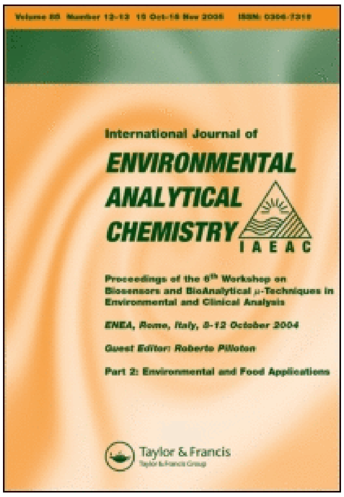

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Comparison of continuous flow analysis including photometric detection and ion-selective electrode potentiometry for the measurement of ammonium nitrogen in wastewater

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Continuous flow analysis (CFA) with photometric detection is widely used to quantify NH_4^+-N. However, low-molecular-weight amines interfere with CFA measurements. Therefore, we compared CFA and ion-selective electrode (ISE) measurements using an ISE25NH4 electrode from Radiometer Analytical for determining NH_4^+-N in wastewater streams in a plant where protein separation media are manufactured. Approximately 50% of the trimethylammonium chloride in one of the samples was recorded by CFA as ammonium nitrogen. Furthermore, CFA spikings using 6 mg N/L NH_4^+-N additions to the wastewater showed less accuracy compared with equivalent ISE spikings. Direct ISE measurements of NH_4^+-N levels in wastewater across the concentration range 0.1–1400 mg N/L typically showed >90% accuracy, with <1% RSD repeatability (both within- and between-day). Furthermore, due to the excellent selectivity of the electrode for NH_4^+-N over Na^+ ($\log K^{\mathrm{Pot}}_{\mathrm{NH4-N,\,Na}}$) = –3.11, the presence of potentially interfering Na^+ ions in selected wastewaters did not affect the readings. ISE measurements obtained by multiple standard addition methodology showed similar levels of accuracy and repeatability, except that the accuracy of the determinations was affected by the non-linear electrode responses to samples with low NH_4^+-N concentrations (<1 mg N/L). Direct ISE and CFA measurements on two types of wastewater streams revealed significant differences ($p < 0.05$). The ISE results showed on average 18 and 112% higher NH_4^+-N concentrations compared with CFA results. The known occasional ammonium increase in one of the streams was not detected by the CFA method.

Keywords: CFA; ISE; Ammonium nitrogen; Wastewater

1. Introduction

Quantification of ammonium nitrogen in wastewaters is important, since measurements of NH_4^+-N concentrations are often used to monitor nitrification reactions in sewage treatment plants [1], and the organic nitrogen (N_{ORG}) contents of wastewater streams are often estimated by subtracting NH_4^+-N, NO_2^--N and NO_3^--N concentrations from total nitrogen (N_{TOT}) determinations.

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Among the existing methods that are frequently used for determining ammonium nitrogen in wastewaters, the Nessler reagent method is well established. The application of Nessler's reagent to factory wastewater is reported to be affected by precipitation formations and matrix effects [2]. It is also previously known that the secondary aromatic amines α-phenyl-naphtylamine and diphenylamine interact with the reagent at prolonged standing times [3]. Meseguer-Lloret *et al.* compared the Nessler reagent method with two other methods: the OPA/NAC-metod where ammonium ions are derivatized with *o*-phtaldialdehyde (OPA)/*N*-acetyl-cysteine (NAC) followed by fluorescence measurement and an ammonia-gas-sensing electrode method [2]. It was concluded that the presence of methylamine, ethylamine, isopropylamine and β-phenylethylamine interfered using the selective electrode method, while the OPA/NAC reagent method was more selective. The limit of detection (LOD) for this method was reported to be 0.07 mg N/L. The excellent ammonium selectivity for the OPA/NAC-reagent method is achieved by exciting at 415 nm and emitting at 485 nm. At 415 nm, no primary amine components are excited [4].

