Application of ion-sensitive sensors in water quality monitoring

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Abstract Within the last years a trend towards in-situ monitoring can be observed, i.e. most new sensors
for water quality monitoring are designed for direct installation in the medium, compact in size and use
measurement principles which minimise maintenance demand. Ion-sensitive sensors (Ion-Sensitive-
Electrode – ISE) are based on a well known measurement principle and recently some manufacturers
have released probe types which are specially adapted for application in water quality monitoring. The
function principle of ISE-sensors, their advantages, limitations and the different methods for sensor
calibration are described. Experiences with ISE-sensors from applications in sewer networks, at different
sampling points within wastewater treatment plants and for surface water monitoring are reported. An
estimation of investment and operation costs in comparison to other sensor types is given.

Keywords Ammonium sensor; in situ; ion sensitive; ISE; nitrate sensor; water quality monitoring

Introduction

Measurement principle

Ion-sensitive probes (Ion-Sensitive-Electrode – ISE) are based on the potentiometric
measurement principle (Cammann, 1979). The probe includes at least two electrodes, a
reference and a measurement electrode. The measurement electrode is equipped with a
special membrane, capable of binding specific ions reversibly. Depending on the activity of
the measured ions in the liquid, a varying number of ions will bind to the measurement
 electrode – resulting in a varying potential difference between the measurement electrode
and the reference electrode, which shows a constant potential in reference to the medium.
The measured potential is put in relation to the activity of the measured ion by means of a
calibration function.

Measurement disturbances

The measurement principle results in a cross-sensitivity to ions with binding properties
towards the measurement electrode similar to the measurement-ion. The so called distur-
bance-ions influence the measured potential difference, which is subsequently interpreted as
a change in the activity of the measurement-ion. For water and wastewater monitoring two of
the most important parameters are ammonium and nitrate.

Table 1 gives an overview on the cross-sensitivities of ISE-sensors on disturbance-ions.
For example, a cross-sensitivity of 1 : 15 of the ammonium electrode on potassium means
that a potassium concentration of 1.5 mg/l results in the same potential difference between the measurement and the reference electrode as an ammonium concentration of 1 mg/l. Since the influence of the disturbance-ions at time of the sensor calibration is compensated automatically, only the concentration variations of the disturbance-ions relative to the concentration at time of the calibration have a negative impact on the measurement.

Table 2 gives typical values for the variation of the K-concentration at different treatment plants.

Considering a typical ammonium concentration of raw or mechanically treated wastewater of 40 mg/l, an ammonium “equivalent-concentration” of 1.5 mg/l due to the influence of potassium would correspond to a measurement error of $\frac{1.5}{40.0} = 3.75\%$ – which usually is acceptable for this application. On the other hand, it becomes obvious that ISE-probes are less suitable for effluent monitoring if no automatic disturbance-ion compensation is carried out, since the measurement signal due to disturbance-ions can be equal to or even larger than the signal due to measurement-ions.

Another disturbing influence can be a high pH-value; with increasing pH-value the ammonia portion also increases, but ammonia is not detected by ammonium sensitive ISE-sensors. An automatic pH-value-compensation can be used to eliminate disturbances due to pH-variations.

**Sensor calibration**

The membrane of the measurement electrode “ages” during its application period due to irreversible bindings with measurement- or disturbance-ions, sectional build up of coatings and mechanical stress. For raw wastewater and surface water a lifespan of 2–3 and 6 months can be expected, respectively. All the above factors result in a drift of the measurement signal.

### Table 1 Properties of ISE-probes for water quality monitoring

<table>
<thead>
<tr>
<th>Sensor type</th>
<th>Ammonium</th>
<th>Nitrate</th>
<th>Potassium*</th>
<th>Chloride*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurement range</td>
<td>$0.1–1,000 \text{ mg_NH}_4\text{-N}/l$</td>
<td>$0.2–7,000 \text{ mg_NO}_3\text{-N}/l$</td>
<td>$0.1–10,000 \text{ mgK}/l$</td>
<td>$0.2–10,000 \text{ mgCl}/l$</td>
</tr>
<tr>
<td>Resolution</td>
<td>$0.1 \text{ mg_NH}_4\text{-N}/l$</td>
<td>$0.1 \text{ mg_NO}_3\text{-N}/l$</td>
<td>$0.1 \text{ mgK}/l$</td>
<td>$0.1 \text{ mgCl}/l$</td>
</tr>
<tr>
<td>Non-linear range</td>
<td>$0.1–1.0 \text{ mg_NH}_4\text{-N}/l$</td>
<td></td>
<td>$0.1–1.0 \text{ mgK}/l$</td>
<td>$0.1–5 \text{ mgCl}/l$</td>
</tr>
<tr>
<td>Cross-sensitivity on main disturbance-ions</td>
<td>Potassium $1:(15–30)$ Chloride $1:300$ Ammonium $1:120$ Bromide $1:1$ Sodium $1:1,300$ Bromide $1:28$ Sodium $1:2,000$ Iodide $20:1$ Iodide $10:1$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Disturbance-ion compensation

