



Application Note No. 235/2016

Ammonium, nitrate, and total nitrogen determination in fly ash

KjelMaster K-375, SpeedDigester K-439, DuMaster D-480



3. Chemicals and Materials

Chemicals for total Kjeldahl nitrogen, ammonium and nitrate determination:

- Sulfuric acid conc 98 %, Merck (1007482500)
- Missouri, BUCHI Kjeldahl Tablet (11057982)
- Sodium hydroxide 32 %, Brenntag (81980-452)
- Boric acid (H_3BO_3) 4 %, 400 g boric acid, Brenntag (80948-155) diluted to 10 L with deionized water, pH adjusted to 4.65
- Sulfuric acid 0.25 mol/L, Riedel-de Haen (53555)
- Neutralization solution for the Scrubber: 600 g sodium carbonate, calcined, technical, Synopharm (0179420) about 2 mL ethanol and a spatula tip of bromthymol blue, Fluka (18460) diluted to 3 L with distilled water

Chemicals for total nitrogen determination according to Dumas:

- L-Aspartic acid, reagent grade $\geq 98\%$ (TLC), Sigma A9256-100G (Aspartic acid is used to determine the daily factor)

For a safe handling, please pay attention to all corresponding MSDS.

4. Samples

Fly ash is a by-product of the combustion of pulverized coal and is composed of small particles. The composition of the fly ash vary considerably, however, all fly ash contain substantial amounts of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and calcium oxide (CaO).

Nowadays, air pollution control standards require a separation of flue gas before being released to the atmosphere. For this, the incurred fly ash can be reused e.g. as fill material or raw material for cement and concrete [5].

The fly ash sample analyzed in this application note was provided from a pulp mill containing organic and inorganic (ammonium nitrate and ammonium sulfate) nitrogen compounds.

5.1. Total Kjeldahl Nitrogen determination

Digestion was performed using the SpeedDigester K-439. To predict the optimum digestion parameters, the KjelOptimizer App was used [6]. The determination of total Kjeldahl nitrogen in fly ash was performed according to the following procedure:

1. Weigh in sample in a Kjeldahl weighing boat and place it in a 300 mL sample tube. The weights of the analysed samples are shown in Table 1.
2. Prepare additional blanks (without sample).

Table 1: Weight for each sample.

Sample	Weight [g]
Fly ash sample for total Kjeldahl nitrogen 1	0.5782
Fly ash sample for total Kjeldahl nitrogen 2	0.5690
Fly ash sample for total Kjeldahl nitrogen 3	0.5756
Fly ash sample for total Kjeldahl nitrogen 4	0.6094

3. Add a Missouri tablet and 10 mL of sulfuric acid (conc. 98 %) to each tube.
4. Connect the Scrubber K-415 to the K-439 for absorbing acidic fumes formed during digestion.
5. Insert the rack with the samples into the K-439 and start the digestion according to the parameters listed in table 2.

Table 2: Temperature profile for digestion with the K-439.

Step	Temperature [°C]	Time [min]
Preheat	350	-
1	480	120
Cool down	-	30

NOTE: If the liquid inside the sample tube is not clear and blue-green, digest for additional 15 min at 480° C.

6. Let the samples cool down to room temperature.
7. Connect the sample tubes to the KjelMaster K-375.
8. Distill and titrate the samples according to the parameters listed in table 3. Start with the blank samples.

Table 3: Parameters for TKN distillation and titration with the KjelMaster K-375.

H ₂ O volume	40 mL	Sensor type	Potentiometric
NaOH (32 %) volume	45 mL	Titration mode	Standard
Reaction time	5 s	Measuring mode	Endpoint pH
Distillation mode	Fixed time	Endpoint pH	4.65
Distillation time	180 s	Stirrer speed titration	7
Stirrer speed distillation	5	Titration start volume	0 mL
Steam output	100 %	Titration algorithm	Optimal
Titration type	Boric acid	Aspiration sample tube	No*
Receiving solution vol.	60 mL	Aspiration receiving vessel	Yes
Titration solution	H ₂ SO ₄ 0.25 mol/L		

*NOTE: Because of the solid particle residues, the sample tube was not aspirated after distillation.