Modified Berthelot reaction methods are commonly used for measuring ammonium nitrogen. In the original Berthelot reaction method (1859), phenol and an oxidizing agent are used to transform ammonium to Indophenol Blue. Using a modified Berthelot reaction method where phenol was replaced with thymol, Moliner-Martínez *et al.* investigated the influence of the presence of surfactants and humic acids on the indophenol reaction [5]. It was found that the surfactants inhibited the formation of the thymol ammonium derivate. The limiting percentages were 0.5% for anionic, 0.001% for cationic and 5.5% for non-ionic surfactants. Laima concluded that a fivefold dilution was necessary in the analysis of NH_4^+ in marine sediments to avoid inhibition of the indophenol colour development. Without the dilution, inhibitions up to 51% were monitored [6]. Laima used a salicylate Berthelot reaction method.

In the present study, a modified Berthelot reaction method which is commonly used in commercial settings and environmental analyses (European Standard Method), including continuous flow analysis (CFA) and photometric detection, was tested. Ammonium ions present in the sample are reacted in alkaline solution with hypochlorite (ClO^-, liberated from dichloroisocyanurate), generating chloroamine. The chloroamine then reacts with salicylate to a blue-green indophenol dye in a nitroprusside-catalysed reaction, and the concentration of the dye is measured in a photometric flow cell [7, 8].

A number of amines, including methylamine, ethylamine, dimethylamine, and diethylamine, are known to interfere with CFA measurements of ammonium, since they also participate in dye-generating reactions, and so their presence leads to overestimates of $NH_4^+{-}N$ contents. Furthermore, $NH_4^+{-}N$ contents may be underestimated if the sample is strongly acidic or buffered, and consequently the pH is < 12.6 after all the reagents have been added [9].

Alternatively, ISE measurements can be performed, using either a direct method or standard addition/subtractions [10]. In the present study, we evaluated both of these approaches for monitoring $NH_4^+{-}N$. The main reason for investigating the ISE methodology was its comparatively low-cost and limited lab-space needs. The membranes in NH_4^+-ISEs usually consist of an ionophore, a plasticizing mediator, and a PVC support matrix. Typically, the ionophore is nonactin, although other ionophores like narsin, monensin, salinomycin, cetyl trimethyl ammonium bromide, and tetrahydrofuran-containing crown ethers have also been used [11, 12]. In the present study, a commercially available NH_4^+-ISE (ISE25NH4) electrode, equipped with a PVC membrane containing an ionophore of unknown origin was chosen. According to the manufacturer's (Radiometer Analytical) specifications, its detection limit for ammonium ions is 3×10^{-6} M (40 µg of $NH_4^+{-}N/L$). K^+ is the only ion that reportedly interferes with ammonium ions measurements by ISE25NH4 electrodes. One benfit of using an ammonium-sensing electrode instead of the previously mentioned ammonia ISE [2] is that volatile amines do not interfere with the measurements. When nonactin is used as an ionophore, the selectivity for NH_4^+ relative to K^+ ($\log K^{Pot}_{NH4-N,K}$) is reportedly –0.92, and depending on the type of plasticizing mediator used, selectivity for NH_4^+ relative to Na^+ ($\log K^{Pot}_{NH4-N,Na}$) is generally in the –1.6 to –2.6 range [13]. Since the wastewaters studied here contained sodium salts and organic cations at various concentrations, it was important to calculate the selectivity coefficients to ensure that the electrode's readings were not significantly affected by these interfering substances.