### Table 2 Examples of the influence of the variation of the K-concentration on an ISE-NH$_4$-N-measurement

<table>
<thead>
<tr>
<th>Plant size [PE]</th>
<th>Sampling point</th>
<th>K-concentration (Min/Average/Max) within 24 hours [mg/l]</th>
<th>Maximum K-concentration variation [mg/l]</th>
<th>Maximum NH$_4$-N-equivalent concentration* [mg/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant A 95,000</td>
<td>Primary clarifier eff.</td>
<td>9.0/12.7/26.0</td>
<td>17.0</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>6.0/12.0/22.5</td>
<td>16.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Plant B 800,000</td>
<td>Primary clarifier eff.</td>
<td>23.0/25.1/29.0</td>
<td>6.0</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>15.5/19.8/23.5</td>
<td>8.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Plant C 2.5 Mio</td>
<td>Primary clarifier eff.</td>
<td>17.0/29.0/39.0</td>
<td>22.0</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>15.0/17.9/22.0</td>
<td>7.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* Assuming a cross-sensitivity of NH$_4$-N/K = 1 : 15
which has to be compensated by means of periodic calibration; several methods are available:

- single-point (offset) calibration, in-line
- two-point calibration (single standard addition)
- multiple-point calibration (Multiple standard addition).

It is recommended to carry out a visual check of the probe before any calibration is started – if necessary the probe should be cleaned manually. Supplementary sensors like temperature or pH should be calibrated before the ISE is calibrated, so that any errors of the automatic temperature or pH-compensation are corrected before the ISE-calibration is started.

For the single-point calibration the probe remains in the liquid, a single reference measurement is carried out. The sampling period should be kept relatively short (approximately 20–30 s). The concentration of the measurement-ion at time of the calibration should be in the upper half of the concentration range at the measurement location. In case the maximum concentration of the measurement-ion is below 5 mg/l a two-point calibration should be carried out in order to consider non-linearities in the lower measurement range.

For the two- and the multiple-point calibration the probe has to be removed from the liquid and put into a bucket with a grab sample or with a standard of known concentration. Using a grab sample of the actual measurement location has the advantage that influences due to disturbance-ions at the time of sampling are compensated automatically. By using standards, reference measurements can be omitted – but a single-point calibration in-situ has to follow any calibration in standards in order to consider influences from disturbance-ions. The calibration standards need to have sufficient ion activity; TISAB-solutions (Total Ionic Strength Adjustment Buffer) can be used to adjust the ionic strength of the calibration samples.

For the two-point calibration the calibration measurements shall be carried out at approximately 20% and 80% of the concentration range of the measurement-ion at the measurement location and an approximate concentration ratio of the calibration samples of $1 : 10$.

A multiple-point calibration can be applied in case the concentration range at the measurement location has a wide span. Especially in the lower concentration range of ammonium ($<5 \text{ mg} \text{NH}_4^-/\text{l}$) non-linearities have to be considered by means of a sectional linear calibration function.

**Sensor properties**

ISE-probes are preferably built as compact dip-in probes, which can be installed directly in the medium. They are also available as flow through cells or applied in automated analysers – these types abandon the simplicity of in-situ installation for the advantage of automatic calibration using standard addition methods. The compact dip-in assembly allows easy installation, which makes them suitable for an appended installation at an existing plant, short term installation for special monitoring campaigns or application in a mobile monitoring station. No additional equipment like sample filtration units, supply pumps and interconnecting pipe work is needed. The probes are equipped with an automatic cleaning system using pressurized air, which proved to work reliably – even in raw wastewater. Results from a test of an ISE-sensor according to ISO/CD 15839 are given in Rieger et al. (2002).

