

Capillary electrophoresis for continuous nitrogen quantification in wastewater treatment processes

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A water quality analyzer based on the working principle of capillary electrophoresis (CE) was developed to determine ionic inorganic nitrogen compounds contained in wastewater samples. The instrument provides simultaneous quantification of anions and cations by superimposing hydrodynamic pumping with electrokinetic motion. It features a single separation capillary with contactless conductivity detection and a sequential injection manifold for fluid handling. Dynamic adaption of the system calibration was enabled by the use of a high precision pressure regulator to cover a wide measurement range showing low relative standard deviations (< 2 %) and high measurement accuracy comparable to conventional wastewater analyzers. The prototype is transportable, integrated in a 19 inch rack and connected to a membrane filter system developed for direct sample aspiration in the wastewater process. For operation on site, only a power supply and a network connection for remote control is necessary. Continuous operation was demonstrated over 24 hours at the aeration tank of a pilot scale wastewater treatment plant at TU Wien and a good correlation with laboratory results was achieved. At this time, there is no device available, on the market, to analyze all nitrogen parameters in one assembly with limited hardware complexity and chemical demand. This entails a significant step forward towards automated water quality monitoring with respect to the implementation of new advanced wastewater treatment technologies.

1. Introduction

In wastewater treatment there is an increasing demand for robust monitoring applications to control new processes, such as mainstream anaerobic ammonium oxidation (Anammox) [1] or treatment of sludge-dewatering effluent (SDE) [2], in order to reduce the energy demand and the emission of greenhouse gases during the treatment process [3]. In particular, partial nitrification in combination with anammox (deammonification) is currently gaining attention of science and industry [4]. The autotrophic process can perform the required nitrogen removal without organic carbon [5] and the partial reduction of ammonium to nitrite reduces the energy demand for aeration compared to the conventional nitrification/denitrification process [6]. Especially nitrite is a crucial parameter for the anammox process. It is an essential nutrient but inhibiting the reaction at concentrations higher than 60 mg/L [7]. Work is currently underway to develop control strategies in order to operate these processes stably in full-scale treatment plants [8]. This requires the simultaneous observation of nutrient parameters in order to investigate and understand the interaction of different processes during wastewater treatment [9]. In order to analyze these parameters during the treatment process some measurement principles are well established, but each with certain limitations.

Nitrate and nitrite absorb light in the UV-range and their direct monitoring by photometry is possible. NH_4^+ , PO_4^{3-} , SO_4^{2-} as well as also NO_3^- and NO_2^- , may be determined by photometric methods following the formation of colored species by addition of selective reagents. NH_4^+ , NO_3^- , Cl^- , Br^- and K^+ , can be

measured potentiometrically with ion-selective electrodes. However, none of these measurement principles is capable of covering all of the parameters. Furthermore, each of these methods has limitations. The direct spectrometric determination of nitrate and nitrite is highly matrix sensitive and requires a case specific calibration model which needs to be developed based on parallel laboratory analyses. For the reagent based methods, a specific set of chemicals is required to induce a specific color reaction for each parameter. Consequently, multiple dosing pumps, valves, etc. need to be installed leading to complex instruments. The use of ion-selective electrodes under field conditions is restricted by a high limit of quantification (LOQ), cross sensitivities and low mechanical ruggedness. Available monitoring instruments therefore only provide a limited number of parameters.

Capillary electrophoresis is a potential alternative which can provide a range of relevant water quality parameters with just a single assembly. Limits of quantification down to the low $\mu\text{mol/L}$ range are another potential benefit of this method [10]. Commercial CE instruments are mainly equipped with an UV detector. This is only partly suitable for the measurement of inorganic ions because most do not absorb in the UV wavelength range [11]. Conductivity detection on the other hand in principle allows the determination of all ionic species and the capacitively coupled contactless conductivity detector (C⁴D) [12] is a convenient practical approach to this measurement. Fundamental aspects and applications of C⁴D can be found in reviews [13–15]. C⁴D can easily be implemented in field portable CE instruments and such devices have, for example, been reported by Kubáň et al. [10], Kappes et al. [16]

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and Hutchinson et al. [17]. A challenge in CE is the sample injection. Very small sample volumes in the nanoliter to picoliter range must be injected in a reproducible way, demanding an automated system with precise timing of all tasks, to make the instrument suitable for routine use in on-site analysis. When cations and anions are to be determined in the same sample, special measures are required as usually either only cations or anions can be determined in a single run.