2. Experimental

2.1 *Materials and sample preparation*

NH_4Cl, KNO_3, conc. HCl, LiCl, and NaCl (all analytical grade) were supplied by Merck, Germany. Milli-Q water (Millipore, Bedford, MA) was used in the preparation of calibration solutions and synthetic wastewater samples. Trimethylammonium chloride (65% in water) was purchased from Chemische Fabrik Berg, Germany. (2,3-Hydroxypropyl) trimethylammonium chloride (HPMAC) was derived from hydrolysis of (2,3-epoxypropyl) trimethylammonium chloride (71% in water) supplied by Degussa, Belgium. HPMAC was prepared by dissolving 10 g of (2,3-epoxypropyl) trimethylammonium chloride in a measuring flask in 750 mL of Milli-Q water. Two grams of NaOH (Analytical Reagent, Prolabo, Rhône Poulenc, France) was added, and finally water was added to a final volume of 1 L. The flask was then placed in a temperature-controlled chamber at 80°C for 90 min. Following this treatment, the measured pH of the solution was 12, and the HPMAC yield was found to be 97% according to LC–MS analysis using a Micromass Quattro II system. The real wastewater samples used in this study were collected at GE Healthcare's site in Uppsala, Sweden where protein-separation media are manufactured. The samples were taken from three different wastewater streams, designated W_A, W_B, and W_C, respectively. The chemical composition of the three streams varies considerably. However, in addition to ammonium ions, trimethylammonium chloride (TMAC), and HPMAC, sodium salts, 2-diethylaminoethanol, polysaccharides, and urea are present in all of them. The $NH_4^+{-}N$ content of W_A samples is typically in the 0–10 mg N/L range, but higher levels can be expected in W_B and W_C samples, since additional ammonium ions are occasionally added to these wastewater streams Furthermore, the urea contents of W_B samples are considerably higher than those of W_A and W_C samples. In Januay 2007, a new sewage treatment plant was put into operation at GE Healthcare in Uppsala with the aim to remove TMAC, HPMAC, and 2-diethylaminoethanol from W_A and W_B. The other constituents remained at their previous concentration levels. The purified W_A and W_B streams are designated W_{A2} and W_{B2}, respectively.

The wastewater samples that were analysed by ISE methods were kept deep-frozen until analyses were performed, at GE Healthcare, Uppsala, while the CFA analyses were carried out at ALcontrol AB, Linköping, Sweden, using samples that were shipped within a day of the sampling.

2.2 *Apparatus and methods*

The CFA analyses were performed according to the European Standard Method EN ISO11732:2005 using a Konelab Aqua 60 system including an UV/VIS detector flow-cell device from Thermo Clinical Labsystems [9]. The absorbance wavelength of choice was 660 nm. For ISE analyses at GE Healthcare, an ammonium-sensitive ISE25NH4-electrode and a double-junction REF251-reference electrode, connected to an ION450 ion meter, were used (all supplied by Radiometer Analytical SAS, France). The outer compartment in the reference electrode was filled with 0.1 M LiCl instead of saturated KCl in accordance with instructions from the manufacturer to prevent diffusion of potassium ions into the sample. Calibration and sample solutions were diluted 1 : 1 by ISA solution (0.2 M LiCl) to final volumes of 100 mL. The calibration solutions were made by diluting a NH_4Cl stock solution (28 g N/L) to 2800, 280, 28, 2.8, 0.28, and 0.014 mg N/L with Milli-Q water. Calibration and sample solutions were mixed with a magnetic stirrer (rod size and speed; 5 × 20 mm and 250 rpm, respectively). On each calibration and analysis occasion, the ambient temperature was recorded with a Fluke 52 II digital thermometer (Fluke, The Netherlands), and the acquired data were manually entered into the ION450 ion meter's software. Synthetic and real wastewater solutions were analysed, using both direct and multiple standard addition (MSA) methods. For MSA runs, 250 µg of ammonium nitrogen (NH_4Cl) was added to 100 mL sample solutions including 50 mL ISA, by pipetting 100 µL of a 2.5 g N/L standard solution stepwise ($n = 7$). The measurements for each concentration were performed in triplicate, and the mean values were used to establish the standard addition curve. The recommended pH interval for the ISE25NH4-electrode, is 3–8. However, at pH 8, approximately 5% of the NH_4^+ ions in a sample will be in the NH_3 form according to the acid–base equilibrium equation:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad (1)$$

where NH_4^+ is a weak acid with a dissociation constant, K_a, of 5.6×10^{-10} at 298.15 K.