**Cost estimation**

Table 3 gives an overview on investment and operation costs provided by manufacturers of ISE-sensors and analysers with sample preparation. The costs are given in Euro per February
Table 3 Cost estimation (investment and operation costs in Euro) for NH$_4$-N measurements with ISE-sensors and classical analysers with sample preparation (errors excepted)

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Type</th>
<th>Measurement principle</th>
<th>Response time</th>
<th>Sample preparation</th>
<th>Investment cost (Analyzer/Sensor)</th>
<th>Investment cost (Sample preparation)</th>
<th>Yearly consumables (Analyzer/Sensor)</th>
<th>Yearly consumables (Sample preparation)</th>
<th>Yearly consumables (Reference measurements)</th>
<th>Construction cost – Piping</th>
<th>Construction cost – Analyzer room</th>
<th>Yearly cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>WTW</td>
<td>Analyzer</td>
<td>NH$_3$-gas-sensitive</td>
<td>3 min</td>
<td>Submersed membrane</td>
<td>8,990</td>
<td>5,405</td>
<td>795</td>
<td>295</td>
<td>75</td>
<td>2,500</td>
<td>18,500</td>
<td>4,519</td>
</tr>
<tr>
<td>WTW</td>
<td>in-situ Sensor (1-Channel)</td>
<td>Ion-sensitive</td>
<td>&lt; 1 min</td>
<td>x</td>
<td>4,983</td>
<td>x</td>
<td>424</td>
<td>424</td>
<td>424</td>
<td>x</td>
<td>x</td>
<td>1,997</td>
</tr>
<tr>
<td>Lange</td>
<td>Analyzer</td>
<td>Indophenol-blue</td>
<td>5 min</td>
<td>Submersed membrane</td>
<td>12,050</td>
<td>5,291</td>
<td>2,125</td>
<td>695</td>
<td>75</td>
<td>2,500</td>
<td>18,500</td>
<td>6,631</td>
</tr>
<tr>
<td>Lange</td>
<td>in-situ Sensor (2-Channel)</td>
<td>Ion-sensitive</td>
<td>13 min</td>
<td>x</td>
<td>9,480</td>
<td>x</td>
<td>942</td>
<td>942</td>
<td>942</td>
<td>x</td>
<td>x</td>
<td>5,115</td>
</tr>
<tr>
<td>Nadler</td>
<td>Analyzer</td>
<td>Stripping method</td>
<td>&lt; 1 min</td>
<td>x</td>
<td>6,880</td>
<td>x</td>
<td>280</td>
<td>280</td>
<td>280</td>
<td>x</td>
<td>x</td>
<td>1,595</td>
</tr>
<tr>
<td>STIP</td>
<td>in-situ Sensor</td>
<td>Indophenol-blue</td>
<td>10 min</td>
<td>x</td>
<td>14,880</td>
<td>x</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>x</td>
<td>x</td>
<td>2,602</td>
</tr>
<tr>
<td>Danfoss</td>
<td>in-situ Analyzer</td>
<td>Indophenol-blue</td>
<td>12 min</td>
<td>x</td>
<td>18,050</td>
<td>x</td>
<td>2,009</td>
<td>2,009</td>
<td>2,009</td>
<td>x</td>
<td>x</td>
<td>4,421</td>
</tr>
</tbody>
</table>
2004. The yearly consumables for the analysers include periodic refill of chemicals and exchange of tubes for the peristaltic pumps. For the ISE-sensors the exchange of membranes, electrolyte and reference electrodes are considered. The yearly cost for reference measurements was estimated based on cost for laboratory material (cuvette tests, pipette tips, filters) – for ISE-sensors 2-weekly control measurements (NH$_4$-N and K as the disturbance-ion), for analyzers a single control measurement (NH$_4$-N) every 6 weeks were assumed. Labour costs for maintenance and control are not included; it was assumed that for all systems the required maintenance demand is approximately equal – for analyzers the main maintenance work covers cleaning, change of tubing and periodic refill of chemicals while for ISE-sensors mainly the reference measurements have to be considered. The depreciation period for the analyser/sensor and construction measures was estimated as 10 years and 25 years, respectively. The interest rate was assumed as 5% p.a.

**Results and discussion**

**Application in sewer systems**

Continuous monitoring in sewer networks can be regarded as one of the most complicated tasks in water quality monitoring. The sensors have to be installed in a way which does not obstruct the free flow in the sewer channel. In combined sewer systems the installation additionally has to allow substantial variations of the water level; with respect to the sensor calibration extreme changes of the wastewater matrix have to be considered. Usually the sensors have to be EX-proved.