Mai et al. [18] reported a CE-based process analyzer employing a sequential injection analysis (SIA) manifold for liquid handling, which was demonstrated for the unattended monitoring of the major inorganic ions in surface water for several days. Both, cations and anions, were determined by carrying out alternate runs applying opposite voltages. A slightly different system, which employed two capillaries for the simultaneous parallel determination of cations and anions, was reported by Pham et al. [19] and demonstrated for the monitoring of ammonia, nitrite and nitrate during denitrification of sewage in an activated sludge reactor.

For the process monitor reported herein a different approach to the concurrent determination of cations and anions was adopted which only requires a single capillary and allows the determination of both groups in a single run. At the trials at the wastewater treatment pilot plant at TU Wien, the focus was on the quantification of the most relevant nitrogen ions NO_2^- , NO_3^- , NH_4^+ in raw wastewater over extended unattended periods. Reference samples were analyzed in the laboratory to verify the results and to ensure high reliability and accuracy during autonomous operation.

2. Experimental setup

2.1 Chemicals and materials

All chemicals were of analytical or reagent grade and purchased from Sigma-Aldrich (St. Louis, Missouri, USA). The multi-ion standards used were prepared from KH_2PO_4 , NH_4Cl , NaNO_3 and NaNO_2 with different dilutions as shown in Table 1. The background electrolyte (BGE) used consisted of 100 mM L-histidine (HIS) / 100 mM 2-(N-Morpholino)ethanesulfonic acid (MES) / 0.13 mM Cetyltrimethylammonium bromide (CTAB) / 1.5 mM 18-crown-6 with a pH of 6 and was freshly prepared each day. Deionized water purified using a system from Seral (Ransbach, Germany) was used for the preparation of all solutions. The capillary was preconditioned with 1 M NaOH for 30 min and deionized water for 30 min prior to flushing with buffer. It was then used for consecutive analyses. Single wastewater samples were passed through 0.45 μm membrane filters and injected directly into the system for analysis. No further treatment was carried out. During continuous measurement, the wastewater was filtered through the 0.2 μm membrane filter, located in the aeration tank of the pilot scale wastewater treatment plant.

Table 1: Concentrations of standard solutions for system calibration

Solution ID	1	2	5	10	30	50
$\text{NH}_4\text{-N}$ [mg / L]	1	2	5	10	30	50
$\text{NO}_3\text{-N}$ [mg / L]	1	2	5	10	30	50
$\text{NO}_2\text{-N}$ [mg / L]	0.1	0.2	0.5	1	3	5
$\text{PO}_4\text{-P}$ [mg / L]	0.3	0.6	1.5	3	9	15
Cl^- [mg / L]	2.4	4.8	12	24	72	120

2.2 Instrumentation

For fluid manipulation, a syringe pump (Cavro XLP 6000, Tecan, Germany) with a 1 mL syringe and a six-port valve (Cavro Smart Valve, Tecan) was used. The interface consisted of two tee pieces (T116-203, LabSmith, USA) that held the separation capillary and the grounded platinum electrode. An automated three-port selector valve (AV201, LabSmith, USA) connected the interface to the syringe pump and the pressure section of the system. To generate the necessary pressure for sample injection and flushing of the capillary, an oil free compressor was used (1-480-9, Implotex, Germany) together with an air particle filter (AF20-02A, SMC, Japan). The generated pressure of 110 psi was reduced with a pressure regulator to 60 psi for flushing of the capillary (AR20-02B-R-A, SMC). Pressure for sample injection was obtained by a pressure reducer (AR20-02B-R-A, SMC) and an automated pressure controller (ITV1010-21N2BL4, SMC) that delivers an adjustable injection pressure between 0.7 psi and 14 psi. A 3/2-port solenoid valve (VT307-5DO1-01F-Q, SMC) enabled the selection between injection pressure and pressure for flushing the capillary. The detector and the accompanying data acquisition hardware was purchased from eDAQ (Australia) ($\text{C}^{4\text{D}}$ amplifier ER225, $\text{C}^{4\text{D}}$ headstage ET120).

