On-line chloride removal from ion chromatography for trace-level analyses of phosphite and other anions by coupled IC-ICPMS

Eva Stueeken[1] and Abu S. Baidya[1]

[1]University of St Andrews

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Abstract

Rationale: Ion chromatography combined with inductively-coupled plasma mass spectrometry is an ideal tool for measuring low concentrations of anionic species such as phosphite; however, the high concentration of chloride and other anions in natural solutions may negatively impact chromatographic separation and data quality. **Method:** We developed an on-line mechanism of removing chloride from the sample within the ion chromatograph, using an additional valve and a separation column that transfers chloride to waste while phosphite and most other anions are retained. We installed this system in a coupled IC-ICPMS system (ICS6000 and Element 2 in medium resolution mode) and determined linearity and detection limits. In addition, we measured phosphorous species by NMR for comparison as an alternative method for phosphite determination. **Results:** Chloride was fully removed from the samples while phosphite was retained and could be analysed by IC-ICPMS. Concentrations could be measured down to 0.003 µmol/L and possibly less with good linearity over the explored range (up to 1.615 µmol/L; $r^2 = 0.999$). In contrast, the detection limit by NMR was 6.46 µmol/L. **Conclusions:** The on-line removal mechanism works well for simplifying sample matrices. It removes the need for costly pre-analytical sample treatment with OnGuard columns. We confirm that IC-ICPMS is the most powerful technique for quantifying phosphite in natural solutions. The new Cl-removal method may also be applicable to analyses of other anions.

1. INTRODUCTION

Ion chromatrography is a common tool for quantifying the concentration of different species of the same element in natural and experimental solutions. Examples include, but are not limited to, nitrate and nitrite, bromide and bromate, chloride and perchlorate, as well as an array of organic compounds. In recent years, with the discovery of reduced phosphorus species in natural settings[1-3], phosphate, phosphite and hypophosphite have moved into the focus of anion chromatography[2, 4-6]. Phosphite has even been detected in ancient sedimentary rocks and holds potential as an important substrate for prebiotic chemistry and early life[7, 8]. Reconstructing its biogeochemical history over geologic time and its distribution in modern environments therefore promises to yield new insights into the evolution of Earth's biosphere. Phosphite is thermodynamically unstable in water (i.e., it forms in the stability field of H_2), but it is kinetically stable, because oxidation to phosphate is slow and primarily catalysed by micro-organisms today[7-9]. Phosphite can be produced biologically[10] or abiotically under dry, hot conditions[8, 11], by lightning[12-14], or from the dissolution of meteoritic FeP-minerals[15]. However, as these pathways are relatively rare, phosphite concentrations can be low in natural fluids (e.g., 0.15-3 µmol/L in waters from Florida[1] and up to 0.45 µmol/L in a eutrophic lake in China[3], but less than 0.06 µmol/L in some geothermal waters[2] and often undetectable). Concentrations at the lower end of this range pose analytical challenges, because the phosphite anion peak is typically dwarfed by those of other anions such as chloride, sulfate, and phosphate in typical chromatographic setups. Saturation of the column and/or detector by those other more abundant anions may impact element separation and detection of phosphite[6].

To overcome this issue, Han et al.[6] as well as Ivey & Foster[4] implemented the use of OnGuard cartridges

that simplify the sample matrix, particularly by the removal of chloride – the most common anionic species in most natural systems. This allowed injection of larger sample volumes (500-800 µL loop size) to overcome the detection limit. By coupling the ion chromatograph (IC) with an inductively-coupled plasma mass spectrometer (ICP-MS), Ivey & Foster[4] were able to achieve detection limits around 0.002 µmol/L for phosphite. However, the authors also noted that OnGuard cartridges can impact the phosphate and phosphite content of the samples, introducing additional uncertainty into the analytical yield. Furthermore, OnGuard cartridges add extra costs and labor to the sample preparation protocol. Alternatively, phosphite can be analysed by UV-VIS spectrophotometry[16]; however, this may suffer from interferences with other ions, and the reported detection limit of 0.36 µmol/L[16] is not as good as with the coupled IC-ICPMS system. Lastly, phosphite measurements can be made by nuclear magnetic resonance (NMR)[1], but this technique is generally not optimized for trace quantities. A detection limit has to our knowledge not yet been published, possibly because it is dependent on numerous instrument parameters (discussed below).

Here we present a new approach of removing chloride from the sample matrix on-line within the ion chromatograph by splitting the sample stream after passage of the chloride fraction through an additional clean-up column. By coupling this method with an Element 2 ICP-MS in medium-resolution mode, this allows us to achieve detection limits better than 0.003 µmol/kg with a small sample volume (37.5 µL loop size on Valve 1, Fig. 1a). We further present data collected by NMR with a detection limit of ca. 6.46 µmol/L, which highlights the value of the IC-ICPMS setup for natural samples.