Therefore, the pH in the real alkaline wastewaters was adjusted with conc. HCl to pH 7, at which only 0.5% of the NH_4^+ ions should theoretically be present in the NH_3 form.

3. Results and discussion

CFA and two chosen ISE methods including direct measurements and MSA were compared by precision, accuracy, and selectivity determinations. LOQ was determined for the two ISE methods. Furthermore, the ISE potentiometric stability was investigated. The presence of significant differences in analysis results for the CFA and the ISE direct measurement method was investigated by performing comparative

Table 1. Accuracy and within-day repeatability determinations of NH_4^+–N concentrations in wastewaters W_A and W_B by the CFA method.

Wastewater ($n = 3$)	Amount added (mg N/L)[a]	Mean (mg N/L) ± SD	%RSD	Yield (%)
W_A (1)[b]	0.0	0.30 ± 0.01	1.9	
W_A (1)	6.0	4.20 ± 0.17	4.1	67
W_B (l)	0.0	29.3 ± 2.3	7.9	
W_B (l)	6.0	32.0 ± 2.7	8.3	67
W_A (2)	0.0	1.2 ± 0.1	4.7	
W_A (2)	15.0	15.7 ± 0.6	3.7	97
W_A (2)	30.0	32.3 ± 0.6	1.8	104
W_B (2)	0.0	7.0 ± 0.4	6.0	
W_B (2)	15.0	21.7 ± 0.1	2.7	100
W_B (2)	30.0	39.3 ± 0.6	1.5	107

[a] NH_4Cl.

[b] Sample collection weeks: week 40, 2005 (I), mixed sample from weeks 5 to 14, 2006 (2).

analyses of chosen wastewater lots. Analysis times, costs, and environmental considerations are also discussed.

3.1 *CFA method*

3.1.1 Precision and accuracy determinations. W_A and W_B wastewater samples were spiked with NH_4Cl solutions at three different concentrations: 6, 15, and 30 mg NH_4^+−N/L. The unspiked and spiked samples ($n = 3$) were analysed by ALcontrol AB (see table 1).

The between-day repeatability of the CFA measurements, estimated by calculating the pooled relative standard deviation for the data set was 4.9%. The yields were notably reduced when small amounts of NH_4^+−N (6 mg N/L) were added. Since the method is preferably used for monitoring minor concentration changes in the chosen effluents, the observed lack of accuracy limits the reliability of these measurements, although the within-day repeatability was consistently high (i.e. the within-day variability was low).

3.1.2 Selectivity. The amines that have been previously reported to interfere in the measurements react in a similar way to the ammonium ions, causing NH_4^+−N concentrations in wastewater samples containing them to be overestimated [9, 14]. In the W_A and W_B wastewaters, high concentrations of TMAC are present, and preliminary results indicated that TMAC interferes strongly in the analysis of NH_4^+−N. Thus, to assess the effects of TMAC on CFA readings quantitatively, W_B samples were spiked with 30 mg of N-TMAC/L and 15 mg of N/L of which was detected as ammonium nitrogen.

3.2 *ISE method (direct measurements)*

3.2.1 Precision, accuracy, and limit of quantification (LOQ). The within-day repeatability ($n = 6$) of direct ISE measurements was evaluated by measuring NH_4^+−N levels