For sample filtration of wastewater, a membrane module (pore size 0.2 μm) was used (PME-2036, ETL, Germany) together with a membrane pump (MAGDOS LA2, Lutz-Jesco, Germany). The sample for analysis was pumped into a self-made 1 mL sample vial, which was connected to port 2 of the 6-port valve and on top to the waste outlet. A dual polarity high-voltage power supply (CZE2000, Spellman Pulborough, UK) with ± 30 kV maximum output voltage and polyimide coated fused silica capillaries of 365 μm OD and 20 μm ID (TSP-020375, BGB, Rheinfelden, Germany) were used for all experiments. For the high voltage end of the capillary, we made a PMMA safety cage holding the glass vessel with 30 mL buffer solution. For control of the complete system, an industrial PC from Bernecker & Rainer (PC910, B&R Industrial Automation, Eggelsberg, Austria) together with an microcontroller board (Arduino Nano 3.0, RS Components, Austria) was incorporated into the device. Two 24 V power supplies from Phoenix Contact (2868664, Phoenix Contact, Blomberg, Germany) generated the power for all components. All connections were made with 1/16" OD and 0.02" ID PEEK tubing. The housing for the hardware was a commercial 19 inch rack (30109791, Conrad Electronic GmbH, Austria).

2.3 On site measurements

The CE system was implemented in a fully automated pilot scale wastewater treatment plant at TU Wien for continuous operation. The plant uses raw wastewater from the university sanitary system and has a total volume of 360 L. The sample aspiration was done in the aeration tank to monitor the biological processes during operation. To assure that the sample in the sample vial was representative of the filtration process, sample was drawn for 4 minutes, delivering 56 mL, before the sample was hydrodynamically injected from the sample vial into the capillary. The dead volume of the filtration system was 13.3 mL. With one filtration cycle, 56 mL were filtered and no dispersion effects occurred.

2.4 System design and operation

We implemented a modified sequential injection analysis system, without the usual holding coil, for continuous and simultaneous separation of inorganic anions and cations in wastewater samples. The schematic drawing of the instrument is shown in Figure 1. The device features one separation

position B-A and V2 on the pressure regulator B-A. The injection parameters for the given capillary inner diameter and capillary length were calculated with the Hagen-Poiseuille equation. The simultaneous separation of anions and cations is enabled by applying + 24 kV at the detector end of the capillary while pressurizing at 13 psi (250 seconds). After all anions have passed the detector, the high voltage is disabled and the pressure is increased to 60 psi, by switching valve V2 to position B-C, to flush the separated cations through the detector (120 seconds). The measurement cycle is completed after 12 minutes and the next cycle starts automatically.

Flushing, conditioning, hydrodynamic injection, data acquisition and sample filtration are controlled by the Instrumentino framework [20]. The syringe pump and the six-port valve are driven by serial communication provided by the Arduino microcontroller board. For online operation, only a 230 V AC power supply and a network connection for remote access, to enable user interaction, is necessary.