With respect to ammonium monitoring it has to be considered, that depending on the sewer network topography 50% or more of the organic nitrogen is not yet hydrolysed, subsequently the measured ammonium represents only 50% or less of the total nitrogen load. Especially in combined sewer systems during storm flows this portion can decrease further. Therefore, parallel laboratory measurements have to be carried out to estimate the NH$_4$-N/total-N-ratio for the different typical conditions at the sampling location.

It has to be acknowledged that such an ISE-measurement in a sewer channel will have a limited trueness; on the other hand the operation of the probe is relatively uncomplicated and delivers a continuous recording of the ammonium concentration which subsequently has to be assessed by experts in the light of the varying conditions at the measurement location.

Figure 1 shows the installation of an ISE-ammonium probe in an open sewer channel closely upstream of a wastewater treatment plant. Due to the *in-situ* installation and the automatic cleaning system continuous monitoring over a period of two months was possible.

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**Figure 1** Installation of an ISE-ammonium probe in an open sewer channel closely upstream of a wastewater treatment plant
The monitoring campaign fulfilled its goal of a qualitative assessment of the nitrogen load dynamics with no maintenance demand.

**Application in wastewater treatment plants**

By application of ISE-probes within WWTPs their advantages fully become apparent. Their compact size reduces the risk of sensor clogging; the cleaning system generally is capable to avoid sensor coating due to fat or precipitation products and sensor fouling.

From a sensor point of view, only a limited number of sensor systems can be operated continuously within the mechanical treatment stage. Experience shows that ISE-probes can be operated reliably with a calibration interval of 10–14 days and a monthly probe check with respect to cleanliness. The influence of disturbance-ions in the mechanical stage is low, since the measurement-ion concentration is in general much larger than the concentration variation of disturbance-ions (see Table 2). At one test site (measurement location = grit chamber influent) some problems with fat coating have been observed; it is assumed that these were caused by an increased fat content of the wastewater due to its content of industrial wastewater from food oil production. The cleaning interval for the automatic cleaning system (pressurized air) was set to 20 minutes, which in retrospect probably was too long. Figure 2 shows results from this measurement location. Left, the frequency distribution of the NH$_4$-N-concentration is shown, the two distribution maxima reflect dry and wet weather periods. The right figure shows the cumulative frequency of the relative residua between the ISE-signal and the laboratory measurements (Lange LCK 303) for spot ($n=62$) and daily composite samples ($n=54$), respectively. For 80% of the measurements the relative residua were lower than 21% for the 24h-average and 28% for the spot samples, respectively. As mentioned above, the main reason of the residua is assumed to be fat coating, since the majority of the residua were negative.

Figure 3 shows results from measurements in primary clarifier effluent. This measurement location is advantageous since the influence from disturbance-ions is still low, while...
risk of sensor fouling or build-up of coatings is considerably lower than in raw wastewater. The right figure shows the cumulative frequency of the relative residua between the ISE-signal and the laboratory measurements (FIA, 2h-composite samples, \( n = 72 \)). For 80% of the measurements the relative residua were lower than 19%.

Thomann et al. (2002) performed tests with an ISE-ammonium-sensor in the primary clarifier effluent and in the lab using standards and wastewater samples. The lab test resulted in a coefficient of variation of 1.8%. The trueness amounted as \(-0.1 \text{ mgNH}_4\text{-N/l}\) over the whole working range. Field tests gave a standard deviation of the differences of 0.62 \text{ mgNH}_4\text{-N/l} at an average measurement value of 19.1 \text{ mgNH}_4\text{-N/l}.

Ammonium and nitrate sensors applied within the biological stage of WWTPs often are used for the aeration control system. Again, the specific properties of ISE-probes are advantageous for an application in this stage. Compared to the mechanical treatment stage, the influence of disturbance-ions can be significantly higher. At plants connected to a combined sewer system or with considerable industrial influence, the potassium concentration in the aeration tank can vary in a range of more than 2 : 1 between dry weather and wet weather, while during dry weather the concentration is relatively constant. One way to compensate this disturbance is a simultaneous measurement of potassium linked with an automatic correction of the measured ammonium value.

Figure 4 shows results from measurements in the aeration tank. Again, the frequency distribution of the \( \text{NH}_4\text{-N}\)-concentration at the measurement location and the cumulative frequency of the relative residua between the ISE-signal (without K-compensation) and the laboratory measurements (Lange LCK 304) for spot samples \((n = 42)\) are shown. For 80% of the measurements the relative residua were lower than 28%. The main reason of the residua is assumed to be the influence from potassium; concentration variations between 20 \text{ mgK/l} and 50 \text{ mgK/l} have been observed at the measurement location. An ISE-NH\(_4\)-N-sensor capable of automatic potassium compensation was later installed at the same measurement location. First results look very promising, but the observation period was too short to include further conclusions into this paper.

