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RESEARCH ARTICLE

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On-line chloride removal from ion chromatography for trace-level analyses of phosphite and other anions by coupled ion chromatography–inductively coupled plasma mass spectrometry

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Rationale: Ion chromatography (IC) combined with inductively coupled plasma mass spectrometry (ICPMS) 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 a sample within an 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 phosphorus 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 chloride-removal method may also be applicable to analyses of other anions.

1 | INTRODUCTION

Ion chromatography (IC) 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 microorganisms 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 and 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 an IC instrument with an inductively coupled plasma mass spectrometry (ICPMS) system, Ivey and Foster[4] were able to achieve detection limits around 0.002 µmol/L for phosphite. Chloride does not interfere isobarically with ^{31}P in the mass spectrometer, but the removal of chloride improves ionic separation in the ion chromatograph[6] and helps protect the mass spectrometer, as large concentrations of matrix elements may lead to the formation of deposits on the plasma cones. However, the authors also noted that OnGuard cartridges can impact the phosphate and phosphite content of samples, introducing additional uncertainty into the analytical yield. Furthermore, OnGuard cartridges add extra costs and labour to the sample preparation protocol. Alternatively, phosphite can be analysed by UV–visible spectrophotometry[16]; however, this may suffer from spectral 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).

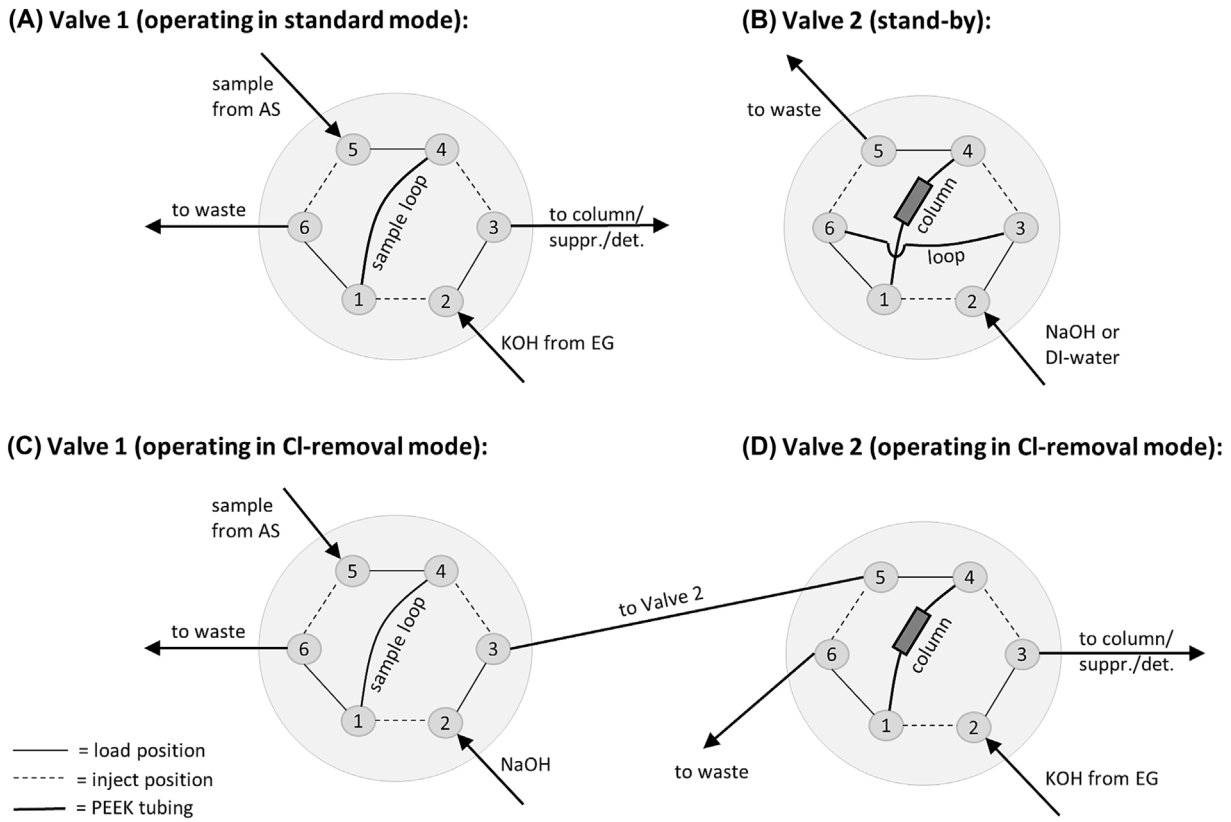

FIGURE 1 Schematic of the change-over valves in the ion chromatograph. Valve 1 is part of the standard setup; valve 2 and the associated small clean-up column were added for chloride removal. (A) Valve 1 during normal operation without the chloride removal step. The tube going to the column, suppressor and conductivity detector can optionally also extend further to transfer the sample into the ICPMS. (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 min.

Here we present a new approach for removing chloride from the sample matrix on-line within an ion chromatograph by splitting the sample stream after passage of the chloride fraction through an additional clean-up column, prior to reaching the separation column and the mass spectrometer. While the use of IC as such is not novel, our work includes a new modification of the system that has to our knowledge not previously been done and which eliminates the need of pre-analytical OnGuard cartridges. By coupling this method with an Element 2 ICPMS 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, Figure 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 (Stag). 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; $Na_2HPO_3{\cdot}5H_2O$, 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 deionized 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 2 mm 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 to 40 mmol/L over the course of each run. Analyses with pyrophosphate were set to last for 55 min, and here the KOH was ramped up between 5.5 and 23 min. After 45 min of total run time, the KOH concentration was decreased back to 1 mmol/L over a duration of 5 min. Analyses of solutions without pyrophosphate were set to last for 27 min; the KOH was ramped up between 5.5 and 23 min and ramped back down between 23 and 26 m. Containers used for samples and standards were soaked in hot 2 M HCl overnight and rinsed several times with deionized water prior to use.