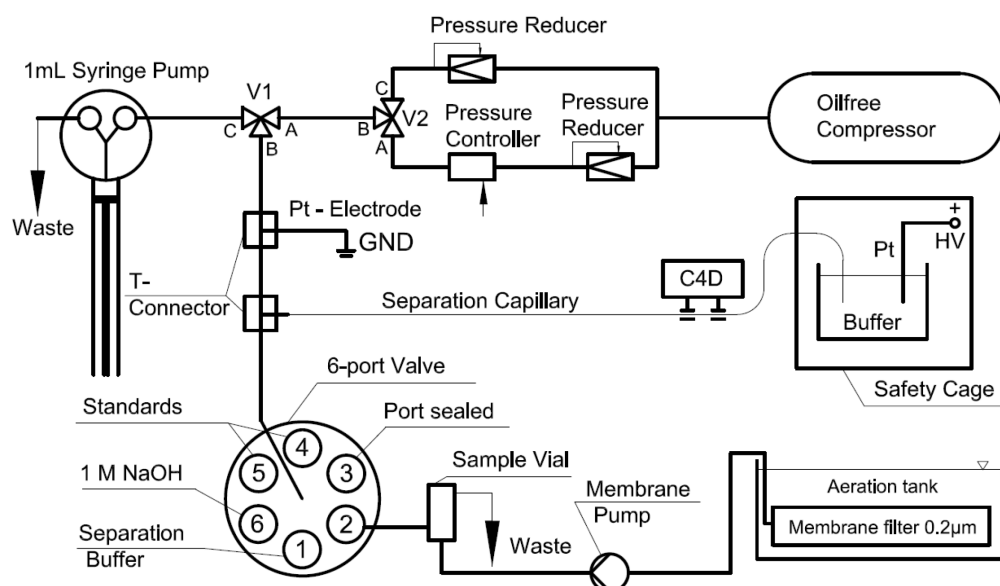


Figure 1: Schematic drawing of the SIA-C⁴D-system for pressure-assisted capillary electrophoresis (C⁴D - contactless conductivity detector; HV - high-voltage power supply).

capillary equipped with platinum high-voltage electrodes and the C⁴D detector at the high-voltage end of the capillary. A syringe pump draws the fluids through the six-port valve, selects the appropriate solution and automates fluid manipulation. One measurement cycle consists of flushing the capillary with consecutive sample aspiration, injection and separation. Flushing is done by pulling the BGE from port 1 into the interface section in front of the separation capillary, switching the valve V2 to the high-pressure branch (B-A) and closing the six-port valve (port 6) for 4 minutes. While the pressure is on the capillary, the membrane pump is activated and conveys the wastewater through the membrane filter into the sample vial. Switching the six-port valve to position 2 and valve V1 to position B-C, while moving the plunger of the syringe pump down, conveys the sample to the tee with the separation capillary for injection. Injection is done with the pressure regulator activated to 10 psi for 4 seconds while valve V1 is in

3. Results and Discussion

3.1. Method development

In order to carry out the separation of both anions and cations in the same run in a single capillary the following procedure was implemented. The electroosmotic flow was reversed by adding CTAB to the BGE. This allows the separation of the anions by applying a positive voltage at the detector end of the capillary. At the same time, the cations move towards the injection end. In order to also move the cations towards the detector, and prevent them from exiting the capillary at the injection end, a hydrodynamic flow towards the detector end was superimposed. As demonstrated previously by Mai et al. [21–23] this is possible without significant penalty due to the imposed laminarity of the flow (potentially causing

bandbroadening) when employing capillaries with internal diameters of 25 μm or less. This is readily possible when employing C^4D . After the separated anions passed the detector the high voltage was disabled and the pressure on the capillary increased to 60 psi. The high flow rate generated in this way moves the cations to the detector and prevents mixing effects of the already separated cations. Through optimization of the capillary length, pressure levels and separation time, it was possible to achieve the required baseline separation of all nitrogen ions.

To establish the required CTAB concentration to obtain the correct EOF its concentration was varied between 0.08 mM and 0.15 mM. Higher CTAB concentrations resulted in split peaks of chloride. This effect was also observed using DDAB as an EOF

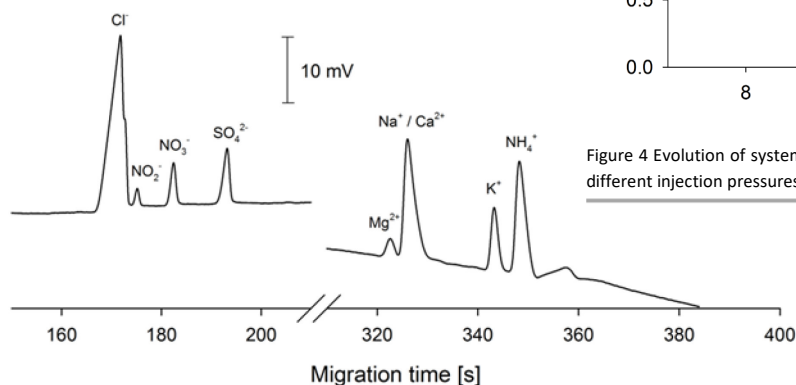


Figure 3: Simultaneous separation of anions and cations in a wastewater sample; Capillary ID: 20 μm , effective length: 68 cm; Buffer solution: 100 mM HIS / 100 mM MES / 0.13 mM CTAB / 1.5 mM 18-crown-6, pH 6; Voltage: + 24 kV