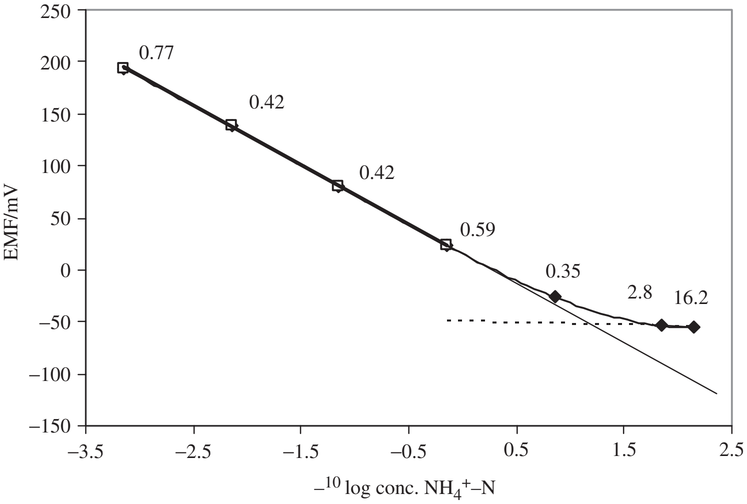

Figure 1. Electromotive force (EMF) response to ammonium nitrogen (mg N/L) of the ISE25NH4 electrode. The % RSD values ($n = 6$) and crosspoint for the extrapolated fourth-order polynomial (◆) and linear fitted (☐) lines are shown in the graph.

Table 2. Accuracy and within-day repeatability of direct ISE measurements ($n = 3$) of NH_4^+–N concentrations in wastewaters W_A and W_B.

Wastewater	Amount added (mg N/L)	Mean (mg N/L) ± SD	%RSD	Yield (%)
W_A	0.0	4.66 ± 0.04	0.88	
W_A	6.0	10.41 ± 0.02	0.22	95.6
W_A	12.0	16.20 ± 0.05	0.30	96.5
W_B	0.0	6.16 ± 0.01	0.15	
W_B	6.0	11.78 ± 0.06	0.51	93.7
W_B	12.0	14.79 ± 0.04	0.24	95.1

[a] Mixed sample from weeks 5 to 14, 2006.

in serially diluted NH_4Cl solutions with seven different concentrations, ranging from 0.007 to 1400 mg N/L. The lowest concentration at which precision was adequately maintained (RSD < 1%) was defined as the LOQ (see figure 1).

The EMF (mV) response was linear for NH_4^+–N concentrations ranging from 0.3 to 1400 mg N/L, with a slope of 57.2 ± 0.2 mV/decade at 294.15 K. The ISE detection limit is often determined by the cross-point method, defined by the intersection of the extrapolated linear mid-range and final low concentration level segments of the calibration curve [15,16]. However, irrespective of the method used to determine the detection/quantification limit, the resulting LOQ was < 0.1 mg N/L.

For accuracy determinations, ISA-diluted W_A and W_B samples were spiked with 6 and 12 mg N/L (NH_4Cl), and measured in triplicate. The within-day repeatability and yield results are summarized in table 2.

The between-day repeatability, estimated by calculating the pooled relative standard deviation for the data set, was 0.46%.

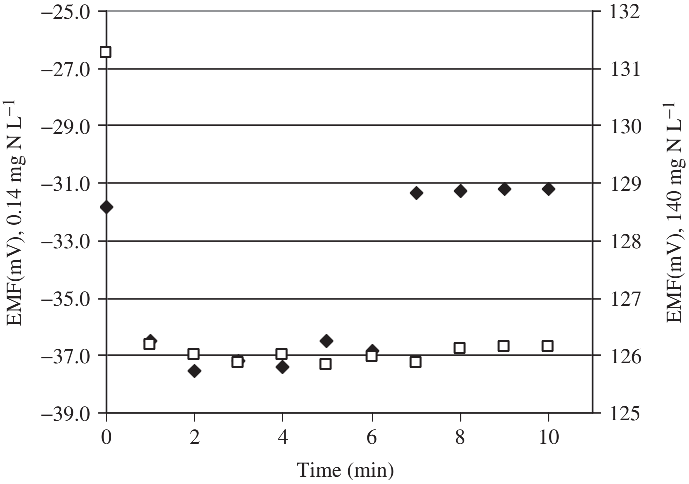

Figure 2. Potentiometric stability of ISE measurements of solutions with 0.14 (◆) and 140 mg N/L (☐) ammonium concentrations taken over 10 min.

