

Reliable Online-Determination of TN_b -It's the 'inner qualities' that makes a difference -

The decisive criteria for the acquisition of an analytical instrument are reliability of operation and the accuracy of the measured results. The determination of the accuracy of the measured values is normally carried out by comparative and reference measurements.

The following essay is about the reliability of online-measurements of the sum parameter TN_b (Total bounded nitrogen). The precondition for the measurement is a complete and reproducible oxidation of the nitrogen compounds. This is guaranteed by the use of the catalytic oxidation with the proven platinum catalyst.

The increasing interest in sum parameters, especially in the online-analytic is a matter of fact. Since the TOC parameter has been well established the TN-parameter is becoming more and more important. Because of various oxidation states in which nitrogen can be present in organic and inorganic compounds, the nitrogen content should be determined exactly, even in mixtures of totally different nitrogen compounds. The determination of the ratio between ammonium and nitrate is of special interest

In 1998 Shimadzu introduced a combined TOC/TN as well as a TN online analyser onto the market. This instrument series oxidise the nitrogen compound in the water samples with the aid of the catalytic combustion (platinum catalyst) at 720 °C to nitrogen oxide (NO). After the reaction with ozone to activated nitrogen dioxide the quantification is performed by chemiluminescence.

Since 1996 the ENV 12260 "Determination of nitrogen – determination of bounded nitrogen after the combustion and oxidation to nitrogen dioxide and chemiluminescence detection" is published.

At the Shimadzu application laboratory several measurements are performed to test the TOCN 4100 according to the efficiency of the TN parameter and the ENV 12260.

1. Comparison of the measurements of ammonium and nitrate compounds

Calibration curves

No.	Standard	Concentration	Area*	Coefficient of variation
1a	Potassium nitrate	100mg/l	33264 ± 175	0,53%
1b	Potassium nitrate	10mg/l	34722 ± 85	0,24%
1c	Potassium nitrate	1mg/l	32095 ± 276	0,86%
2a	Ammonium sulphate	100mg/l	33882 ± 396	1,17%
2b	Ammonium sulphate	10mg/l	36325 ± 301	0,83%
2c	Ammonium sulphate	1mg/l	30010 ± 429	1,43%

*mean value of three injections

Results of the measurements

Sample solution	Calibration curve	Result	Coefficient of variation	Recovery rate
Potassium nitrate 100 mg/l	2a (NH ₄)	100,7 ± 1,14mg/l**	1,14%	100,7%
Potassium nitrate 10 mg/l	2b(NH ₄)	9,55± 1,14mg/l **	1,14%	95,5%
Potassium nitrate 1mg/l	2c (NH ₄)	0,991± 0,007mg/l**	0,71%	99,1%
Ammonium sulphate 100mg/l	1a (NO ₃)	102,5 ± 1,00mg/l **	0,97%	102,5%
Ammonium sulphate 10mg/l	1b (NO ₃)	10,67± 0,08mg/l****	0,75%	106,7%
Ammonium sulphate 1mg/l	1c (NO ₃)	1,017± 0,008mg/l****	0,76%	101,7%

**mean value of 5 injections

****mean value of 4 injections

There is a slight difference in the determination of ammonium and nitrate compounds. This is nevertheless acceptable.

To keep the difference as small as possible, the calibration of the instrument in the ENV 12260 is performed with a mixed standard composed of potassium nitrate and ammonium sulphate. This comparison was tested with the TOCN 4100 as well.

Calibration curves

No.	Standard	Concentration	Area*	Coefficient of variation
1	Potassium nitrate	50mg/l	33952 ± 140	0,41%
2	Ammonium sulphate	50mg/l	35005 ± 599	1,71%
3	Mixed Standard**	50mg/l	35324 ± 359	1,02%

*mean value of three injections

** mixture of potassium nitrate and ammonium sulphate

Results of the measurements

Sample solution 50mg/l	Calibration curve	Result***	Coefficient of variation	Recovery rate
Potassium nitrate	2 (NH ₄)	47.63 ± 0,29mg/l	0,60%	95,3%
Potassium nitrate	3 (Mix)	49,20 ± 0,62mg/l	1,25%	98,4%
Ammonium sulphate	1(NO ₃)	51,60 ± 0,30mg/l	0,57%	103,2%
Ammonium sulphate	3(Mix)	51,07 ± 0,44mg/l	0,87%	102,1%
Mixed standard	1(NO ₃)	50,05 ± 0,22mg/l	0,44%	100,0%
Mixed standard	2(NH ₄)	49.58 ± 0,29mg/l	0,58%	99,2%

*** Mean value of 6 injections

The good recovery rates of the ammonium and nitrate compounds could be improved by a calibration performed with a mixed standard.