modifier. A concentration of 0.13 mM CTAB was found to be a good compromise to keep NH_4^+ in the capillary due to sufficiently high and stable EOF with no split peaks during separation. Adding 1.5 mM crown-ether (18-crown-6), to separate K^+ from NH_4^+ by complexing potassium and thus lowering its mobility, enables a baseline separation of K^+ from NH_4^+ up to 50 mg/L $\text{NH}_4\text{-N}$. The ionic strength of the BGE was adapted to produce sharp symmetric peaks with good resolution in the required concentration range of nitrogen ions in wastewater samples. The pH of the running buffer was kept near the pH of wastewater to avoid sample decomposition and to have all nitrogen ions fully charged to receive the full possible response on the detector. The sequence of detection was thus anions first (fast ones before slow ones) followed by the cations (slow ones first). An example of a separation of wastewater is shown in Figure 2.

3.2 System calibration

The system was calibrated using six concentrations of standard solutions (Table 1). Each standard was separated four times to check the relative standard deviation (RSD) and the stability of the system. Peak size evolution was investigated over different injection pressures, starting from 4 psi up to 12 psi for 4 seconds, using 2 psi steps. Figure 3 shows that injection pressures between 8 psi and 12 psi give the best results with respect to the RSD, which stays below 2%. The reason for the high RSD when small injection pressures are used could be a small hydrostatic reflux with adverse turbulence effects at the beginning of the sample zone while the excess sample is

removed. In order to improve the RSD in this pressure range, it is necessary to adjust the flow rate and the volume of the trailing solution in the tee piece of the separation capillary. The resulting slopes of these calibration curves show linear behavior (Figure 4) that permits dynamic adaption of the measurement

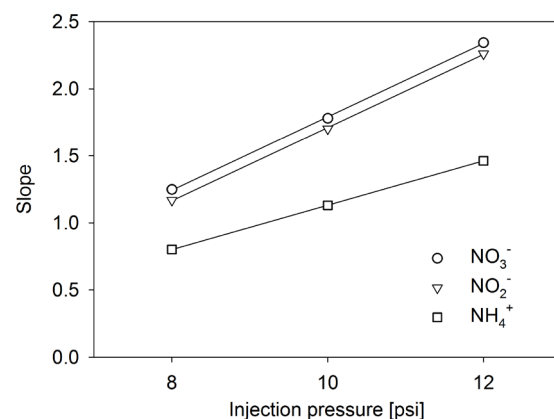


Figure 4 Evolution of system sensitivity for nitrate, nitrite and ammonium using different injection pressures for system calibration

range during operation. When peaks overlap, it is possible to reduce the injection pressure. In case of disappearing peaks, the pressure can be increased. This enables the option of a dynamic system calibration through variation of injection pressure which is a useful feature when analyzing wastewater samples. Monitoring of the effluent of a wastewater treatment plant

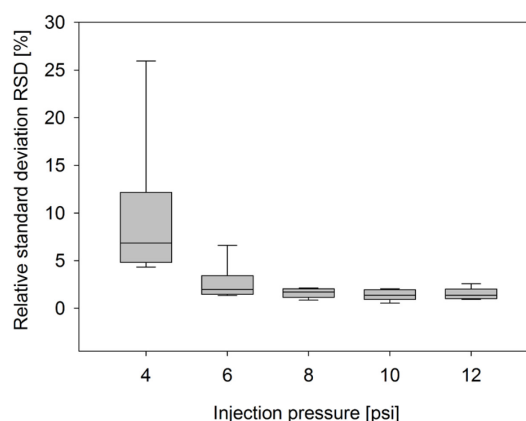


Figure 2: Relative standard deviations of peak areas using different injection pressures (n=4 per standard solution)

requires a low LOD because of the conducted nitrogen removal during the treatment process. Usually only small amounts of nitrate can be found in the effluent. When one of the nitrogen parameters starts to rise abnormally, it is possible to identify problems in the cleaning process. Measurements at the influent of a treatment plant requires the separation of high $\text{NH}_4\text{-N}$

concentrations with respective low injection pressures to separate ammonium from potassium. In most cases, this means that nitrate and nitrite can no longer be quantified, as they occur only in very low concentrations in the influent. Therefore, it has to be considered that the change of the injection quantity always has an effect on all ions.

