosphoric acid production problems and solutions. Industrial minerals. 1997;355:61-71.
14. Revie RW. Uhlig's corrosion handbook: John Wiley & Sons; 2011.
15. Ramteke L, Sahayam A, Ghosh A, Rambabu U, Reddy M, Popat K, et al. Study of fluoride content in some commercial phosphate fertilizers. Journal of Fluorine Chemistry. 2018;210:149-55.
16. Smee BW, Hall G, Koop D. Analysis of fluoride, chloride, nitrate and sulphate in natural waters using ion chromatography. Journal of Geochemical Exploration. 1978;10(3):245-58.
17. Guo W, Jin L, Hu S, Guo Q. Method development for the determination of total fluorine in foods by tandem inductively coupled plasma mass spectrometry with a mass-shift strategy. Journal of Agricultural and Food Chemistry. 2017;65(16):3406-12.
18. Beauchemin D. Inductively coupled plasma mass spectrometry. Analytical chemistry. 2008;80(12):4455-86.
19. Agatemor C, Beauchemin D. Matrix effects in inductively coupled plasma mass spectrometry: A review. Analytica Chimica Acta. 2011;706(1):66-83.
20. Masson P, Dalix T, Bussière S. Determination of Major and Trace Elements in Plant Samples by Inductively Coupled Plasma–Mass Spectrometry. Communications in Soil Science and Plant Analysis. 2010;41(3):231-43.
21. Becker JS, Boulyga SF, Pickhardt C, Becker J, Buddrus S, Przybylski M. Determination of phosphorus in small amounts of protein samples by ICP–MS. Analytical and Bioanalytical Chemistry. 2003;375(4):561-6.

22. Michalski R. Ion Chromatography as a Reference Method for Determination of Inorganic Ions in Water and Wastewater. Critical Reviews in Analytical Chemistry. 2006;36(2):107-27.