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Rapid sample clean-up procedure for aminophosphonate determination by LC/MS analysis

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1. Introduction

Aminophosphonates are utilised as complexing agents of detergents, antiscaling agents in water treatment or as dispersing agents applied in paper and textile industry [1]. Despite of its broad application, the analysis of these substances is still challenging. Earlier methods developed for ion chromatography (IC) [2–5] and capillary electrophoresis (CE) were limited due to interferences by major cations and anions in the water [6,7]. Other separation methods such as high performance liquid chromatography (HPLC) [8] and liquid chromatography (LC) coupled with mass spectrometry (MS) coupled by particle-beam interface (PB) (LC/PB-MS) [9] were recently introduced as very promising analytical methods for determination of phosphonates in natural and surface water samples. However, in both studies the authors pointed out that their methods were strongly affected by the interfering sample matrix mainly through inorganic salts decreasing the sensitivity, especially if applied to environmental samples.

Matrix effects caused through inorganic salts can negatively affect LC-ESI-MS analysis. Those obstacles can start rising with simple surface water or TW samples containing anions and cation in higher concentrations compared to purified water for analysis. According to Schmidt et al. [10] anions such as sulphate and chloride from water samples can be discharged during the chromatographic run by including a switching step between the pre-column and the main

chromatographic column. The removal of cation seems to be a greater challenge since phosphonates form metal complexes. Therefore, Schmidt et al. [10] recommended additional sample purification with cation exchange resin (CER).

More recently, Wang et al. [11] introduced a method for LC-MS/MS analysis of common aminophosphonates from environmental samples. This method includes sample purification with CER and enrichment on SPE according to Schmidt et al. [10] prior to methylation. The authors demonstrated the sensitivity of the method for common aminophosphonates. However, the sample clean-up with CER is poorly suitable to purify amino(methylenephosphonic acid) (AMPA). This metabolite is strongly absorbed at the CER. If intermediates such as AMPA and iminodi(methylenephosphonic acid) (IDMP) should be analysed together with the parent compounds further optimisation of the clean-up process is required to run all compounds in a single LC/MS analysis.

In this work, we optimised the application of the strong acidic ion exchange resin Dowex 50WX8 as a rapid and simple sample clean-up procedure for the phosphonates hydroxyethylidene(diphosphonic acid) (HEDP), aminotris(methylenephosphonic acid) (ATMP), ethylenediaminetetra(methylenephosphonic acid) (EDTMP) and diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) and their major intermediates AMPA and IDMP. We compared four different sample clean-up conditions in ultra-pure water (UPW) and in TW for all six phosphonates. TW was used in this study as a model for natural water

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Abbreviations

AMPA	amino(methylenephosphonic acid)
ATMP	aminotris(methylenephosphonic acid)
AES	atomic emission spectroscopy
CER	cation exchange resin
DTPMP	diethylenetriaminopenta(methylenephosphonic acid)
EDTMP	ethylenediaminetetra(methylenephosphonic acid)

ESI	electrospray ionization
HDTMP	hexamethylenediaminetetra(methylenephosphonic acid)
HEDP	hydroxyethylidene(diphosphonic acid)
IDMP	iminodi(methylenephosphonic acid)
PB	particle-beam interface
PSD	process standard deviation
TW	tap water
UPW	ultra-pure water

with common cation concentrations. For better comparison, references without sample clean-up were prepared for both UPW and TW. Finally we applied the sample clean-up procedure to a sample from industrial laundry service.

2. Material and methods

2.1. Chemicals and reagents

The standard phosphonates HEDP, ATMP, EDTMP and DTPMP were provided by "Zschimmer & Schwarz Mohsdorf" (Burgstädt, Germany). The standards AMPA and IDMP and the internal standard glyphosate were purchased from Sigma Aldrich (Steinheim, Germany). All standards were of analytical grade or better with purity > 99%. The chemical structures are presented elsewhere (Fig. 1 in Ref. [12]).