Table 2 shows the results of the applied calibration procedure. The resulting monitoring range is sufficient to analyze wastewater processes concerning nitrogen transformation and removal. During the investigations of the possible concentration ranges, overlapping peaks of chloride and nitrite were found when the chloride peak exceeded a peak area of 110 mVs that corresponds to 120 mg/L Cl^- .

Table 2: Calibration ranges, limits of detection (LOD) and reproducibility of examined nitrogen parameters

Ions	Range [mg/L]	Correlation coefficient	LOD [mg/L] ^{a)}	RSD [%] residence time (n=4)	RSD [%] peak area (n=4)
$\text{NO}_2\text{-N}$	0.1 – 5	0.9986	0.03	0.43	1.34
$\text{NO}_3\text{-N}$	1 – 50	0.9988	0.08	0.47	0.52
$\text{NH}_4\text{-N}$	1 – 50	0.9978	0.11	0.96	0.97

^{a)} LOD determined using the slope of calibration line [24]

3.3 Performance with wastewater samples

To check the matrix sensitivity of the CE system, single wastewater samples were analyzed from different wastewater treatment plants and processes. SDE samples were diluted to fit the calibration range. All samples were analyzed in our laboratory with a segmented flow analyzer (SFA) and the corresponding DIN methods. DIN EN ISO 11732:2005-05 for $\text{NH}_4\text{-N}$ and DIN EN ISO 13395:1996 for $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$. On average, the recovery rates were 102 % for $\text{NO}_3\text{-N}$, 104 % for $\text{NO}_2\text{-N}$ and 104 % for $\text{NH}_4\text{-N}$, analyzing 15 different samples. This in comparison to conventional wastewater analyzers is a common measurement accuracy [25–27].

For the continuous monitoring of nitrogen ions, the developed membrane filter system was installed in the aeration tank of the pilot scale wastewater plant at the TU Wien. The influent of the plant is provided by a section of the sanitary system from the university. At the start of the experiments, there was no nitrogen available in the plant because it was Monday and no students or employees used the toilets on the weekend. To increase the nitrogen concentration, we added 57.6 g urea into the plant and conducted five consecutive runs of wastewater, followed by one run of standard solution (ID: 30), to prove the stability of the system during separations (Figure 5). The relative standard deviations of the peak areas of standard solution were slightly higher during 24 hours of operation than obtained from calibration (Table 2). Nitrite showed an RSD of 2.1 %, nitrate 0.7 % and ammonia 1.2 %. During the first 8 hours, reference samples were taken from the waste port of the sample vial for laboratory analysis. The results of the ammonium investigation are shown in Figure 6. The calculated recovery rate for ammonium-nitrogen is between 94 % and 103 %.

After the urea dosing, there is a very steep ammonium-nitrogen increase for one hour. This is followed by a smoother increase of $\text{NH}_4\text{-N}$, which results from urease activity [28], the onset of nitrogen transformation and the influent of new ammonium-nitrogen into the plant.

Corresponding results for $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ of the 24-hour investigation are shown in Figure 7, which again agreed with laboratory reference values ($\text{NO}_3\text{N Ref}$, $\text{NO}_2\text{N Ref}$). The recovery rate of CE results compared to laboratory reference values were 90 % – 104 % for $\text{NO}_3\text{-N}$ and 92 % – 108 % for $\text{NO}_2\text{-N}$. The nitrate-

nitrogen concentration follows a saw tooth pattern during the first 12 hours resulting from the nitrification and denitrification process in the aeration tank. The aeration tank is intermittently operated with 20 minutes of stirring followed by 40 minutes of stirring and aeration to 2 mg/L oxygen concentration. During aeration, the nitrate concentration increases due to nitrification. In the second phase, nitrate is reduced to molecular nitrogen. After 16 hours the dosing of carbon into the plant was stopped to inhibit the denitrification which led to a