The ICPMS instrument 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 each run, the ICPMS system was tuned with a multi-element solution at a concentration of 1 ng/g in 5% HNO_3 (Thermo Scientific p/n 1099601). The instrument was operated in medium-resolution mode (measured resolution was *ca* 4200 $\Delta m/m$) to avoid HNO interferences with phosphorus at m/z 31. The Element 2 offers this medium-resolution capability, which means that an additional entrance slit is inserted into the ion transfer optics between the torch and the magnet that narrows the ion beam, leading to a higher mass resolving power, though at the expense of lower signal counts. Also a high-resolution mode is available (where $\Delta m/m$ is *ca* 10 000), but this mode is not required for ^{31}P. We stress that the chloride removal method implemented in this study does not overcome the need of the medium-resolution mode, because chloride does not form any species that interfere isobarically with ^{31}P. However, as noted above and by previous authors,[4,6] the simplification of the sample matrix optimizes ionic separation in the ion chromatograph and it protects the mass spectrometer from accumulating deposits on the plasma cones over time. Oxide formation in the plasma was determined from the ratio of uranium oxide to uranium (UO/O) during tuning and was found to be consistently in the range of *ca* 3–5%.

The NMR system 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 setup

In the standard IC setup, the sample is transferred from the autosampler to a loop that is attached to a rheodyne valve (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 (Figure 1A). For on-line chloride removal, the IC was modified with the installation of an additional rheodyne valve (Sunquest Scientific p/n 061961; hereafter valve 2). This was placed between the sample loop on valve 1 and the guard

column (Figures 1C and 1D), following the design of Lloyd Billingham from Sunquest Scientific. The software (Chromeleon) was modified such that valve 2 remained in load position for an additional 2.5 min after valve 1 had switched from 'load' to 'inject' (Figure 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). The clean-up column on valve 2 was an AG11-HC 4 × 50 mm 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 (Figures 1C and 1D). 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 after the installation. After 2.5 min, 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 (Figure 1B). The clean-up column was flushed with NaOH and kept moist via the external gradient pump. This solution was sent to waste and did therefore not interfere with analyses carried out in standard mode.

2.3 | Coupling of IC to ICPMS

The IC instrument was physically connected to the ICPMS system with black PEEK tubing. This tubing was spun between the outlet of the conductivity detector on the IC and the inlet of the nebulizer on the ICPMS. 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 ICPMS, the suppressor is regenerated with the waste solution from the detector).

