

Determination of total Nitrogen (TN)

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1. definitions
2. methods for the determination of TN
 - a. methods for the digestion step
 - b. methods for the detection/determination of $\text{NO}_3^-/\text{NH}_3/\text{NO}$
3. automated TN-analyser systems
4. norms
5. results of the 2. WRT for TN
6. adapted methods for TN

Determination of total Nitrogen (TN)

1. Definitions

Total Nitrogen:

$$\text{TN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+ + \text{N}_{\text{org}}$$

Dissolved inorganic Nitrogen:

$$\text{DIN} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$$

Dissolved organic Nitrogen:

$$\text{DON} = \text{TN} - \text{NO}_3^- - \text{NO}_2^- - \text{NH}_4^+$$

Kjeldahl Nitrogen:

$$\text{N}_{\text{Kjeldahl}} = \text{NH}_4^+ + \text{N}_{\text{org}}$$

$$\text{TN} = \text{N}_{\text{Kjeldahl}} + \text{NO}_3^- + \text{NO}_2^-$$

Determination of total Nitrogen (TN)

2. Determination methods for TN

always 2 steps:

1. digestion of the organic matter, which contains nitrogen, to NH_4^+ , NO_3^- or NO
2. detection/determination of $\text{NO}_3^-/\text{NH}_4^+/\text{NO}$

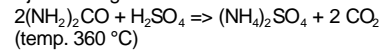
Determination of total Nitrogen (TN)

2a. Digestion methods

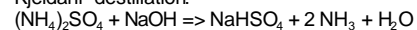
1. Kjeldahl:
 - a. determination of $\text{N}_{\text{Kjeldahl}}$ with Kjeldahl-digestion

reactions:

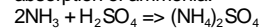
Kjeldahl- digestion:



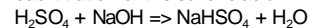
Kjeldahl- destillation:



absorption of ammonia:



backtitration of the sulfuric acid:



Determination of total Nitrogen (TN)

1. Kjeldahl:
 - a. determination of $\text{N}_{\text{Kjeldahl}}$ with Kjeldahl-digestion

problems:

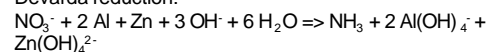
- chose of catalyst: HgO , Se (both very toxic!), $\text{CuSO}_4/\text{TiO}_2$
- interferences: NO_3^- (may be reduced to NH_4^+ or react with NH_4^+ to $\text{N}_2/\text{N}_2\text{O}$)
- H_2S (from org. sulphur) interferes the acidimetry of NH_3

Determination of total Nitrogen (TN)

1. Kjeldahl:
 - a. determination of TN with Devarda-reduction and Kjeldahl-digestion

reactions:

Devarda-reduction:



then Kjeldahl digestion

Determination of total Nitrogen (TN)

1. Kjeldahl (KJELD):
- b. determination of TN with Devarda-reduction and Kjeldahl-digestion

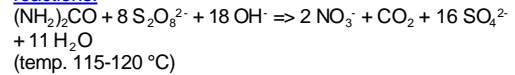
problems: (same as 1.a.)

- chose of catalyst: HgO, Se (both very toxic!), $\text{CuSO}_4/\text{TiO}_2$
- interferences: NO_3^- (may be reduced to NH_4^+ or react with NH_4^+ to $\text{N}_2/\text{N}_2\text{O}$)
- H_2S (from org. sulphur) interferes the acidimetry of NH_3

Determination of total Nitrogen (TN)

2. peroxodisulfate-digestion
- a. with H_3BO_3 und NaOH (Koroleff) (PSB)

reactions:



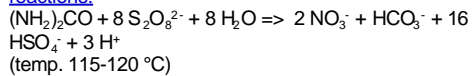
problems:

- normally no problems, if the concentration of peroxodisulfate is high enough
- some organic 5-rings with N are not digested

Determination of total Nitrogen (TN)

2. peroxodisulfate-digestion
- b. with H_2SO_4 (PSH)

reactions:



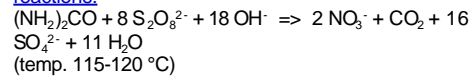
problems:

- normally no problems, if the concentration of peroxodisulfate is high enough
- sometimes problems with total oxidation of NH_4^+
- some organic 5-rings with N are not digested

Determination of total Nitrogen (TN)

2. peroxodisulfate-digestion
- c. with NaOH (PSOH)

reactions:



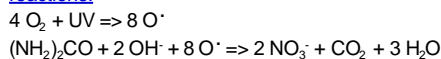
problems:

- possibility of NH_3 -loss concerning the high pH
- the concentration of peroxodisulfate must be high enough
- some organic 5-rings with N are not digested

Determination of total Nitrogen (TN)

3. UV-light-digestion

reactions:



problems:

- some organic substances are not digested by UV-light
- chose of the right UV-lamp

Determination of total Nitrogen (TN)

4. combined peroxodisulfate/UV-light-digestion

reactions:

see above

problems:

- some organic 5-rings with N are not digested

5. combined peroxodisulfate/mikrowave-digestion

reactions:

see above

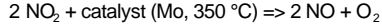
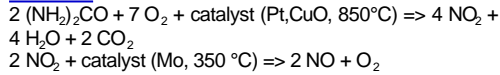
problems:

- some organic 5-rings with N are not digested

Determination of total Nitrogen (TN)

6. catalytic high temperature combustion to NO (CHML)

reactions:



problems:

- catalyst: the right combination of catalyst and oven temperature (for example Co, Cr, 850°C) has to be chosen

Determination of total Nitrogen (TN)

2b. methods for the detection/determination of NO₂/NH₃/NO

1. NO₂:

- spectrophotometry: UV-detection at 210-220 nm
- spectrophotometry: Cd-Reduction to NO₂ and detection as diazo-compound
- spectrophotometry: Cu/Hydrazin-Reduction detection as diazo-compound
- IC (with and without suppression)
- Ion capillary electrophoresis (CIA)

Determination of total Nitrogen (TN)

2. NH₄⁺:

- NH₃-distillation, acid absorption and back-titration (Kjeldahl)
- IC (with and without suppression)
- spectrophotometry: detection as indophenole-blue

3. NO:

- Chemoluminescence-detection (CHML)
reaction: $2 \text{NO} + \text{O}_3 \Rightarrow 2 \text{NO}_2 + \text{O}_2 + \text{h}\nu$

Determination of total Nitrogen (TN)

3. automated TN-analyser systems

- TN-Analyser** with catalytic high temperature combustion (A5) and chemoluminescence detection (B3a)
- Continuous flow Analyser** with peroxodisulfate- (A2) or combined peroxodisulfate/UV-digestion (A4) and spectrophotometric NO₃- determination (B1)

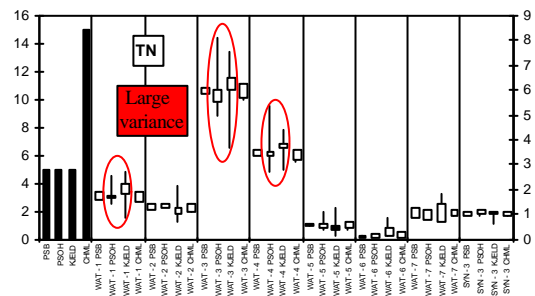
Determination of total Nitrogen (TN)