Ultra-pure water (LC/MS grade) was in-house generated (Adrona Sia Crystal EX, Lithuania). The cation exchange resin Dowex 50WX8 with 100–200 mesh (hydrogen form) was purchased from Acros Organics (Geel, Belgium) and had a stated exchange wet volume capacity of 1.7 meq mL⁻¹. Acetonitril of LC/MS grade was purchased from VWR (Darmstadt, Germany), CH₃COONH₄ of analytical grade was purchased from VWR (Leuven, Belgium) and CsCl of optical grade was supplied from Acros Organics (New Jersey, USA). The ICP standard solution IV (23 elements in 2% nitric acid – 1000 mg L⁻¹) was purchased from Roth (Karlsruhe, Germany).

2.2. Sample clean-up procedure with Dowex 50WX8

A detailed description of the preparation of the standard solutions and the performance of the clean-up procedure is presented at [12]. All CER columns were packed manually with Dowex 50WX8. The bond

elution reservoir (Agilent Technologies, USA) was set on a vacuum filtration unit (VacMaster sample processing station; Biotage, Sweden), fitted with a frit (1/2 inch; Agilent Technologies, USA) at the bottom and filled up with 2.5 mL well homogenised wet Dowex 50WX8 (H form) material corresponding to a packed column height of 1.5 cm (1.75 g wet resin). The CER bed was covered with a frit. The packed CER bed was then rinsed with 20 mL UPW prior to the sample clean-up procedure. Subsequently, 4 mL of the standard sample solution was added on the CER column bed and filtered. The initial eluent of 2 mL was discarded and the final eluent of 2 mL was collected and further analysed with LC/MS and/or AES. All filtration steps were carried out at a flow rate of 1 mL min⁻¹.

2.3. LC/MS analyses

Phosphonates were analysed by liquid chromatography-electrospray ionization-mass spectrometry (LC-ESI-MS) using a Finnigan MAT LC/MS (LC spectral system P4000, LCQ MS Detector, autosampler AS 3000, Metal PEEK-coated column LUNA HILIC 100 × 2.0 mm, 3.0 μm/200 Å, Aschaffenburg, Germany). Prior to the analyses, all liquid samples were mixed with 50% acetonitrile (VWR, Darmstadt, Germany). The gradient elution was performed with solvent A (100% ultra-pure water) and solvent B (10% ultra-pure water/90% acetonitrile) at 35 °C at a flow rate of 0.2 mL min⁻¹. Both solvents A and B contained 2.5 mM CH₃COONH₄. The analysis was run for 43 min by first holding 100% of solvent B for 2 min. The gradient was then concavely increased to 10% A for 1 min and was held for 2 min. The gradient was further concavely increased to 30% A for 1 min and held again for 2 min. Subsequently, the gradient was again concavely increased to 50% A for 2 min and held for 10 min. Afterwards, the gradient was concavely increased to 60% A for 5 min and held for another 5 min, before the gradient was concavely