2. Control check according to the ENV 12260

In the ENV 12260 the oxidability of the system is tested with a control check. For that, the TOCN 4100 was calibrated with a mixed standard of KNO_3 and $(\text{NH}_4)_2\text{SO}_4$ (100mg/l TN). The control sample is composed of glycine with a TN concentration of 100mg/l.

Control sample	Desired value	Measured value, mean value	Number of injections	Coefficient of variation	Recovery rate
Glycine	100mg/l	99.4±0.90mg/l	7	0.90%	99.4%

3. Recovery rates in comparison to the ENV 12260

Test sample	Recovery rates in % TOCN 4100	Recovery rates in % ENV 12260
Ammonium sulphate	100 – 106	95 – 100
Potassium nitrate	95 – 101	97 – 105
Sodium nitrate	99	101
Coffin	99	98
Glycine	99	95 – 99
Urea	101	92 – 99
Nicotine acid	102	98 – 102
Glutamine acid	96 – 100	97
Nitrophenoles	94 – 100	93 - 102
Nitraniline	100	91 – 100
Potassiumhexacyanoferrate (II)	99	92 – 96
Synthetic mixture 1)	99	-
Synthetic mixture 2)		

1) ($\text{NO}_3:\text{NH}_4:\text{Urea}:\text{Nicotin acid}$, ratio 1:1:2:1 sum 125 mg/l N

2) ($\text{NO}_3:\text{NH}_4:\text{Nitrophenol}:\text{Nitranilin}$, ratio 1:1:1:1 sum 50 mg/l N

The recovery rate of this control sample was 99,4 %. This result and the other recovery rates point out, that the in the ENV required temperature of more than 1000 °C is not necessary. The TOCN 4100 determines the common nitrogen compounds safely.

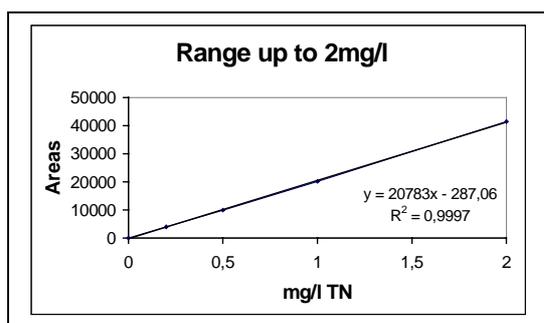
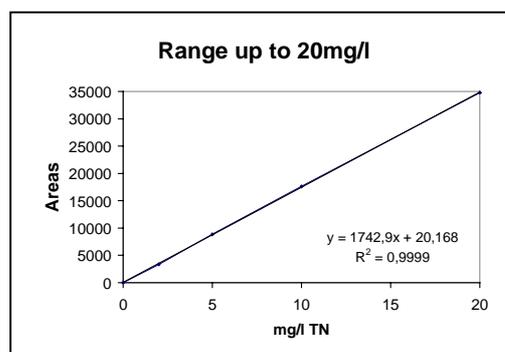
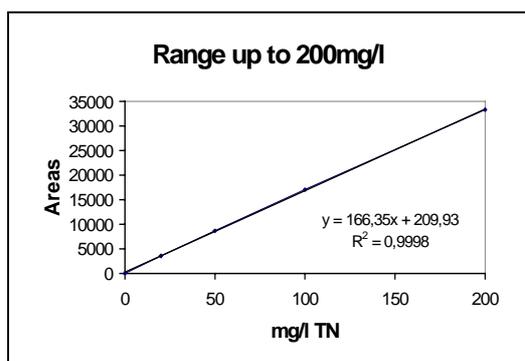
4. Simultaneous measurements of TOC and TN

The measurements were carried out with a combined TOC/TN analyser. This means the instrument is able to determine TOC and TN by just one injection. The simultaneous determination was proved by means of a standard solution of nicotine acid of 100 mg/l. Nicotine acid contains 58,5 % carbon and 11,4 % nitrogen.

The simultaneous determination delivered a TOC of 59,7 mg/l and a TN of 11,6 mg/l, corresponding to a recovery rate of 102 % for both parameters.

5. Linearity of the TOCN 4100

The TOCN has got a measuring range of up to 200 mg/l for TN. This range is guaranteed by different injection volumes and detector sensitivities. To prove the linearity of the chemiluminescence detector, the range was divided into three parts. Four standard solutions with different concentrations were measured in this range.



6. Discussion

The high quality of the results show, that the requirements concerning the determination of the TN with the TOCN 4100 can be fulfilled. The instrument delivers reliable values over the whole range and the recovery rates show that even totally different nitrogen compounds can be recovered.

Besides the excellent TN determination the online TOCN 4100 and TN 4100 have many features making them a reliable all-round partner in the online analytic field.

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