In Figure 5 the results from the ISE-sensor tests within WWTP’s are summarized. For comparison reasons, also results achieved with a classical analyzer with sample filtration in an aeration tank (Analyzer_AT) are included. At this measurement location also an ISE-sensor was applied, which showed a significantly better trueness than the results shown in Figure 4. It is assumed that this was due to a substantially lower influence of potassium. Also it can be seen that the trueness of the ISE-sensor in the primary clarifier effluent is comparable to the trueness of the analyzer in the aeration tank.

Overall it can be concluded that ISE-NH\(_4\)-N-sensors enable continuous measurements in raw and mechanically treated wastewater with a relative trueness in the range of \( \pm 15\% \).

**Figure 4** NH\(_4\)-N-measurement in the aeration tank. Left: Frequency distribution of the NH\(_4\)-N-concentration at the measurement location. Right: Cumulative error frequency of an ISE-NH\(_4\)-N-sensor without K-compensation
to $\pm 20\%$. The main disturbance influence seems to be fat coating, which can be compensated by means of selecting a measurement location after the grit and grease chamber or by setting a short cleaning interval. Though it has to be considered, that mechanical stress of the membrane (also induced by the cleaning system) shortens the membrane lifespan. In the aeration tank good results have been achieved in case the influence of disturbance-ions was low or automatic disturbance-ion compensation was applied. Effluent monitoring seems to be less suitable since the noise due to disturbance-ions can be in the range of or even larger than the signal from the measurement-ions.

**Surface water monitoring**

Here, the measured concentrations are low compared to wastewater treatment plants, but also the water matrix is long term constant. The variation of concentration of the disturbance-ions is small and can therefore be compensated by means of sensor calibration. Another advantage of the application of ISE-probes is that the river monitoring stations can be built very compact and almost no auxiliary equipment is needed besides an air compressor for the air cleaning system.

For a monitoring station at the Danube River near Vienna (Pressl *et al.*, 2004), ISE-probes have been adapted to allow submersed operation (Figure 6, middle). This was necessary due to considerable variations of the water level over the course of the year, which were in the range of 7.5 m. In August 2002 heavy floods occurred while in summer 2003 the water level

**Figure 5** Cumulative error frequency of ISE-$\text{NH}_4$-N-sensors for different applications within WWTPs

**Figure 6** Compact water quality monitoring station at the Danube near Vienna and ISE-probe installation in the river Mur (right). Left: Water level too low (probes dry). Middle: Submersion depth approx. 1 m
decreased to an extent that the sensors fell dry. A different installation was possible for the river Mur in Graz; a snow discharge ramp of the municipality allowed a pendulum installation (Figure 6, right).

The monitoring station at the Danube River is also equipped with a submersible UV/VIS spectrometer; this enables parallel monitoring of nitrate with two different methods. Figure 7 shows that the two methods deliver equivalent results over the course of one week.

**Conclusions**

Ion-sensitive-probes have strong advantages in open channel installations; the dip-in assembly allows appended installation at an existing plant, short term installation for special monitoring campaigns or application in a mobile monitoring station. Their compact size also allowed application in a new type of surface water monitoring station, where all sensors were installed in-situ. Periodic calibration is an integral part of the measurement method in order to compensate drift of the measurement electrode. The influence of disturbance-ions is depending on the cross-sensitivities of the measurement membrane on the disturbance-ions and the ratio between the concentration of the measurement-ion and the variations of the concentration of the disturbance-ions. The method of calibration has to be selected depending on the chosen application; in the low concentration range non-linearities of the measurement electrode have to be considered.

ISE-sensors have proven to be applicable for many applications within water quality monitoring (sewer networks, WWTPs and surface water). In sewer networks it has to be considered that the NH₄-N/total-N-ratio can vary significantly in combined sewer networks; only the NH₄-N-fraction is measured by means of the ISE-sensor. Good results were achieved in the mechanical stage of WWTPs. For application in the biological stage and even more for effluent monitoring the influence of disturbance-ions can be significant. In case a high trueness is required automatic compensation of the main disturbance-ion is recommended; for effluent monitoring it can be considered mandatory since the noise due to disturbance-ions can be in the range of the signal from measurement-ions. Good results were also achieved for nitrate monitoring in rivers.

**References**