2. MATERIALS AND METHODS

2.1. Reagents and equipment

All sample preparation and IC-ICPMS analyses were carried out in the St Andrews Isotope Geochemistry laboratory (StAIG). NMR analyses were carried out in the School of Chemistry at the University of St Andrews. Solutions containing chloride, nitrite, nitrate, sulfate, phosphite, phosphate and in some cases hypophosphite and pyrophosphate were prepared in LDPE bottles from pure reagents (NaCl, Sigma-Aldrich p/n 1.06404.0500; KNO_2, Fisher Scientific p/n 11328016; $NaNO_3$, Fisher Scientific p/n 10696842; $MgSO_4$, Fisher Scientific p/n 11377658; Na_2HPO_2, Fisher Scientific p/n 222791000; $Na_2HPO_3.5H_2O$, Fisher Scientific p/n 11994281; Na_2HPO_4, Acros Organics p/n 204855000; $K_4P_2O_7$, Fisher Scientific p/n 10378860) dissolved in 18.2 MΩ[?]cm^{-1}deionized water, which was generated with a Smart2Pure system. During the analysis, a 1 mmol/L NaOH solution was used, which was prepared each day by dilution of a concentrated stock solution (500 g/L, carbonate-free NaOH, VWR p/n 87938.290). This stock bottle was stored and handled with minimal agitation to avoid mixing with atmospheric CO_2 gas that may lead to elevated carbonate concentrations. An aliquot of 0.16 ml was pipetted into 2 L of DI-water, and the pipette was dipped as deeply into the stock bottle as possible to avoid carbonate-enriched solution from the upper layer closest to the lid. The bottle with the diluted 1 mmol/L NaOH solution was only shaken up after purging with N_2 to remove air. The headspace was then pressurized with N_2 to further avoid ingrowth of atmospheric CO_2 during the analysis. For the NMR analysis, 10-20 % heavy water (D_2O) was used (Sigma-Aldrich p/n 151882-100G) to prepare a 0.6 ml sample solution.

The ion chromatograph used in this study was a Dionex ICS-6000 from Thermo Fisher, equipped with an AS-AP autosampler, a 37.5 µL sample loop, a gradient pump, an eluent generator with an RFIC degasser, a CR-ATC 600, an EGC 500 KOH cartridge, an AG17-C guard column, an AS17-C analytical column, an ADRS 600 2mm suppressor, and a conductivity detector (Thermo Scientific p/n 061830). It was run with a constant flow rate of 0.5 ml/min. KOH was used as an eluent, and its concentration was ramped from 1 mmol/L to 40 mmol/L over the course of each run. Analyses with pyrophosphate were set to last for 55 minutes, and here the KOH was ramped up between 5.5-23 minutes. After 45 minutes of total run time, the KOH concentration was decreased back to 1 mmol/L over a duration of 5 minutes. Analyses of solutions without pyrophosphate were set to last for 27 minutes, the KOH was ramped up between 5.5-23 minutes and ramped back down between 23-26 minutes. Containers used for samples and standards were soaked in hot 2M HCl overnight and rinsed several times with deionized water prior to use.

The ICP-MS was an Element 2 from Thermo Fisher. It was equipped with a Scott quartz spray chamber and a quartz nebulizer rated for a solution flow rate of 1 ml/min. Argon gas flow rates were 16 L/min for the cool gas flow, 0.8 L/min for the auxiliary flow, and 1 L/min for the sample carrier flow. The RF power was set to 1250 W. Prior to the start of the run, the ICP-MS was tuned with a multi-element solution at a concentration of 1 ppb in 5% HNO_3 (Thermo Scientific p/n 1099601). The instrument was operated in medium resolution mode (measured resolution was ca. 4200 Δm/m) to avoid HNO interferences with phosphorus at m/z 31. Oxide % measured determined from UO/O was ca. 3-5%.

The NMR used in this study was a Bruker AVIII 500 MHz NMR instrument equipped with nitrogen cooled broadband cryoprobe. It was operated in proton-decoupled mode with 3000-7000 scans per analysis.