The plasma of the ICPMS was kept on throughout the day; however, data were only collected during a 3 min window around the arrival of the phosphite peak from each solution. This required that the analysis on the ICPMS was started manually after *ca* 12 min into the IC analysis of each solution. The ICPMS method for this analysis was set up with 750 runs and 1 pass, equivalent to 3 min per analysis. In the sequence file, the chromatographic output mode was selected for each sample. It is possible to run the ICPMS in automatic mode where data collection extends over the entire 55 min duration of the IC run and is externally triggered via a relay cable between the IC and the ICPMS as soon as the autosampler on the IC moves to the next solution. However, we decided against this option, because it would imply that the entrance slit plate used for medium resolution in the ICPMS would be corroded quickly over the course of several analyses. Instead, we manually started the data collection on the ICPMS *ca* 1 min before the expected arrival of the phosphite peak at the conductivity detector on the IC. The peak itself lasted for *ca* 40 s. The ICPMS method (i.e. data collection at the *m/z* of phosphorus) was allowed to run for 3 min, providing sufficient data before and after the phosphite peak to determine analytical background levels.

For further protection of the ICPMS from unwanted ions (in our case, everything other than phosphite), it is possible to break the physical connection between the IC and ICPMS outside of the 3 min window of data collection. Breaking the connection means that the outlet of the IC would be directed to the waste while the ICPMS takes up pure water or 2% HNO_3. Doing this may be advantages for samples with a high phosphate/phosphite ratio, where the arrival of the phosphate peak in the ICPMS may lead to elevated background levels at the *m/z* of ^{31}P.

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 Lab for further processing. Here, we used Origin Lab for smoothing the data (using the fast Fourier transform filter with a points of window value of 15), subtracting background levels and calculating 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 h. 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 ng/g) to 1,614 µmol/L (50 µg/g) 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 (Figures 1C and 1D) revealed complete removal of chloride while phosphite and other ions contained in the solution were retained (Figures 2B and 2D). A comparison with the normal mode (Figures 2A and 2C) 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 min. It may be possible to also cut off anions that