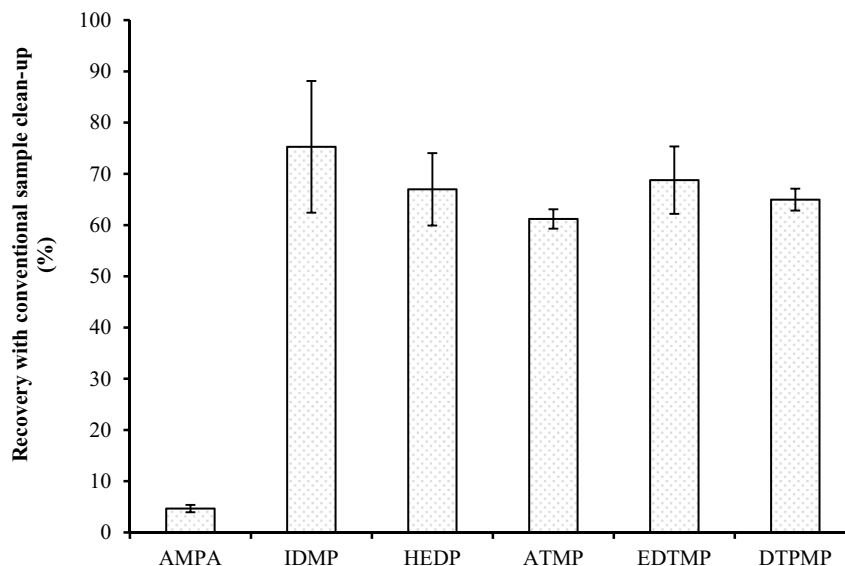


Fig. 1. Determined recovery values of standard phosphonates in TW after sample clean-up procedure with Dowex 50WX8 compared to standard phosphonates in UPW.

increased back to 100% B for 3 min and held for 10 min. The MS detector settings were as follows: The negative polarity ionization was 3.5 kV and the spray capillary temperature was 220 °C. Selected ion monitoring (SIM) was chosen for quantification. The following mass-to-charge (m/z) ratios were used for identification: DTPMP 572, EDTMP 435, ATMP 298, HEDP 205, IDMP 204, and AMPA 110.

2.4. Atomic emission spectroscopy (AES)

The concentrations of Ca^{2+} and Mg^{2+} of treated samples were determined using 4100 MP-AES system from Agilent (Mulgrave, Australia). Prior to routine measurement, the AES was always calibrated using ICP standard solution IV. For routine measurement, 0.5 mL of the sample was first diluted with 9.5 mL ultra-pure water and then mixed with 0.4 mL CsCl solution (50 g L^{-1}). The emission of Ca^{2+} was measured at 393.366 nm and 422.673 nm. The emission of Mg^{2+} was measured at 280.271 nm and 285.213 nm. The limit of detection was $1 \mu\text{g L}^{-1}$.

2.5. Total phosphorus analysis

For the determination of total phosphorous, chemical digestion was carried out by adding 200 mg of "Oxisolv" (Merck, Darmstadt, Germany) into 5 mL sample volume. The samples were treated using the microwave digestion unit MARS 5 (CEM, Kamp-Lintfort, Germany). The samples were linearly heated to 170 °C within 3 min and were held for another 3 min. Subsequent cooling down of the samples to room temperature, total phosphorus was measured as o-PO_4^{3-} with a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan) according to the European standard procedure EN ISO 6878:2004.

3. Results and discussion

3.1. Application of the sample clean-up procedure with Dowex 50WX8

The sample clean-up procedure with Dowex 50WX8 enhanced the sample quality, especially for the TW samples, which were not measurable without clean-up (Fig. 4 in Ref. [12]). The main effect of clean-up procedure was to remove disturbing cations from the TW while the phosphonates were completely eluted from the CER column. In particular, Ca^{2+} and Mg^{2+} are known to disturb the LC/MS analysis [9]. According to Schmidt et al. [10] the CER transfers the metal phosphonate complexes into the free acids and therefore similar results as

for standard phosphonates in UPW are obtained.

For more detailed quantitative analysis, we determined the phosphonate concentration in TW compared to UPW before and after clean-up. Five different concentrations of every standard were measured (5 mg L^{-1} , 10 mg L^{-1} , 25 mg L^{-1} , 50 mg L^{-1} and 100 mg L^{-1}). Without clean-up most samples were not detectable in the LC/MS. After the clean-up, the recoveries of most samples increased to more than 60% for IDMP, HEDP, ATMP, EDTMP and DTPMP (Fig. 1). Only the smallest phosphonate AMPA resulted in very low recovery with less than 5%. Stefan and Meghea [13] stated that the selectivity of the ion exchange resin is influenced by the structural characteristics of the absorbance such as the electrical load, the crystallographic radius of the ions, van der Waals or covalent radius, electronegativity and the functional groups of the resin. AMPA has a relatively low electronegative charge compared with the other phosphonates and is the only tested phosphonate with a free amino group capable to protonate. In consequence, AMPA exchanges easily with hydrogen ions and is almost completely retained on the resin.