2.2. Chloride removal set-up

In the standard IC set-up, the sample is transferred from the autosampler to a loop that is attached to a Valco-style (hereafter Valve 1). Initially, Valve 1 remains in load position until sample transfer is complete. Then it switches to inject position, and KOH that comes from the eluent generator pushes the sample from the sample loop to the guard and separator column (Fig. 1a). For on-line chloride removal, the IC was modified with the installation of an additional valve (hereafter Valve 2, supplied by Sunquest Scientific). This was placed between the sample loop on Valve 1 and the guard column (Fig. 1c, d). The software (Chromeleon) was modified such that Valve 2 remained in load position for an additional 2.5 minutes after Valve 1 had switched from 'load' to 'inject' (Fig. 1). During this time, a 1 mmol/L NaOH solution at a flow rate of 1 ml/min was used to push the sample from the loop on Valve 1 to the clean-up column installed on Valve 2. This additional NaOH solution was supplied by an external pump (Dionex GP50 Gradient Pump). Alternatively, an N_2-pressurized reservoir may be used. The clean-up column on Valve 2 was a AG11-HC 4x50mm column, which separates anions contained in the solution similar to the guard and analytical columns. Chloride eluted first and was allowed to pass into the waste (Fig. 1c, d). Valve 2 was switched from 'load' to 'inject' after chloride had passed but prior to the elution of other anions from the clean-up column. The timing was calibrated manually at the start of the installation. After 2.5 minutes, Valve 2 switched automatically to 'inject', and the KOH eluent pushed the sample out of the clean-up column onto the guard column.

When the instrument was not in chloride-removal mode, Valve 2 was set to stand-by (Fig. 1b). The clean-up column was flushed with NaOH and kept moist with DI-water supplied from the external gradient pump. This solution was sent to waste and did therefore not interfere with analyses carried out in standard mode.

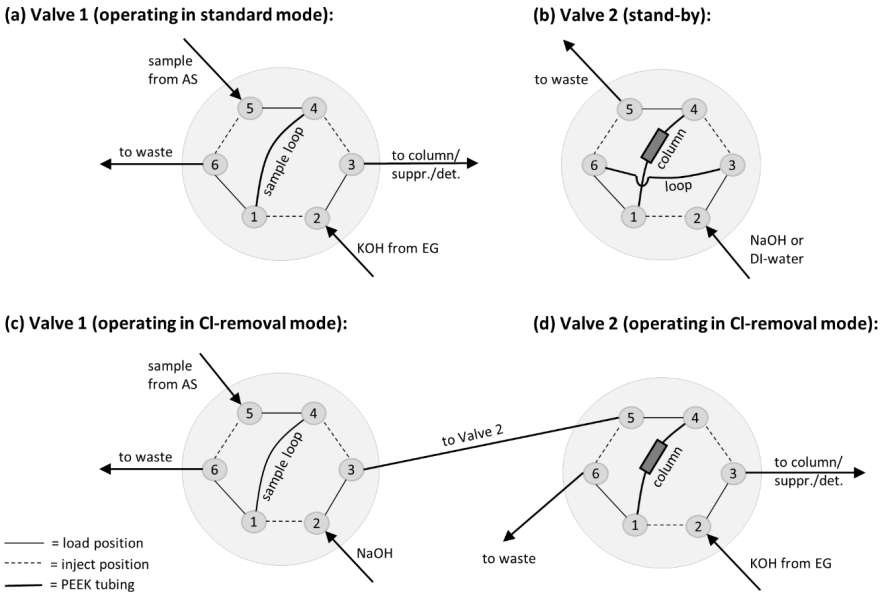


Figure 1: Schematic of the change-over valves in the ion chromatograph. *Valve 1 is the part of the standard setup; Valve 2 and the associated small clean-up column were added for chloride removal. (a) Valve 1 during normal operation without the chloride removal step. The tube going to the column, suppressor, and conductivity detector can optionally also extend further to transfer the sample into the ICP-MS. (b) Valve 2 in stand-by mode when chloride removal is not needed. Here the small column is constantly flushed with water to keep it hydrated. (c) Valve 1 in chloride removal mode. NaOH is introduced by an additional pump. (d) Valve 2 in chloride removal mode, receiving solution from Valve 1, when Valve 1 is in the 'inject' position. Valve 2 is in the 'load' position while receiving sample from Valve 1 and switches to 'inject' after 2.5 minutes.*

2.3. Coupling of IC to ICP-MS

The IC was connected to the ICP-MS with black PEEK tubing. This was spun between the outlet of the conductivity detector on the IC and the inlet of the nebulizer on the ICP-MS. When the instruments were connected in this way, the suppressor on the IC was regenerated with an external water supply at a flow rate of ca. 0.5-1 ml/min, delivered from an N_2-pressurized container. (When the IC is not connected to the ICP-MS, the suppressor is regenerated with the waste solution from the detector). The ICP-MS method for this analysis was set up with 750 runs and 1 pass, equivalent to 3 minutes per analysis. In the sequence file, the chromatographic output mode was selected for each sample. While it is possible to run the ICP-MS in automatic mode where a new analysis is externally triggered via a relay cable between the IC and the ICP-MS, we decided against this option, because it would imply that the slit plate used for medium resolution in the ICP-MS would be corroded quickly over the course of several analyses that last up to 55 minutes each. Instead, we manually started the analysis on the ICP-MS ca. 1 minute before the expected arrival of the phosphite peak at the conductivity detector on the IC. The peak itself lasted for ca. 40 seconds. The ICP-MS method was allowed to run for 3 minutes, providing sufficient data before and after the phosphite peak to determine analytical background levels.