3.2.2 Potentiometric stability (drift). Potentiometric measurements of two NH_4Cl solutions (one with 0.14 and the other with 140 mg N/L) were continuously recorded for 10 min at 294.15 K, and the responses were converted to mg N/L units. For the 0.14 mg N/L sample, the response was stable after 6 min, and after 10 min the reported concentration was 3% higher than the initial value (0 min). The response for the 140 mg N/Lsample decreased rapidly within the first 3 min and then stabilized. For this sample, the reported concentration was 3% lower than the initial value (see figure 2).

3.2.3 Potentiometric selectivity coefficients. Potentiometric selectivity coefficients ($\log K^{\mathrm{Pot}}_{\mathrm{NH4-N,B}}$), describing the selectivity of the membrane for $NH_4{}^+$-N relative to each interfering ion, B, were determined by the separate solution method and expressed in mg/L (rather than the more common molar units) in accordance with general practice in environmental analyses [17–21]. According to the manufacturer, Radiometer Analytical, the only ion that is known to interfere significantly with measurements by this electrode is K^+. However, the electrode's selectivity for NH_4^+-N over trimethyl ammonium ions (TMA), Na^+, and (2,3-hydroxypropyl) trimethylammonium ions (HPMA) was also investigated, since substantial amounts of these ions are present in the W_A and W_B wastewaters. Selectivity coefficients were determined for each of these species, using solutions with four different B-ion concentrations (7, 70, 700, and 1400 mg/L). The EMF responses (E_B) for the ions were determined from the resulting calibration curves, and the corresponding NH_4^+-N concentrations ($E_A = E_B$) were then calculated (see table 3).

In contrast to the CFA method, no interference from TMAC was detected. However, although the electrode's NH_4^+-N selectivity over Na^+ is high, the levels of NaCl in W_A and W_B samples were sufficiently high (ca. 500 mg Na^+/L) to prompt the suspicion that they may interfere with the electrode's NH_4^+-N measurements. The selectivity coefficient (–3.11) obtained indicates that Na^+ may have significant effects at

Table 3. Selectivity coefficients for the ISE25NH4-membrane obtained using the separate solution method.

Ion (mg/L)	Log $K_{\mathrm{NH4\text{-}N,\ B}}$
K^+ (7)	–1.22
K^+ (70)	–1.25
Na^+ (1400)	–3.11
TMA (700)	nd[a]
HPMA (70)	–3.64
HPMA (700)	–4.59

[a] No EMF response was detected at this concentration

Table 4. Within-day repeatability ($n=3$) and accuracy of ISE (MSA) measurements of solutions with various ammonium concentrations.

Conc. (mg N/L)	0.10	1.00	10.00	50.00
Mean calculated conc. (mg N/L) ± SD	0.15 ± 0.004	1.00 ± 0.005	9.67 ± 0.05	52.41 ± 0.20
%RSD	2.66	0.50	0.54	0.51
Yield (%)	153	100	96.7	101

concentrations exceeding 1 g/L. Thus, additional measures to account for its effects do not seem to be required in this application.

3.3 *ISE method (MSA)*

3.3.1 Precision, accuracy, and LOQ. The accuracy of the MSA method was assessed by taking ISE measurements of samples with various known NH_4^+-N concentrations. The within-day repeatability was estimated from the least square-fitted slopes of graphs in which the added amount of NH_4^+-N (μg) was plotted against the expression $(V_0 + V_{\mathrm{std}})10^{\frac{\Delta E}{s}}$ [22, 23]. As for direct ISE measurements, LOQ was defined as the lowest concentration at which precision was maintained (1.0 mg N/L; see table 4).

For the highest concentrations, correlation coefficients obtained by least-square fitting were >0.9985. However, at 0.1 mg N/L, the errors were significantly higher, and the recorded yield (153%) was influenced by the non-linear response at low concentrations (see figure 1). Therefore, the responses were recalibrated for low levels of NH_4^+-N using data acquired solely from solutions with 0–140 μg of NH_4^+-N/L. The correlation coefficient for the second-order polynomial equation fitted to these data was 0.9993 (see figure 3).

