Secrets revealed

Sea water: TN determination in the ultra trace range

TOC-V_{CSH} with TNM-1

The TN_b (total nitrogen) parameter originates from wastewater analysis applications as an alternative to the Kjeldahl determination. Just like the history of TOC sum parameter development, application areas for TN_b are rapidly increasing. In addition to the TN_b determination in the ppm concentration range for environmental applications, there is also increasing interest in determination of total nitrogen content in the ultra trace range, for instance in sea water analysis. For this purpose, Shimadzu has increased the maximum injection volume to 300 µL and subsequently lowered the detection limit.

Determination of the detection limit from blank value studies

In order to determine the detection limit x_{NG}, $\hat{N}$ parallel measurements were carried out on N independently prepared blank samples. From all obtained values, the mean $\bar{y}_B$ and the standard deviation s_y, was calculated.

$$x_{NG} = \frac{s_y}{m} \cdot t \cdot \sqrt{\frac{1}{\hat{N}} + \frac{1}{N}}$$

s_y = standard deviation of the N blank value measurements
N = number of blank values
$\hat{N}$ = number of parallel measurements
t = t-value (table with one-sided t-test, f = N - 1, P = 95 %)
m = increase in the calibration function

In order to calculate the detection limit for the total nitrogen determination, 7 blank water samples (obtained from a Millipore system) with injection volumes of 300 µL were measured (Table 1).

Sample	Area
1	1.089
2	1.105
3	1.117
4	1.072
5	1.02
6	1.034
7	1.074
Mean value	1.073
Standard deviation	0.035

Table 1: Results of the blank water measurements

Calculation of the detection limit: The t-value is 1.94, according to the one-sided t-test table (f = 7 - 1 and P = 95 %).

$$x_{NG} = \frac{0.035}{0.057} \cdot 1.94 \cdot \sqrt{\frac{1}{1} + \frac{1}{7}} = 1.3\ \mu g/L\ TN$$

This indicates clearly that the determination of the detection limit depends on the quality of the water used and on the calibration curve. Based on this fact, Shimadzu officially specifies a detection limit of 5 µg/L TN.

Calibration curve 1,000 µg/L TN

For the calibration curve, seven standard solutions were prepared in the range of 50 to 1,000 µg/L. The standard solution was a mixed standard of ammonium sulphate and potassium nitrate as recommended according to ENV 12260. Each point was measured three times at an injection volume of 300 µL.

Concentration (µg/l)	Area (mean value)
50	3.877
100	6.595
200	11.89
400	22.76
600	34.91
800	46.45
1000	57.85

Table 2: Data for the TN calibration curve 1,000 µg/L

Characteristic parameters

Calibration function:
y = 0.057 x + 0.668
Regression coefficient:
0.9998

TN determination in sea water

One of the application areas for trace-level TN determination is sea water analysis. Whether the special matrix (3.5 % salt solution) has an effect on the determination is debatable. In order to answer this question, the following tests were performed:

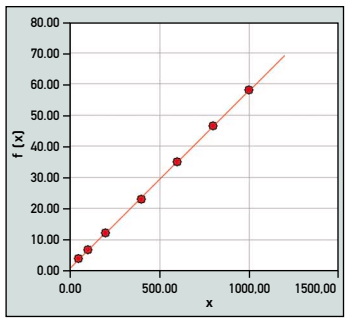

Figure 2: Calibration curve 1,000 µg/L

from water

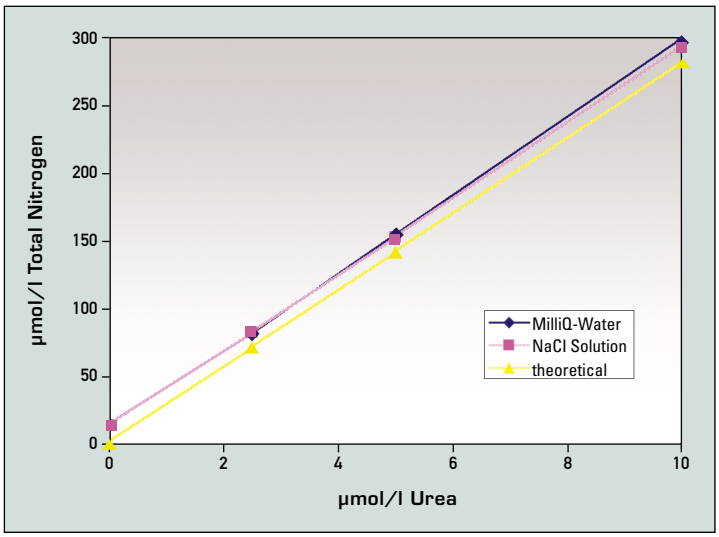

Figure 3: Determination of the urea solution

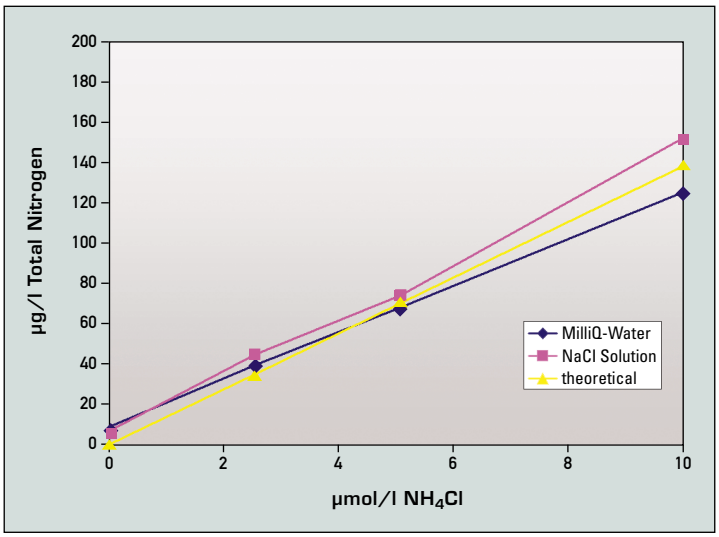

Figure 4: Determination of ammonium chloride solution

Determination of urea

Urea solutions at concentrations of 0, 2.5, 5 and 10 µmol/L in Millipore water and in NaCl solution (3.5 %) were prepared and subsequently measured. For this sample series, the maximum injection volume of 300 µL was used.

Figure 3 shows the results of these tests. The concentrations of the prepared urea solutions are plotted against the results of the TN determinations. Important here is that urea contains two nitrogen atoms. The yellow line represents the theoretically calculated results. As can be seen, there is no distinction between the Millipore water solution and the NaCl solution. Both lines are shifted parallel with respect to the yellow line around the blank value. The blank value therefore plays a decisive role in trace analysis.

Determination of the NH_4Cl solution

The experiments were repeated using ammonium chloride as standard. Figure 4 shows the results. A somewhat greater deviation can be seen compared with the previous test samples. Important is that ammonium chloride only contains one nitrogen atom, so the measuring range is even lower.

Determination of potassium nitrate solution at different injection volumes

For the measurement of sea water samples the effect of salt on the catalyst has to be taken into account. A high salt impact increases the maintenance requirements of the instrument. In this sample series the potassium nitrate solutions in NaCl solution were measured at different injection volumes. (Figure 5). The largest effect on the determination of the blank water samples was the injection volume. The deviation at an injection volume of 150 µL is larger. The remaining values, however, show very good results – for both the 150 µL as well as for the 300 µL injection volumes.

Conclusions

Using larger injection volumes of 300 µL, a determination limit of 5 µg/L can be attained. Whether this maximum injection volume is always useful depends on the type of application and the main objective of the user.

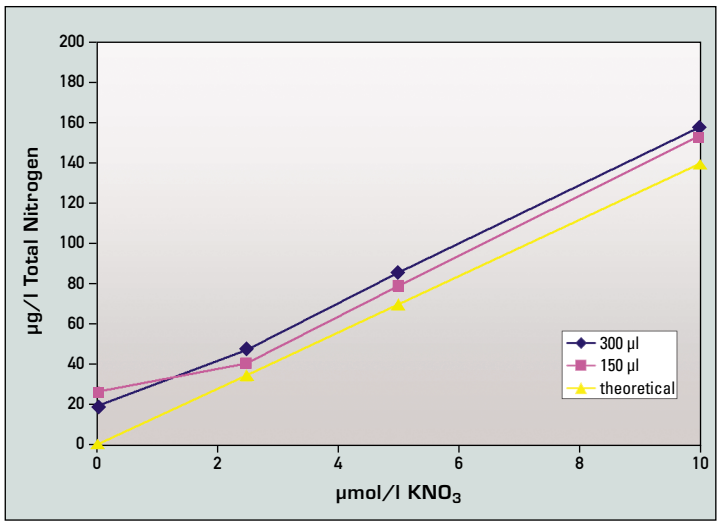

Figure 5: Determination of potassium nitrate solution at different injection volumes