The final data were accessed via the Show program under Chromatogram > From Info File > Display Chromatogram, followed by Display > Data View and File > Export (select ASCII format). This dataset could be opened in Excel or Origin (Origin Lab) for further processing. Here, we used Origin for smoothing the data (using the fast furrier transform filter with a points of window value of 15), subtract background levels, and calculate the area under the peak as a metric for signal intensity. We also calculated the peak height, but the calibration curve was found to be less scattered when peak area was used instead. The method was tested with a series of standards containing 0.003 to 1.614 µmol/L phosphite (corresponding to 0.1 to 50 ppb P).

2.4. Nuclear Magnetic Resonance

For the NMR, solutions were mixed with 10-20% D_2O to make a total volume of 0.6 ml. The solutions were analyzed in proton-decoupled mode with 3000-7000 scan. Typical run time for a 7000 scan was around 4 hours. The ^{31}P chemical shifts are referenced to phosphoric acid having a chemical shift of 0δ. Standards of known concentration (0.026 µmol/L (8 ppb) to 1614 µmol/L (50 ppm) P were analysed to find the detection limit and building calibration curves. After acquiring the data, phase correction, background correction, peak identification, and area integral calculation were executed in MestReNova software. Area integrals of the peaks were used for building the calibration curve.

3. RESULTS AND DISCUSSION

3.1. Removal of chloride in ion chromatograph

The chromatograms of the IC in chloride-removal mode (Fig. 1c, d) revealed complete removal of chloride while phosphite and other ions contained in the solution were retained (Fig. 2b). The comparison to the normal mode (Fig. 2a) shows that also nitrite was removed by this method as it elutes close to chloride. However, nitrate, phosphite, sulfate and phosphate were retained. Chloride removal was incomplete when the delay on Valve 2 (i.e., the time before Valve 2 switches form 'load' to 'inject' mode) was less than 2 minutes.

It may be possible to also cut off anions that elute later than phosphite (such as sulfate or phosphate) by switching Valve 2 back to 'load' as soon as phosphite has been pushed from the clean-up column to the guard column. This was not explored in this study.

The chromatograms with the Cl-removal method display a larger carbonate peak than those generated in normal mode (Fig. 2) despite the use of carbonate-free NaOH. We suspect that some carbonate was already dissolved in the samples and standards, derived from atmospheric CO_2. Additional CO_2 may have dissolved in the NaOH solution during preparation. Care was taken to minimize ingrowth of atmospheric CO_2 (Section 2.1), but we could not guarantee complete avoidance. The retention time of carbonate is only slightly longer than that of phosphite, and therefore the carbonate peak may reduce confidence in the detection and quantification of phosphite with the conductivity detector on the IC. However, this problem is resolved by IC-ICPMS coupling, as the ICP-MS measures phosphite by mass and is therefore not impacted by the presence of carbonate ions.