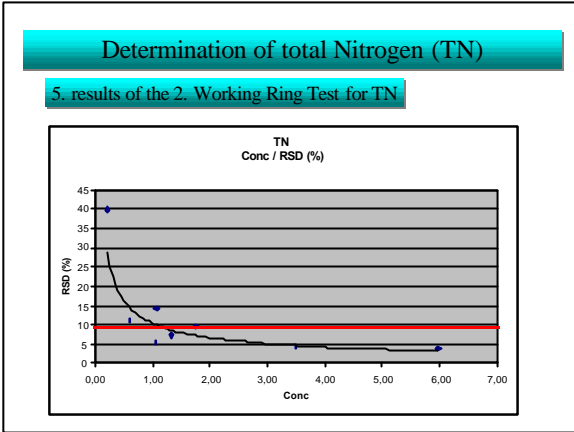
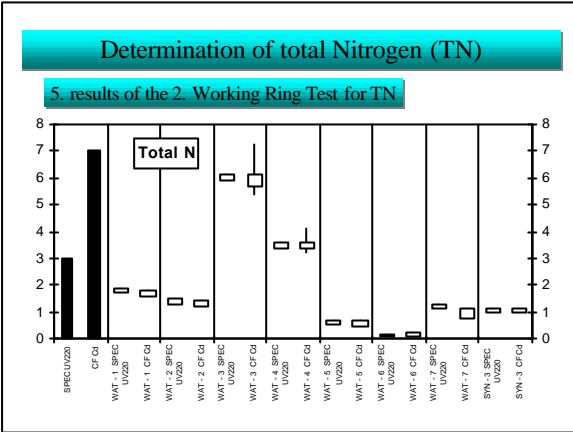
4. norms

- N_{Kjeld} in waters: DIN EN 25663 (Kjeldahl-digestion and distillation)
- TN in waters: DIN EN ISO 11905-1 or DIN 38409 H-36 (peroxodisulfate CF or FIA)
- TN in waters: DIN EN ISO 11905-2 or DIN 38409 H-34 (chemoluminescence)
- TN in Calciumchloride soil extracts: DIN ISO 14255 (peroxodisulfate CF or FIA)

Determination of total Nitrogen (TN)

5. results of the 2. Working Ring Test for TN





Determination of total Nitrogen (TN)

Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
57	CV-057	KJELD		7.14	4.33	2.59	2.52	2.00	2.97	1.50	1.01
14	SR-014	KJELD		6.46	3.78	2.14	1.23	0.73	1.07	0.50	0.36
3	SE-003	KJELD		2.77	2.48	0.52	0.84			0.50	0.15
2	NL-002	KJELD	IC CS	6.11	3.84	1.91	1.10	1.33	1.10	0.35	0.41
Mean				5.62	3.61	1.79	1.42	1.32	1.71	0.71	0.48
STD %				34.63	21.92	49.90	52.74	59.52	63.61	74.31	76.65
Expected values				5.98	3.46	1.77	1.32	1.10	1.06	0.58	0.18

conclusion:
the Kjeldahl method should be listed as a not permitted analytical method

Determination of total Nitrogen (TN)

Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
7	IT-007	PSB	SPEC UV220	5.94	3.41	1.79	1.44	1.22	1.12	0.57	0.11
28	IT-028	PSB	SPEC UV220	6.09	3.58	1.90	1.44	1.29	1.13	0.65	0.16
49	SI-049	PSB	SPEC UV220	6.01	3.49	1.77	1.34	1.20	1.07	0.61	0.16
Mean				6.01	3.49	1.82	1.41	1.24	1.11	0.61	0.14
STD %				1.25	2.44	3.76	4.13	3.92	2.96	6.57	20.74
Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
13	DE-013	PSB	CF Cj	5.93	3.49	1.60	1.22	0.92	0.99	0.54	0.00
48	DE-048	PSB	CF Cj	6.15	3.67	1.77	1.28	0.94	1.06	0.65	0.12
Mean				6.04	3.58	1.69	1.26	0.93	1.03	0.61	0.06
STD %				2.58	3.56	7.13	3.89	1.92	4.83	13.07	141.42
Expected values				5.98	3.46	1.77	1.32	1.10	1.06	0.58	0.18

conclusion:
the PSB method is a good digestion method and can also be used in a cont. flow system combined with NO₃ detection

Determination of total Nitrogen (TN)

Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
31	DE-031	PSH	CF Cj	6.02	3.45	1.82	1.35	0.85	1.09	0.57	0.10
44	DE-044	PSH	CF Cj	x	x	1.77	1.38	1.26	1.15	0.71	0.23
Mean				6.02	3.45	1.80	1.37	1.05	1.12	0.64	0.17
STD %						1.97	1.55	27.44	3.79	15.47	55.71
Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
23	EE-023	PSOH	CF Cj	5.54	3.45	1.73	1.38	0.80		0.58	0.27
39	FI-039	PSOH	CF Cj	5.96	3.53	1.76	1.34	1.11	1.05	0.61	0.18
33	NO-033	PSOH	CF Cj	5.98	3.46	1.75	1.41	0.94		0.54	0.15
56	DE-056	PSOH	CF Cu Hyd	5.80	3.42	1.73	1.32	0.95	1.13	0.57	0.15
Mean				5.82	3.47	1.74	1.35	0.95	1.09	0.59	0.19
STD %				3.49	1.34	0.95	2.96	13.33	5.19	5.02	30.29
Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
73	RU-073	PSOH	SPEC Cj	9.28	6.45	2.99	1.42	1.20	1.57	1.44	0.26
Mean				9.28	6.45	2.99	1.42	1.20	1.57	1.44	0.26
STD %											
Expected values				5.98	3.46	1.77	1.32	1.10	1.06	0.58	0.18

conclusion:
the PSH and the PSOH method are good digestion methods in a cont. flow system combined with NO₃ detection

Determination of total Nitrogen (TN)

Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
12	CH-012	CHML		x	3.27	1.52	1.19	1.00	0.95	0.56	0.18
4	DE-004	CHML		5.89	3.52	1.79	1.39	1.16	1.11	x	0.00
27	DE-027	CHML		6.40	3.27	1.80	1.43	1.13	1.00	0.53	0.00
8	FR-008	CHML		6.10	3.40	1.83	1.29	1.15	1.14	0.71	0.34
52	DE-052	CHML		6.20	3.50	2.00	1.40	1.20		0.70	0.30
64	DE-064	CHML		5.73	3.35	1.68	1.18			1.00	0.53
65	DE-065	CHML		5.71	3.21	1.77	1.21	1.10	0.99	0.61	0.26
77	DE-077	CHML		6.21	3.59	1.88	1.29	0.99	1.05	0.54	0.13
9	DK-009	CHML		5.70	x	1.63	1.23	0.97	1.04	0.52	0.15
3	FR-003	CHML		6.33	3.44	2.05	1.45	1.14	1.00	0.61	0.19
32	GB-032	CHML		5.71	3.46	1.60	1.31	1.07	1.07	0.60	0.17
26	IT-026	CHML		5.92	3.42	1.74	1.21	0.89	1.09	0.58	0.20
55	LV-055	CHML		6.00	3.72	1.80	1.47	1.06		0.73	0.29
53	NL-053	CHML		6.01	3.31	x	x	1.06		x	
Mean				6.09	3.42	1.75	1.31	1.07	1.04	0.60	0.18
STD %				4.07	4.17	8.42	8.04	8.27	5.56	12.40	58.45
Expected values				5.98	3.46	1.77	1.32	1.10	1.06	0.58	0.18

conclusion:
the CHML method is a good digestion+ detection method

Determination of total Nitrogen (TN)

Lab.#	Lab.code	Method	Method	WAT - 3	WAT - 4	WAT - 1	WAT - 2	WAT - 7	SYN - 3	WAT - 5	WAT - 6
36	RU036		CIA	5,63	3,78	1,47	1,28	x	0,99	0,55	0,13
38	RU038		CIA	5,80	3,40	1,60	1,30	1,20	1,02	0,63	0,24
Mean				5,72	3,59	1,54	1,29	1,20	1,01	0,59	0,19
STD %				2,10	7,48	5,99	1,10		2,11	9,59	42,04
Expected values				5,98	3,46	1,77	1,32	1,10	1,06	0,58	0,18

conclusion:
the CIA method (ion capillary electrophoresis) is also a usable detection method

Determination of total Nitrogen (TN)

6. adapted methods for TN

1. TN-Analyser with chemoluminescence detection (CHML)
2. Peroxodisulfate digestion (PSB, PSH, PSOH), also in combination with UV-light and in continuous flow systems combined with NO₃- or UV 220-detection