AMPA is a very important metabolite of environmental samples of different sources such as glyphosate or can be released as breakdown product though sunlight irradiation of aminophosphonates [14]. Therefore, AMPA ought to be not neglected. With regard to the sample clean-up, we focussed further on improving also the successful elution of purified AMPA in order to perform a single LC/MS analysis for all phosphonates and preventing additional derivatisation steps.

3.2. Optimisation of the sample clean-up procedure with Dowex 50WX8

The sample clean-up procedure was further optimised to improve the elution of AMPA. In the first optimisation step, we investigated the incubation time more in detail. The detailed method description is presented elsewhere (Fig. 3 in Ref. [12]).

Comparing the two incubation times of 0 min and 1 min, we did not find a significant difference on the recovery values. In both cases, the recovery was almost identical with up to 38.2% (Fig. 2). However, the incubation time of 0 min resulted in most cases in higher imprecision ($37.0 \pm 10.9\%$) indicated by a higher relative standard deviation compared with the incubation time of 1 min ($38.2 \pm 4.8\%$). With increasing incubation time up to 5 and 10 min, the AMPA recovery decreased to $19.9 \pm 4.4\%$ and $14.4 \pm 3.8\%$, respectively. We conclude that increasing the incubation time unfortunately increases further the ion exchange of AMPA on the resin due to diffusion processes. No cations were determined for all four tested incubation times performing

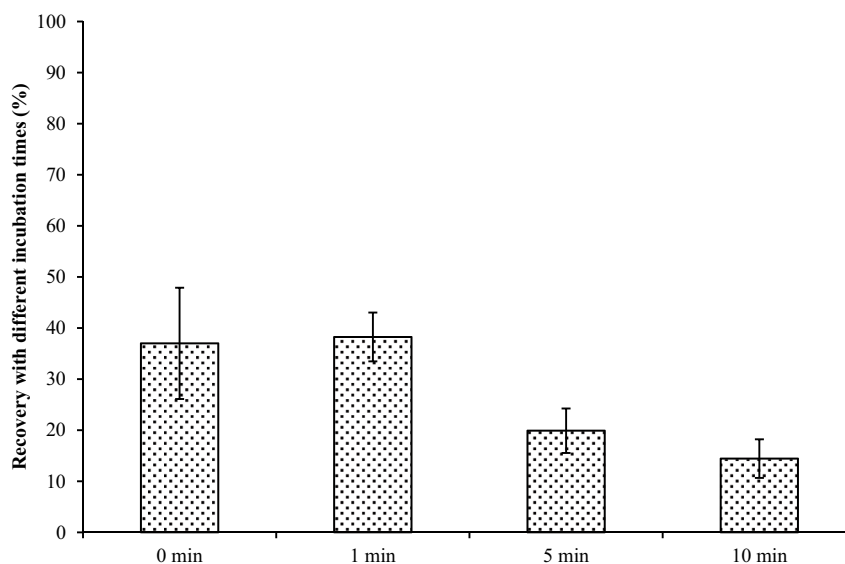


Fig. 2. Application of different incubations times of 10 mg L^{-1} AMPA solubilised in tap water on Dowex. The analyses were carried out by LC/MS measurements.