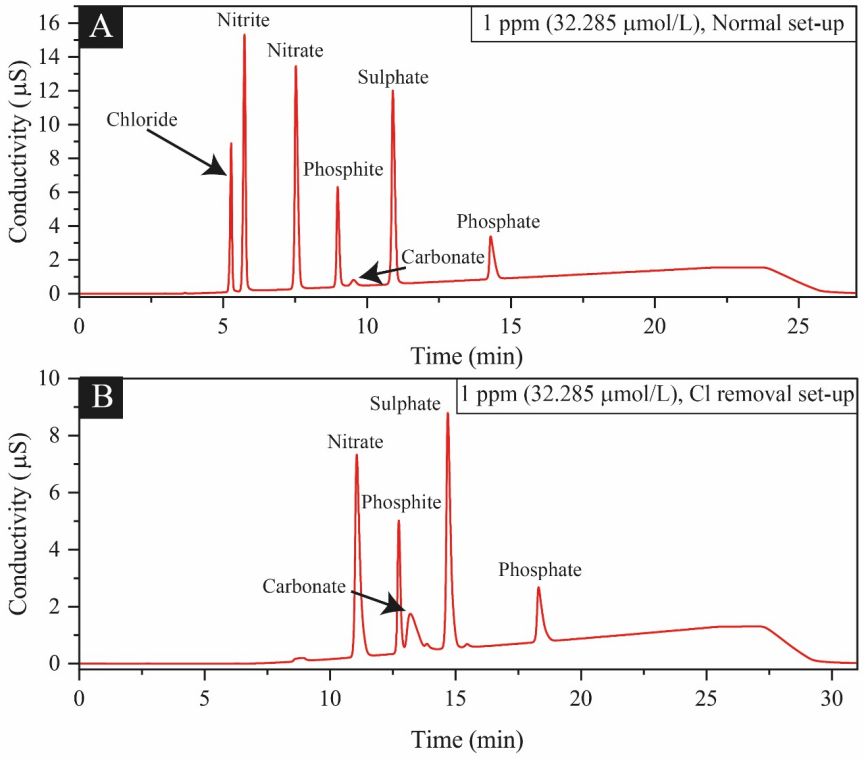


Figure 2: IC traces with and without chloride removal set-up. *A. Peaks of a 1 ppm solution (all species are at the same concentration) in normal set-up. B. Peaks of the same solution in Cl-removal set-up. The latter does not contain chloride or nitrite but displays a slightly larger carbonate peak. The shift in retention time for all ions in panel B compared to panel A is expected, because the Cl-removal setup increases the path length for the solution as it travels from the autosampler to the detector. Both panels show an increase in the baseline over the course of the run which is due to the ramp-up of the KOH concentration.*

3.2. Calibration and detection limits of IC and IC-ICPMS

We generated calibration curves with the IC in standard mode (without chloride removal), and with the coupled IC-ICPMS setup with chloride removal, using both the conductivity detector in the IC and the SEM detector in the ICP-MS. In all cases, the data show good linearity over the concentration ranges that were tested, with correlation coefficients (r^2) better than 0.999 (Fig. 3, 4). As shown in Fig. 3, the performance of

the conductivity detector in the IC is not negatively impacted by the presence of the Cl-removal setup. Good linearity was obtained with and without chloride removal, as illustrated here with phosphite and nitrate. This observation demonstrates that the Cl-removal may also be useful for analyses of ions such as nitrate that cannot be analysed by ICP-MS. Furthermore, it gives confidence that the clean-up column does not introduce random error performs as expected.

Regarding detection limits, the coupling of the IC to the ICP-MS resulted in significant improvement, as expected. In standard mode without chloride removal (Fig. 3a), we were able to confidently quantify phosphite peaks down to ca. 0.32 µmol/L (10 ppb P) using the conductivity detector alone. With the IC-ICPMS setup and the SEM detector in the ICP-MS, a resolvable peak was obtained for as little as 0.003 µmol/L (0.1 ppb P, Fig. 4a). Slightly lower concentrations may still be detectable. Our results are thus similar to the detection limit of 0.002 µmol/L reported by Ivey & Foster (2005)[4], despite a significantly smaller sample loop (37 µL instead of 800 µL). Reproducibility in our IC-ICPMS setup was 13% at 0.032 µmol/L.

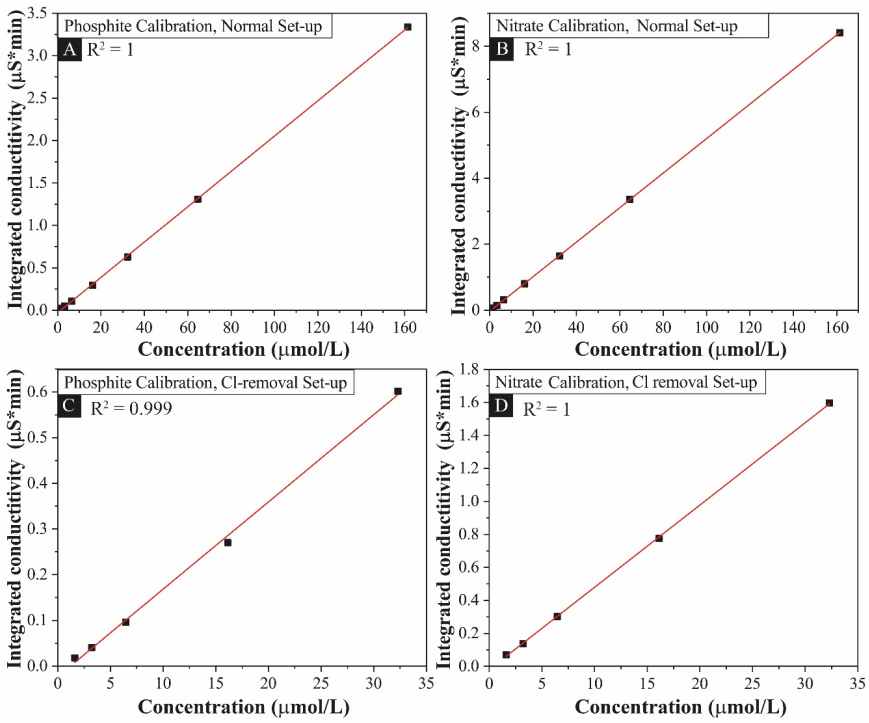
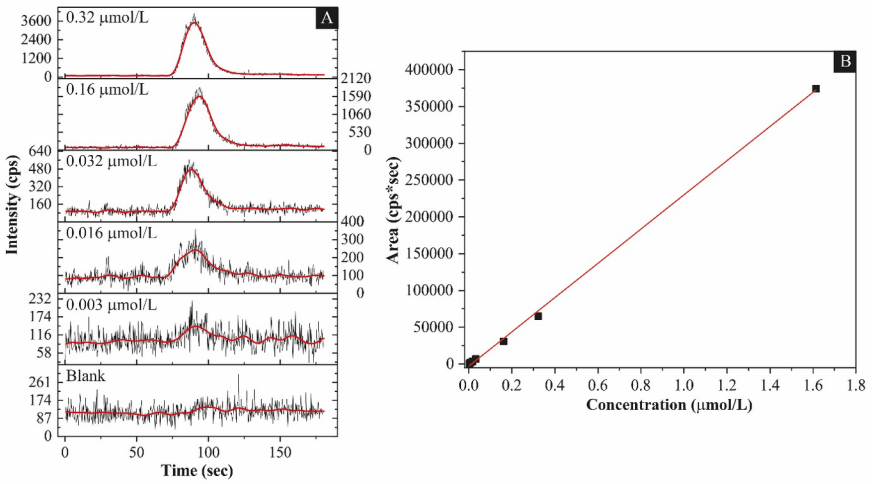