Thus, least-square MSA-fitting of data obtained at low NH_4^+-N levels will lead to erroneously low *k*-values, and since C_0 is defined as k^{-1}, the reported yield will be too high [23]. Simple algorithms are available for non-linear MSA fittings [24]. However, for the present application, a 1 mg N/L LOQ was sufficient, so there would be no need to apply such algorithms in routine practice.

The ISA diluted samples (W_A and W_B) were spiked with 6 mg of N/L (NH_4Cl). The within-day repeatability and yield results are summarized in table 5.

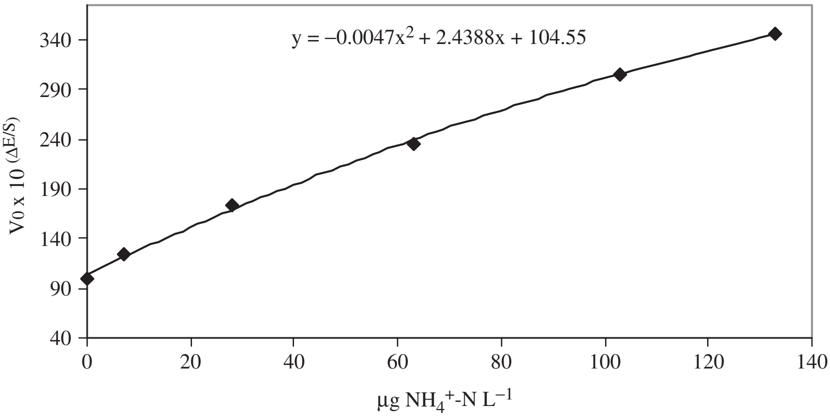

Figure 3. Potentiometric responses in the low-NH_4^+-N concentration range.

Table 5. Accuracy and within-day repeatability of ISE (MSA) determination of NH_4^+-N concentrations in wastewaters W_A and W_B.

Wastewater[a]	Amount added (mg N/L)	Calculated conc. (mg N/L) ± SD	%RSD	Yield (%)
W_A	0.0	4.51 ± 0.02	0.49	
W_A	6.0	10.25 ± 0.05	0.53	95.6
W_B	0.0	6.31 ± 0.03	0.51	
W_B	6.0	12.67 ± 0.03	0.26	106.0

[a] Mixed samples from weeks 5 to 14, 2006.

Using the stepwise addition ($n = 7$) technique outlined in section 3.2 for the unspiked and the spiked W_A-sample, the within-day repeatability and yield results were found to be in accordance with corresponding ISE direct measurement values. Concerning the W_B-sample accuracy, the calculated yield result was slightly increased.

3.4 *Comparison of CFA, ISE (direct measurement), and ISE (MSA): results*

A representative sample of each of the W_A, W_B, and W_C wastewaters was collected in 2006 and analysed by each of the three investigated methods. Furthermore, several samples of the purified W_A and W_B wastewaters (W_{A2} and W_{B2}) were collected on different weeks in 2007 and analysed using CFA and ISE direct measurements (see table 6). ISE (MSA) measurements were not included, since it was decided to routinely use the ISE direct measurement method for these water types.

The results obtained for the W_A sample using the three methods deviated significantly, with higher levels of NH_4^+-N being detected by both of the ISE-methods than by the CFA method. The sodium ion concentrations were similar in the W_A, W_B, and W_C samples (ca. 500 mg Na^+/L). Thus, interference by Na^+ with the ISE measurements is unlikely to be the cause of this deviation, since the critical interfering Na^+ concentration level was previously found to be > 1 g/L (see above). The analysed

Table 6. Amounts of ammonium (mg N/L) in three wastewater streams according to the CFA and ISE methods.