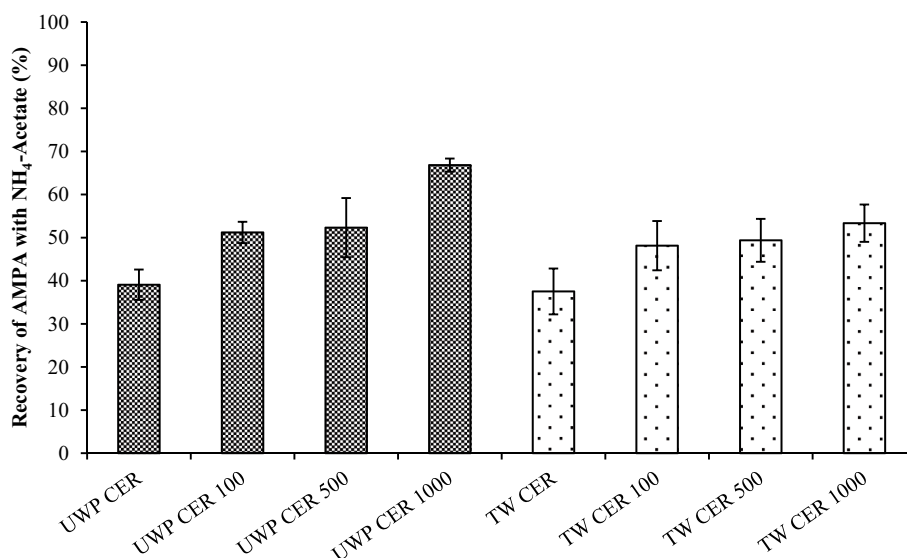


Fig. 3. Influence of different NH₄-Acetate concentrations on the CER treatment of AMPA (10 mg L⁻¹). All standards were adjusted at pH 7.0.

Table 1

Determined recoveries (%) of phosphonates with different ammonium acetate concentrations during sample clean-up.

Treatment	AMPA	IDMP	HEDP	ATMP	EDTMP	DTPMP	
UPW	without CER	100	100	100	100	100	
	with CER	37.2 ± 1.59	49.0 ± 3.34	97.6 ± 2.33	96.7 ± 4.51	97.5 ± 2.26	53.1 ± 1.68
	CER 100	54.5 ± 2.28	54.8 ± 2.40	63.5 ± 2.70	> 100	53.6 ± 1.76	39.9 ± 2.10
	CER 1000	62.6 ± 2.55	58.4 ± 1.70	48.7 ± 2.42	> 100	50.2 ± 3.81	82.9 ± 3.42
TW	without CER	34.0 ± 1.18	-	-	-	-	-
	with CER	49.7 ± 1.27	63.6 ± 1.95	72.0 ± 2.91	52.5 ± 3.14	76.1 ± 3.36	72.6 ± 2.53
	CER 100	48.5 ± 2.03	61.5 ± 2.59	52.1 ± 2.17	58.8 ± 2.78	> 100	67.6 ± 3.50
	CER 1000	53.1 ± 1.59	57.1 ± 2.31	31.4 ± 3.13	59.7 ± 3.09	98.6 ± 3.86	55.9 ± 2.41

CER – cation exchange resin.

CER 100 – sample contain 100 mg L⁻¹ ammonium acetate.

CER 1000 – sample contain 1000 mg L⁻¹ ammonium acetate.

n = 3 (number of experiments).

Table 2

Application of the optimised sample clean-up procedure to industrial laundry sewage.

	AMPA	IDMP	HEDP	ATMP	EDTMP	DTPMP
Sample 1 (mg L ⁻¹)	18.20	11.11	14.98	36.29	56.13	39.14
Sample 2 (mg L ⁻¹)	24.70	8.69	15.79	37.38	52.44	34.33
Sample 3 (mg L ⁻¹)	20.01	8.33	12.91	38.15	59.00	36.81
Mean (mg L ⁻¹)	20.97	9.38	14.56	37.27	55.86	36.76
SD	3.35	1.51	1.49	0.94	3.29	2.41
RSD (%)	15.97	16.0	10.23	2.52	5.88	6.55
Sample 1 (mg P L ⁻¹)	5.08	3.36	4.50	11.28	15.95	10.58
Sample 2 (mg P L ⁻¹)	6.89	2.63	4.75	11.61	14.90	9.28
Sample 3 (mg P L ⁻¹)	5.58	2.52	3.88	11.85	16.76	9.95
Mean (mg P L ⁻¹)	5.85	2.83	4.38	11.58	15.87	9.93
SD	0.94	0.46	0.45	0.29	0.93	0.65
RSD (%)	16.06	16.25	10.27	2.50	5.86	6.54

n = 3 (number of experiments).