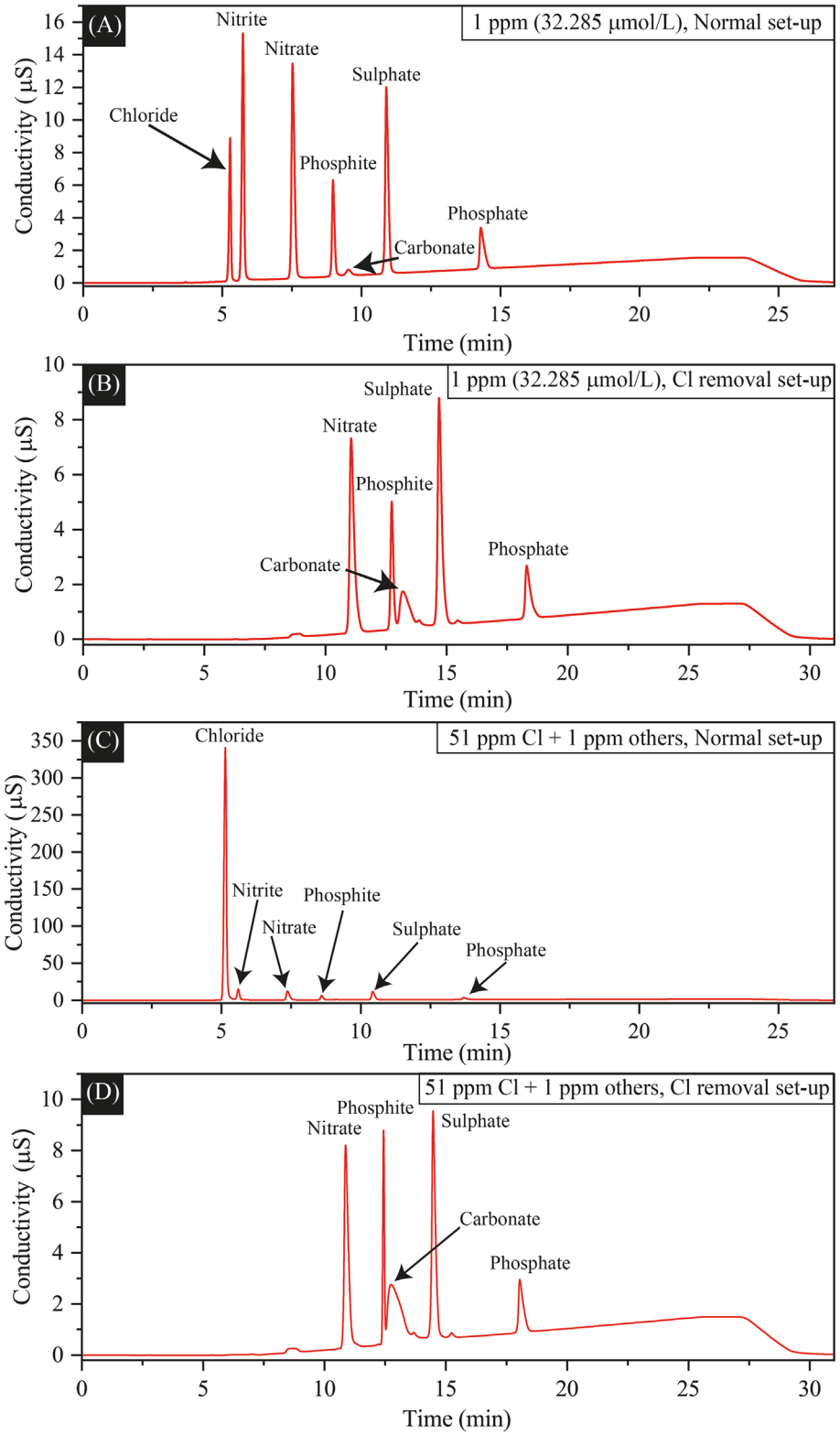

FIGURE 2 IC traces with and without chloride removal setup. (A) Peaks of a 1 µg/g solution (all species are at the same concentration) in normal setup. (B) Peaks of the same solution in chloride-removal setup. (C) Normal setup with a solution containing 51 µg/g chloride and 1 µg/g for all other ions. (D) The same solution as in (C) but analysed with the chloride-removal setup, demonstrating that chloride removal also operates at high chloride concentrations. The chromatograms in (B) and (D) do not contain chloride or nitrite but display a slightly larger carbonate peak compared with (A) and (C). The shift in retention time for all ions in (B) compared with (A) is expected, because the chloride-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. In (D), the phosphite peak sits on top of a larger carbonate peak compared to (B) due to aging of the NaOH solution and associated ingrowth of carbonate. Although the phosphite peak is still resolvable, this close association between phosphite and carbonate illustrates the utility of the IC/ICPMS coupling, where phosphite can be analysed as a peak on *m/z* 31, independently from carbonate. Raw chromatographic data are provided in Data S2. [Color figure can be viewed at wileyonlinelibrary.com]

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 chloride-removal method display a larger carbonate peak than those generated in normal mode (Figure 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 ICPMS measures phosphite by mass and is therefore not impacted by the presence of carbonate ions. As noted above, isobaric interferences on ^{31}P were avoided in the mass spectrometer by use of the medium-resolution mode.

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 of the IC and the SEM detector of the ICPMS. In all cases, the data show good linearity over the concentration ranges that were tested, with correlation coefficients (r^2) better than 0.999 (Figures 3 and 4). As shown in Figure 3, the performance of the conductivity detector in the IC is not negatively impacted by the presence of the chloride-removal setup. Good linearity was obtained with and without chloride removal, as illustrated here with phosphite and nitrate. This observation demonstrates that the chloride removal may also be useful for analyses of ions such as nitrate that cannot be analysed by ICPMS. Furthermore, it gives confidence that the clean-up column does not introduce random error.