Figure 3: Calibration curves for phosphite and nitrate in normal and Cl-removal set-ups with the IC conductivity detector. *A and B: Calibration for phosphite and nitrate in normal set-up. C and D: Calibration for phosphite and nitrate in Cl-removal set-up. Correlation coefficients (r^2) values are > 0.999 for all cases suggesting no disruption of other peaks by Cl removal.*



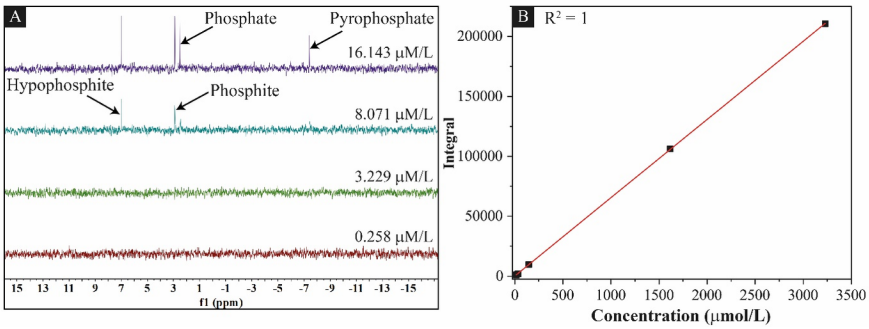
Φιγυρε 4: Ι*-*ΙΠΜΣ τραςες ανδ ςαλιβρατιον ςυρε φορ πηοσπηιτε*. A: ήροματογραμ οφ α βλανκ ανδ οφ πηοσπηιτε-βεαρινγ σολυτιονς ωιτη ςονςεντρατιονς φρομ 0.1 το 10 ππβ (0.003 το 0.32 µµολ/Λ). Ρεδ λινες αρε σμοοτηενεδ ςυρες οβταινεδ βψ ΦΦΤ φιλτερινγ ωιτη α ποιντς οφ ωινδοω αλυε οφ 15. Τηε 0.003 µµολ/Λ (0.1 ππβ) σολυτιον ηας α δετεςταβλε πηοσπηιτε πεακ ας ςομπαρεδ το τηε βλανκ. Β: Πηοσπηιτε ςαλιβρατιον ςυρε ωιτη τηε πεακ ιντεγραλ δατα.*

3.3. Comparison of IC-ICPMS to alternative methods

Previous workers also used NMR to quantify phosphite concentrations in solutions[1]. Our own measurements reveal a detection limit around 6.46 µmol/L (200 ppb), which is substantially higher than what is achievable by IC or IC-ICPMS. To first order, this method therefore appears less suitable for phosphite-lean samples than IC, IC-ICPMS and even UV-VIS spectrophotometry (Table 1). However, we note that in NMR, the detection limit depends on the strength of the magnetic field (i.e., resonance frequency), the nature of the probe, and the number of scans (which in turn determine the length of the run per sample). In our case, the strength of the magnetic field was 500 MHz. The detection limit could be comparatively lower ($<$ 200 ppb) in an instrument with a stronger magnetic field (e.g., 700 mHz) and higher ($>$ 200 ppb), if the magnetic field is weaker (e.g., 400 mHz). The NMR used in this study is equipped with a liquid-nitrogen-cooled broadband cryoprobe. If an uncooled probe were used, it is estimated that the detection limit could be roughly 2.5 times higher (nearly 500 ppb) if all other parameters remain the same. Finally, we performed 7000 scans for phosphite analysis, which equated to 4 hours of run time per sample, but it is possible to detect even lower concentrations if the samples are analyzed with a higher number of scans and accordingly longer runs.