AES analyses. We, further, assume that the increased recoveries for the two incubation times of 0 min and 1 min were a result of multiple exchange processes on the CER column. The presence of cation ion such as Ca²⁺, Mg²⁺ and Na⁺ caused certainly gradients depending on the electric load of the ions, the ion radius and the pH. Consequently, Mg²⁺ should be the first ion exchanged on the CER followed by Ca²⁺, Na⁺ and at last AMPA. The latter is further protonated due to the decreasing pH caused through the increasing hydrogen ion concentration in the liquid phase on the CER column. Thus, extending the incubation time

up to 5 min or even 10 min can easily lead to further AMPA protonation which is then exchanged on the resin. Therefore, we decided to continue our second optimisation step with an incubation time of 1 min since the measurement resulted in higher precision.

The second optimisation step aimed at minimising the exchange of protonated AMPA on the resin by adding different ammonium acetate (CH₃COONH₄) concentration (i.e. 100 mg L⁻¹, 500 mg L⁻¹ or 1000 mg L⁻¹) as competing exchange ion in both UPW and TW standards. Ammonium acetate in acidic methanol was recently recommended to increase the recoveries of sample clean-up of chlormequat applying SPE-C₁₈ cartridge for LC/MS [15].

We found highest AMPA recovery with 66.8 ± 1.5% in UPW with addition of 1000 mg L⁻¹ CH₃COONH₄ (Fig. 3). The two concentrations 100 mg L⁻¹ and 500 mg L⁻¹ resulted in comparable recoveries and averaged 51.2 ± 2.5% and 52.3 ± 6.9%, respectively. The reference sample without CH₃COONH₄ addition resulted in the lowest recovery with 39.1 ± 3.5%. We found a similar trend for the AMPA standards dissolved in TW. The AMPA reference sample without CH₃COONH₄ addition resulted in 37.5 ± 5.3% recovery. With 100 mg L⁻¹ CH₃COONH₄ addition the AMPA recovery increased to 48.1 ± 5.7%. Further CH₃COONH₄ addition resulted in only minor increase, i.e. 49.4 ± 5.0% and 53.4 ± 4.3% recovery for 500 mg L⁻¹ and 1000 mg L⁻¹ of CH₃COONH₄ addition respectively.

In general, we found that the addition of CH₃COONH₄ resulted in higher recoveries for both water qualities. However, the recoveries for the AMPA standards in UPW were always higher compared with the TW standard samples. We assume this is due to the different ion gradients

and pH gradients occurring during the clean-up process. As mentioned above, the CER exchanges Ca^{2+} , Mg^{2+} and Na^+ and also ammonium (NH_4^+). The AMPA standards in UPW provide only the cation NH_4^+ as counter ion. We assume this results in a weaker pH gradient and therefore AMPA is less protonated. As a result, the recovery of AMPA in UPW is always higher compared to TW, due to the presence of Ca^{2+} , Mg^{2+} and Na^+ . These cations and the addition of $\text{CH}_3\text{COONH}_4$ produce a stronger ion gradient and thereby also a pH gradient promoting the protonation of AMPA. For that reason, the recovery is lower compared with the AMPA standards in UPW. We, further, speculate that an additional increased $\text{CH}_3\text{COONH}_4$ concentration was not further enhancing the AMPA recovery in TW.

In fact, we believe that our optimisation of the sample clean-up might be a very valuable contribution to the newly developed method of Wang et al. [11] who also apply a strong cation exchange resin to purify phosphonate samples prior to derivatisation. Wang et al. did not demonstrate the sensitivity with regard to AMPA. Combining our optimised sample clean-up with this LC-MS/MS method could lead to a single LC/MS analysis for the phosphonate parent compounds and their major intermediates.