Regarding detection limits, the coupling of the IC to the ICPMS resulted in significant improvement, as expected. In standard mode without chloride removal (Figure 3A), we were able to confidently quantify phosphite peaks down to *ca* 0.32 µmol/L (10 ng/g P) using the conductivity detector alone. With the IC/ICPMS setup and the

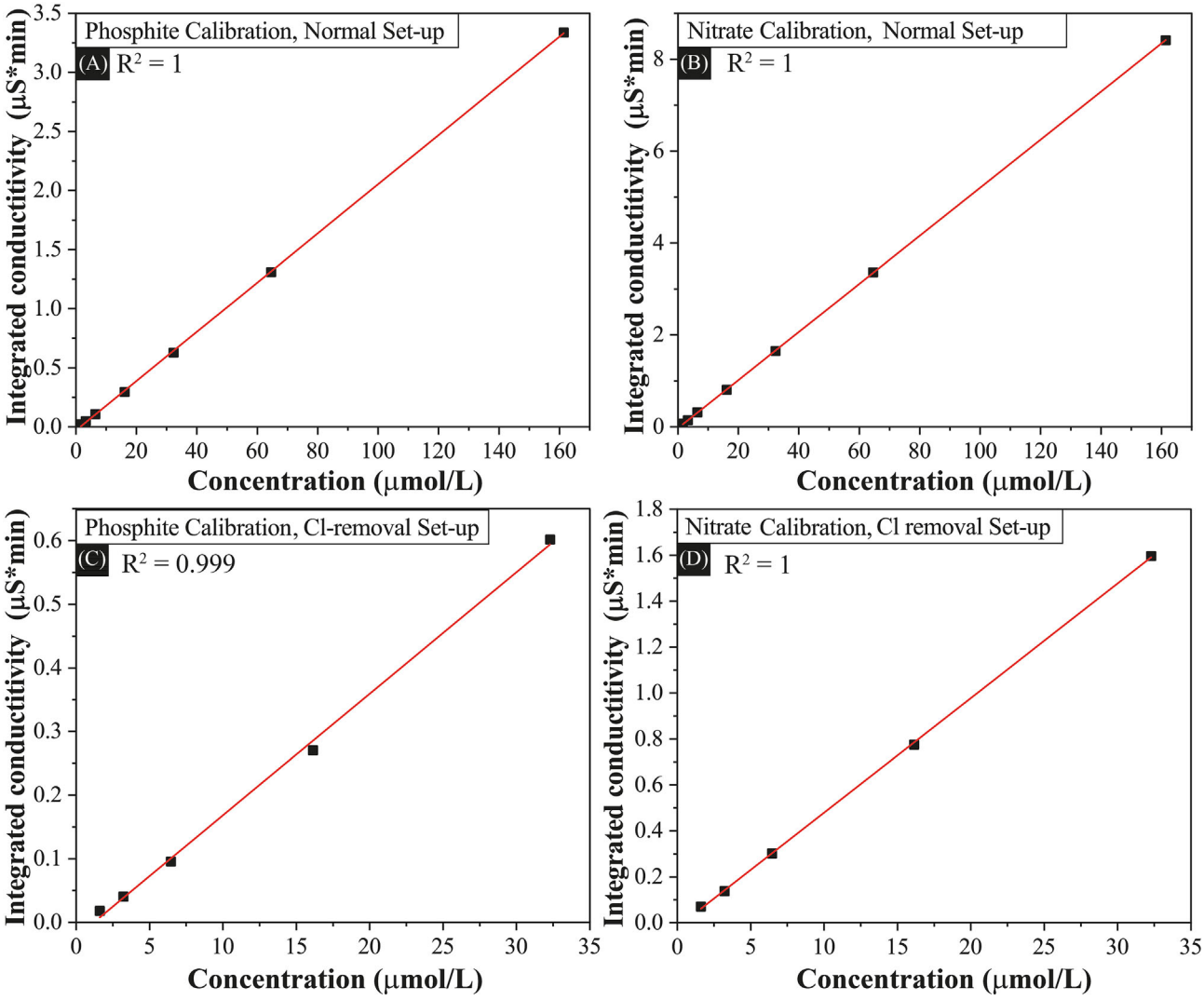

FIGURE 3 Calibration curves for phosphite and nitrate in normal and chloride-removal setups with the IC conductivity detector. (A, B) Calibration for phosphite and nitrate in normal setup. (C, D) Calibration for phosphite and nitrate in chloride-removal setup. Correlation coefficient (r^2) values are >0.999 for all cases suggesting no disruption of other peaks by chloride removal. Tabulated data are provided in Data S1. [Color figure can be viewed at wileyonlinelibrary.com]