Sample type	CFA ± SD[a]	ISE (direct readings) ± SD	ISE (MSA) ± SD
W_A	1.21 ± 0.06	4.52 ± 0.05	4.71 ± 0.05
W_B	7.05 ± 0.34	6.33 ± 0.06	6.21 ± 0.06
W_C	22.02 ± 1.10	24.72 ± 0.25	23.6 ± 0.24
W_{A2}, week 16	1.70 ± 0.08	1.43 ± 0.02	
W_{A2}, week 17	2.73 ± 0.13	3.80 ± 0.04	
W_{A2}, week 18	3.50 ± 0.17	3.80 ± 0.04	
W_{A2}, week 19	1.10 ± 0.05	1.33 ± 0.01	
W_{A2}, week 20	4.80 ± 0.24	6.22 ± 0.06	
W_{A2}, week 21	0.87 ± 0.04	1.10 ± 0.01	
W_{B2}, week 16	1.40 ± 0.07	3.62 ± 0.04	
W_{B2}, week 17	1.13 ± 0.06	3.85 ± 0.04	
W_{B2}, week 18	2.40 ± 0.12	4.59 ± 0.05	
W_{B2}, week 19	7.63 ± 0.37	8.88 ± 0.09	
W_{B2}, week 20	3.80 ± 0.19	6.18 ± 0.06	
W_{B2}, week 21	1.20 ± 0.06	2.45 ± 0.02	

[a] SD values originate from previously determined between-day repeatabilities for the CFA method and the two ISE methods (CFA: 4.9% RSD, ISE methods: 1% RSD).

W_{A2} and W_{B2} samples containing negligible amounts of TMAC, HPMAC, and 2-diethylaminoethanol showed higher levels of NH_4^+-N for ISE except for sample W_{A2}, week 16. For W_{A2} and W_{B2} samples, the ISE direct measurement method showed on average 18 and 112% higher results, respectively, compared with CFA. Paired *t*-tests revealed that these recorded differences were significant ($p < 0.05$) using the mean standard deviations for the CFA and ISE results from table 6 in the calculations. As previously mentioned, the W_B and W_{B2} streams are occasionally enriched with NH_4^+-N. From table 6, it is clear that at least for four of the 6-week ISE measurements, the W_{B2} concentration levels exceed the corresponding W_{A2} results while for CFA measurements, 4-week samples show elevated results in the W_{A2} streams. The reason for the discrepancy in the CFA method is not known but may be correlated to matrix effects that possibly can be overcome by simply diluting the samples [6]. Concerning the W_B sample that was analysed using CFA and both ISE methods, the higher $NH_4{}^+$-N analysis result may be explained by a positive interference from TMAC.

3.5 *Additional comments concerning the use of CFA, ISE (direct measurement), and ISE (MSA) methods*

The total estimated analysis time for one sample using the fully automatized CFA method is 5 min. For ISE methods, the corresponding analysis times are approximately 30 min for direct measurements and 45 min for MSA measurements. The Konelab Aqua 60 system used for CFA analysis is approximately 15 times more expensive than the ISE equipment and is aimed at large-scale routine analysis purposes. Considering environmental aspects using the investigated methods, dichloroisocyanuric acid and sodium nitroprusside used in CFA analysis are toxic.

4. Conclusions

We have demonstrated that ISE measurements using an ISE25NH4 electrode are well suited for the analysis of ammonium nitrogen in complex wastewater streams, providing greater precision and accuracy than the CFA method for determining low concentrations of $NH_4^+{-}N$. Direct ISE measurements are preferred over MSA for their convenience and sensitivity (low LOQ). CFA and direct ISE measurements in wastewater streams from which the organic nitrogen compounds TMAC, HPMAC, and 2-dietyhlaminoethanol were removed (W_{A2} and W_{B2}) revealed results that differed significantly ($p < 0.05$). For selected week samples, the W_{A2} and W_{B2} mean analysis results were 18 and 112% higher, respectively, using the ISE method. It is believed that the CFA measurements on W_{B2} water are interfered by matrix effects, thereby presenting falsely low analysis results. The known occasional $NH_4^+{-}N$ increase in W_{B2} waters compared with W_{A2} waters was not verified using CFA.

In cases where ISE is to be used to analyse ammonium nitrogen in wastewaters, the possibility that potassium and sodium ions may be present at concentrations that interfere significantly with the measurements must be considered. Interferences from other major contaminants are preferably investigated by selectivity studies.

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