We applied our optimised clean-up procedure also to the phosphonates IDMP, HEDP, ATMP, EDTMP and DTPMP in order to match the best condition for a single LC/MS analysis. Eight different test conditions, including addition of $\text{CH}_3\text{COONH}_4$ in UPW and TW, were tested with standard mixture solutions. We validated the different sample clean-up procedures based on the slope of the calibration curves and determined the recovery (Table 1). The individuals calibration results for the six aminophosphonates AMPA, IDMP, HEDP, ATMP, EDTMP and DTPMP are presented elsewhere (Tables 1 and 2 in Ref. [12]).

3.3. Applicability to industrial wastewater

In order to prove the applicability of our optimised sample clean-up procedure, we analysed a wastewater sample from industrial laundry service located in Berlin (Germany). Higher concentrations as commonly found in natural water samples were expected for different aminophosphonates from this specific sewage sample (Table 2). The LC/MS analysis was performed in triplicates of the sewage sample. We determined the highest phosphonate concentration for EDTMP, which averaged $55.86 \pm 3.29 \text{ mg L}^{-1}$ (corresponding to $15.87 \pm 0.93 \text{ mgP L}^{-1}$). Both ATMP and DTPMP were determined with almost similar concentrations having $37.27 \pm 0.94 \text{ mg L}^{-1}$ and $36.76 \pm 2.41 \text{ mg L}^{-1}$ (corresponding to $11.58 \pm 0.29 \text{ mgP L}^{-1}$ and $9.93 \pm 0.65 \text{ mgP L}^{-1}$) respectively. HEDP was also determined and averaged $14.56 \pm 1.49 \text{ mg L}^{-1}$ (corresponding to $4.83 \pm 0.45 \text{ mgP L}^{-1}$). The intermediates AMPA and IDMP were determined with average concentrations of $20.97 \pm 3.35 \text{ mg L}^{-1}$ and $9.38 \pm 1.51 \text{ mg L}^{-1}$, corresponding to $5.85 \pm 0.9 \text{ mgP L}^{-1}$ and $2.83 \pm 0.46 \text{ mgP L}^{-1}$, respectively. On the bases of our LC/MS analyses, we calculated the sum of total phosphorus of $50.44 \pm 0.34 \text{ mgP L}^{-1}$ corresponding to the phosphorus concentration related on the determined phosphonates. We also analysed the fraction of soluble unreactive phosphorus of the wastewater sample and determined an average concentration of $52.6 \pm 0.54 \text{ mgP L}^{-1}$.

The phosphorus concentration either determined by TP or LC/MS analyses were very close and confirmed each other. However, the TP analysis did not allow detailed conclusion or any differentiation about different phosphorus containing aminophosphonates. The results of the LC/MS analyses demonstrated very precise identification and quantification by applying our optimised sample clean-up procedure prior to the LC/MS measurements. Thus, the developed sample clean-up procedure is applicable as sample pre-treatment where the detection limits of aminophosphonates are in the range of milligram per litre and delivers excellent results.

3.4. Conclusion

We have investigated the application of the strong cation exchange resin Dowex 50WX8 for the sample clean-up of four the phosphonates HEDP, ATMP, EDTMP, DTPMP and their two major intermediates AMPA and IDMP. Commonly, cation exchange resins such as Dowex are used to enrich and selectively separate cations. We, however, applied Dowex 50WX8 successfully to remove the cations from phosphonate samples cation concentration similar to natural waters. The optimised sample clean-up procedure allows a single LC/MS analysis of common aminophosphonates and their intermediates. We recommend the addition of $1000 \text{ mg L}^{-1} \text{ CH}_3\text{COONH}_4$ to the sample prior to the clean-up enhancing the elution of AMPA from the CER. The application to an industrial wastewater sample was successfully demonstrated. This clean-up method is simple, rapid, precise and delivers an adequate sensitivity. However, coupling our clean-up procedure with online SPE or combining with other more sensitive LC/MS methods as recently published will further enhance a single LC/MS analysis of phosphonate parent compounds and their intermediates at trace-level concentrations.

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Declaration of competing interest

The authors declare no conflict of interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2019.120454>.

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