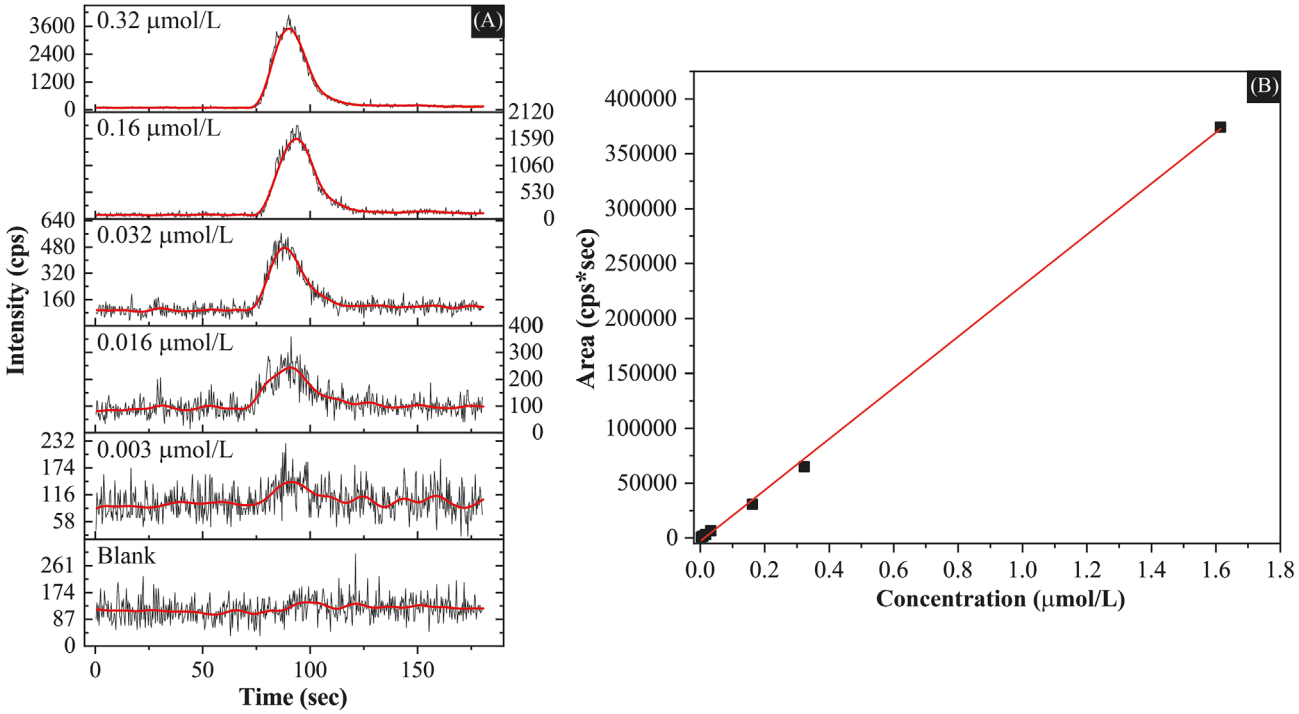

FIGURE 4 IC/ICPMS traces and calibration curve for phosphite. (A) Chromatogram of a blank and of phosphite-bearing solutions with concentrations from 0.1 to 10 ng/g (0.003 to 0.32 µmol/L). Red lines are smoothened curves obtained by fast Fourier transform filtering with a points of window value of 15. The 0.003 µmol/L (0.1 ppb) solution has a detectable phosphite peak as compared to the blank. (B) Phosphite calibration curve with the peak integral data. Tabulated data are provided in Data S1. [Color figure can be viewed at wileyonlinelibrary.com]