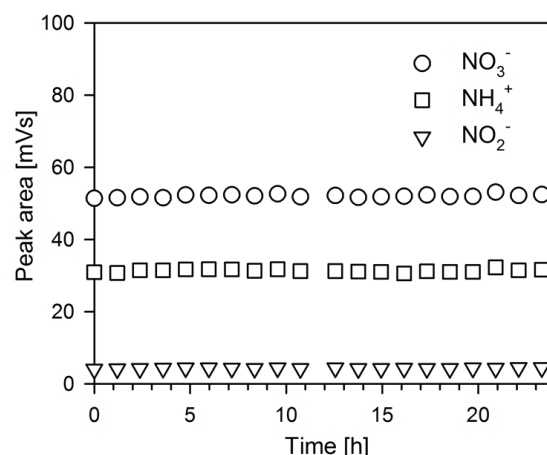


Figure 5: Stability investigation of peak areas of standard solution (ID: 30), during continuous wastewater monitoring

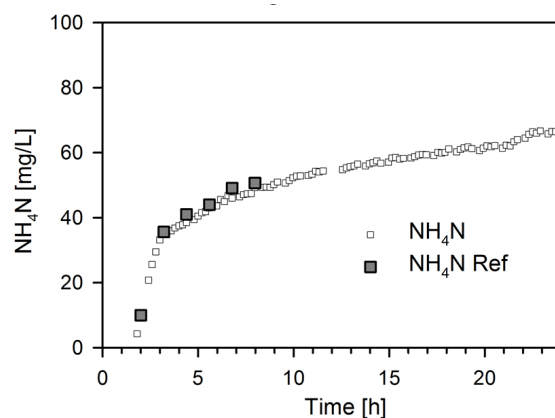


Figure 6: Ammonium-nitrogen concentrations of CE and laboratory reference in aeration tank

steady increase of nitrate-nitrogen concentration in the aeration tank.

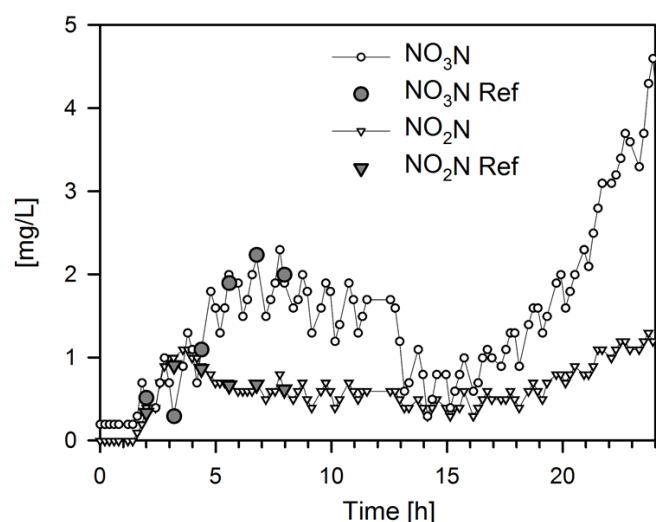


Figure 7: Nitrate-nitrogen and nitrite-nitrogen concentrations with corresponding reference values in the aeration tank during 24 hours of investigation

The observed measurement errors are partially induced by temperature variations in the laboratory facility. By incrementing the temperature of the device in a climate chamber, the peak area increased by 1.8 % for NO_2^- and NO_3^- and 1.3 % for NH_4^+ for a temperature increase of 2°C, for a range of 30°C to 40°C.

4. Conclusions

It could be demonstrated that the shown approach of superimposing electrokinetic motion with hydrodynamic pumping enables the separation of inorganic nitrogen ions in wastewater samples with good performance in terms of RSD and accuracy. It is possible to monitor new wastewater treatment processes in the shown measurement ranges of nitrogen ions. The achieved ranges are sufficient to observe nitrification and denitrification processes in municipal wastewater treatment plants as well as the monitoring and investigation of mainstream deammonification processes. In addition, the implementation of this monitoring strategy in research opens up many possibilities to gain new insights into this novel processes and supports the development of new full-scale control strategies.

The cycle time of 12 minutes is sufficient to monitor those biological processes over extended time periods with persistent system stability. By using high quality industrial hardware, we overcome known CE limitations of low reproducibility of separations due to injection errors. For a practical implementation of the system, a precise temperature control is desirable. Additionally, a software package performing automated peak area integration and calibration will be necessary.

Conflicts of interest

There are no conflicts to declare.

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