A major advantage of NMR is its ability to detect a much wider range of phosphorus species, including various polyphosphates[17]. These are relatively large molecules that would likely be difficult to elute from the separator column of an IC. And to our knowledge, no UV-VIS method has so far been developed to measure polyphosphates other than pyrophosphate in solution. Hence NMR, despite its limitations in the detection limit, analytical time and installation costs (Table 1), is perhaps the best method for measuring polyphosphate species. It is also unaffected by the presence of chloride or other interferences.

UV-VIS spectrophotometry is probably the most cost-effective method for phosphite[16] as well as phosphate[18] measurements, and it too can be conducted in the presence of high chloride concentrations[16]. However, other interferences may persist, and its detection limit is significantly higher than with the IC and ICP-MS, making it unsuitable for many environmental samples.



Φιγυρε 5: Σελεστεδ ^{31}Π NMP παττερνς ανδ ςαλιβρατιον ςυρε φορ πηοσπηιτε ωιτη NMP δατα. *A: NMP παττερνς φορ 4 διφφερεντ στανδαρδς (8, 100, 250, ανδ 500 ππβ) ςονταινινγ 4 διφφερεντ σπεςιες (ηψποπηοσπηιτε, πηοσπηιτε, πηοσπηατε, πψροπηοσπηατε). 8 ανδ 100 ππβ στανδαρδς (0.258 ανδ 3.229 µM/Λ) αρε νοτ δετεςτεδ ιν τηε πρεσεντ αναλψτιςαλ ςονδιτιονς. B: ἄλιβρατιον ςυρε φορ πηοσπηιτε ωιτη πεακ ιντεγραλ δατα ωιτη α P^2 αλυε νεαρλψ 1.*

Table 1: Method comparison. *The detection limit is given in nanogram phosphorus per gram of solution.*

Method	Δετεςτιον λιμιτ [µµολ/Λ]	Advantages	Disadvantages	References
IC	0.002-0.32 (Dependent on size of the sample loop and column type; detection limit may be impacted by the presence of carbonate eluting close to phosphite)	Relatively cost-effective; separation from most interferences	Low detection limit requires large sample volume, possibly causing saturation by other ions; possibly interferences by ions with similar retention times; can analyse multiple P species but not all	This study; [6]
IC + ICP-MS	0.002-0.003 (Dependent on the size of the sample loop)	Low detection limits achievable with small sample sizes; separation of interferents with similar retention times in the IC	High installation costs; can analyse multiple P species but not all	This study; [4, 6]
UV-VIS spectrophotometry	0.36	Most cost effective; separation from many interferences; fast	High detection limit; some interferences may persist; can analyse multiple P species but not all	[16]

Method	Δετεχτιον λιμιτ [μμολ/Λ]	Advantages	Disadvantages	References
NMR	6.46 (Dependent on length of run or number of scans, strength of the magnet, type of probe)	Can analyse greatest variety of P species; separation from interferences	High installation costs; slow analysis; high detection limit	This study

4. CONCLUSION

Our results show that on-line removal of chloride with the clean-up column and split valve (Valve 2 in Fig. 1d) in the ion chromatograph is a viable method for simplifying the matrix of natural and experimental solutions for phosphite analysis. For an element such as phosphite, this tool can be combined with coupling of the IC to an ICP-MS to achieve detection limits below 0.003 μmol/L (< 0.1 ppb P), in line with previous studies[4, 6] but without the need for a large sample loop or pre-analytical sample treatment with OnGuard cartridges.

Without the ICP-MS, the removal of chloride also simplifies analyses with the conductivity detector of the IC alone, except for ions that elute close to chloride (as those may be difficult to separate from chloride) or those close to carbonate. The latter may be elevated by the introduction of external NaOH. The carbonate problem may be mitigated if a degasser is installed in-line with the NaOH supply, but we did not explore that in this study. However, even without carbonate-removal from the NaOH solution, we would expect that ions such as nitrate, sulfate or phosphate, which typically have much shorter or much longer retention times than carbonate with the AS17-C analytical column, would be easier to quantify at low concentrations after on-line removal of chloride with the setup described in this study. Our results show good linearity in the conductivity detector both with and without the Cl-removal setup. In addition, it may be possible to further modify the timing in the software such that additional ions can be cut out from the sample. Our study therefore presents a new approach for optimizing ion chromatography and taking full advantage of the low detection limits of ICP-MS.