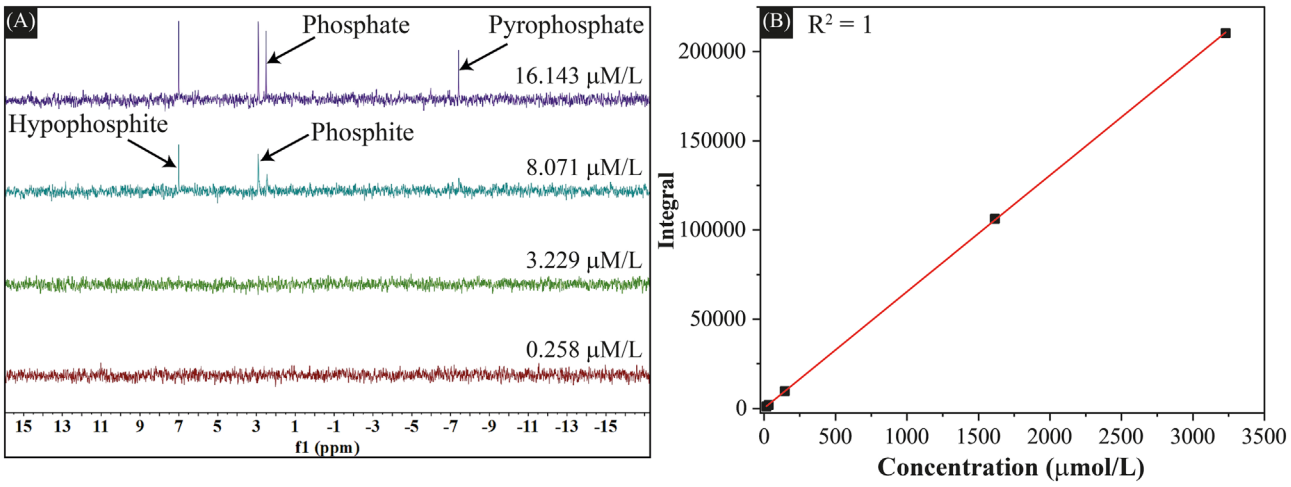

FIGURE 5 Selected ^{31}P NMR patterns and calibration curve for phosphite with NMR data. (A) NMR patterns for four different standards (8, 100, 250 and 500 ng/g) containing four different species (hypophosphite, phosphite, phosphate, pyrophosphate). Around 8 and 100 ng/g standards (0.258 and 3.229 µmol/L) are not detected in the present analytical conditions. (B) Calibration curve for phosphite with peak integral data with an r^2 value nearly 1. Tabulated data are provided in Data S1. [Color figure can be viewed at wileyonlinelibrary.com]

SEM detector in the ICPMS, a resolvable peak was obtained for as little as 0.003 µmol/L (0.1 ng/g P; Figure 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 and Foster,[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.

3.3 | Comparison of IC-ICPMS to alternative methods

Previous workers also used NMR to quantify phosphite concentrations in solutions.[1] Our own measurements (Figure 5) reveal a detection limit of around 6.46 µmol/L (200 ppb), which is

TABLE 1 Method comparison; the detection limit is given in nanograms of phosphorus per gram of solution.

Method	Detection limit (µmol/L)	Advantages	Disadvantages	Ref.
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 analyze multiple P species but not all	This study; 6
IC + ICPMS	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–visible spectrophotometry	*ca* 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
NMR	*ca* 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

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–visible 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 instrument 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 h of run time per sample, but it is possible to detect even lower concentrations if the samples are analysed 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–visible method has so far been developed to measure polyphosphates other than pyrophosphate in solution. Hence NMR, despite its limitations in terms of 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–visible 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 spectral interferences may persist, and its detection limit is significantly higher than that of IC and ICPMS, making it unsuitable for many environmental samples.

4 | CONCLUSION

Our results show that on-line removal of chloride with the clean-up column and split valve (valve 2 in Figure 1D) in an ion chromatograph is a viable method for simplifying the matrix of natural and experimental solutions for phosphite analysis. For a species such as phosphite, this tool can be combined with coupling of the IC to an ICPMS system 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 ICPMS, 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 chloride-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 IC and taking full advantage of the low detection limits of ICPMS.

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–visible spectrophotometry. NMR holds the major advantage that it can detect a more diverse range of phosphorus species, including large polyphosphate ions, while UV–visible 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.

AUTHOR CONTRIBUTIONS

Eva E. Stüeken conceived the project, acquired funding, provided analytical facilities, helped interpret the data and wrote the manuscript. Abu S. Baidya performed all analyses, led the data interpretation, created figures and contributed to the writing of the manuscript.

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PEER REVIEW

The peer review history for this article is available at https://www.webofscience.com/api/gateway/wos/peer-review/10.1002/rcm.9665.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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