We conclude that IC-ICPMS coupling with on-line chloride removal provides perhaps the best way forward for phosphite analyses at low concentrations, because detection limits are significantly better compared to NMR and UV-VIS spectrophotometry. NMR holds the major advantage that it can detect a more diverse range of phosphorus species, including large polyphosphate ions, while UV-VIS spectrophotometry is the most cost-effective method for phosphite analysis, but neither of the two methods is able to achieve similar detection limits. The IC-ICPMS approach may therefore be ideally suited for unlocking phosphorus redox chemistry in the environment.

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REFERENCES

[1] Pasek MA, Sampson JM, Atlas Z. Redox chemistry in the phosphorus biogeochemical cycle. *Proceedings of the National Academy of Sciences* . 2014;111:15468-15473.

[2] McDowell MM, Ivey MM, Lee ME, Firpo VVVD, Salmassi TM, Khachikian CS, Foster KL. Detection of hypophosphite, phosphite, adn orthophosphate in natural geothermal water by ion chromatography. *Journal of Chromatography A* . 2004;1039:105-111.

[3] Han C, Geng J, Ren H, Gao S, Xie X, Wang X. Phosphite in sedimentary interstitial water of Lake Taihu, a large eutrophic shallow lake in China. *Environmental Science & Technology* . 2013;47:5679-5685.

[4] Ivey MM, Foster KL. Detection of phosphorus oxyanions in synthetic geothermal water using ion chromatography–mass spectrometry techniques. *Journal of Chromatography A* . 2005;1098:95-103.

[5] Pech H, Henry A, Khachikian CS, Salmassi TM, Hanrahan G, Foster KL. Detection of geothermal phosphite using high-performance liquid chromatography. *Environmental Science & Technology* . 2009;43:7671-7675.

[6] Han C, Geng J, Xie X, Wang X, Ren H, Gao S. Determination of phosphite in a eutrophic freshwater lake by suppressed conductivity ion chromatography. *Environmental Science & Technology* . 2012;46:10667-10674.

[7] Pasek MA, Harnmeijer JP, Buick R, Gull M, Atlas Z. Evidence for reactive reduced phosphorus species in the early Archean ocean.*Proceedings of the National Academy of Sciences* . 2013;110:10089-10094.

[8] Herschy B, Chang SJ, Blake R, Lepland A, Abbott-Lyon H, Sampson J, Atlas Z, Kee TP, Pasek MA. Archean phosphorus liberation induced by iron redox geochemistry. *Nature Communications* . 2018;9:doi:10.1038/s41467-41018-03835-41463.

[9] Schink B, Friedrich M. Phosphite oxidation by sulphate reduction. *Nature* . 2000;406:37.

[10] Liu W, Zhang Y, Yu M, Xu J, Du H, Zhang R, Wu D, Xie X. Role of phosphite in the environmental phosphorus cycle. *Science of The Total Environment* . 2023;881:doi: 10.1016/j.scitotenv.2023.163463.

[11] Pasek MA, Omran A, Feng T, Gull M, Lang C, Abbatiello J, Garong L, Johnston R, Ryan J, Abbott-Lyon H. Serpentinization as a route to liberating phosphorus on habitable worlds. *Geochimica et Cosmochimica Acta* . 2022;336:332-340.

[12] Pasek M, Block K. Lightning-induced reduction of phosphorus oxidation state. *Nature Geoscience* . 2009;2:553-556.

[13] Hess BL, Piazolo S, Harvey J. Lightning strikes as a major facilitator of prebiotic phosphorus reduction on early Earth.*Nature Communications* . 2021;12:doi: 10.1038/s41467-41021-21849-41462.

[14] Glindemann D, De Graaf RM, Schwartz AW. Chemical reduction of phosphate on the primitive Earth. *Origins of Life and Evolution of the Biosphere* . 1999;29:555-561.

[15] Pasek MA, Lauretta DS. Aqueous corrosion of phosphide minerals from iron meteorites: a highly reactive source of prebiotic phosphorus on the surface of the early Earth. *Astrobiology* . 2005;5:515-535.

[16] Barco RA, Patil DG, Xu W, Ke L, Khachikian CS, Hanrahan G, Salmassi TM. The development of iodide-based methods for batch and on-line determinations of phosphite in aqueous samples. *Talanta* . 2006;69:1292-1299.

[17] Pasek MA, Kee TP, Bryant DE, Pavlov AA, Lunine JI. Production of potentially prebiotic condensed phosphates by phosphorus redox chemistry. *Angewandte Chemie* . 2008;120:8036-8038.

[18] Nagul EA, McKelvie ID, Worsfold P, Kolev SD. The molybdenum blue reaction for the determination of orthophosphate revisited: Opening the black box. *Analytica Chimica Acta* . 2015;890:60-82.