5.2. Ammonium determination (no digestion)

The not digested fly ash sample is suspended in water fixed to the K-375 and further alkalized. The alkalization with sodium hydroxide converts the ammonium (NH_4^+) to volatile ammonia (NH_3). The direct distillation of ammonium in fly ash was determined as follows:

1. Weight in each sample in a 500 mL sample tube as described in table 4.

Table 4: Weight for each sample.

Sample	Weight [g]
Ammonium and nitrate Sample 1	0.8205
Ammonium and nitrate Sample 2	0.8588
Ammonium and nitrate Sample 3	0.8173
Ammonium and nitrate Sample 4	0.8789

2. Connect the sample tube to the K-375 distillation unit.
3. Distill and titrate the sample according to the parameters listed in Table 5. Start with the blank samples.

Table 5: Parameters for NH_3 distillation and titration with the KjelMaster K-375.

H_2O volume	10 mL	Sensor type	Potentiometric
NaOH (32%) volume	20 mL	Titration mode	Standard
Reaction time	5 s	Measuring mode	Endpoint pH
Distillation mode	Fixed time	Endpoint pH	4.65
Distillation time	240 s	Stirrer speed titration	7
Stirrer speed distillation	5	Titration start volume	0 mL
Steam output	100 %	Titration algorithm	Optimal
Titration type	Boric acid	Aspiration sample tube	No
Receiving solution vol.	50 mL	Aspiration receiving vessel	Yes
Titration solution	H_2SO_4 0.25 mol/L		

Important: After distillation place the distilled sample into a sample rack and let it cool down to ambient temperature. After cooling down, the nitrate determination according to Devarda (described below) is performed using the same samples again.

5.3. Nitrate determination (Devarda method)

To save time and sample, the same sample already analysed for its ammonium content was used for nitrate determination. Therefore, the sample from ammonium determination was cooled down to room temperature and then the Devarda alloy was added. The procedure for nitrate determination was:

1. Add ± 3 g Devarda alloy to the cooled down sample tube of the ammonium determination.
2. Connect the sample tube to the K-375 distillation unit.

NOTE: When the Devarda alloy is added, immediately connect the sample tube to the distillation unit and start distillation method.

3. Distill and titrate the samples according to the parameters listed in Table 6. Start with the blank samples.

Table 6: Parameters for $\text{NO}_2 / \text{NO}_3$ distillation and titration with the KjelMaster K-375.

H_2O volume	0 mL	Sensor type	Potentiometric
NaOH (32%) volume	20 mL	Titration mode	Standard
Reaction time	300 s	Measuring mode	Endpoint pH
Distillation mode	Fixed time	Endpoint pH	4.65
Distillation time	300 s	Stirrer speed titration	7
Stirrer speed distillation	5	Titration start volume	0 mL
Steam output	100 %	Titration algorithm	Optimal
Titration type	Boric acid	Aspiration sample tube	No
Receiving solution vol.	50 mL	Aspiration receiving vessel	Yes
Titration solution	H_2SO_4 0.25 mol/L		

5.4. Total nitrogen determination (Dumas method)

The determination of total nitrogen in fly ash was performed according to the following procedure:

1. Weight in around 250 mg sample on the foil and press it with the manual pressing tool (Figure 2).
2. Check the tightness of the packed sample visually. The tin foil must be wrapped completely around the whole sample.
3. Start or “wake-up” the DuMaster D-480, check the maintenance intervals of the instrument.



Figure 2: Manual pressing tool for tin foil packed samples.

NOTE: Use the “sleep-mode” but do not switch off the instrument if the pause time is less than 5 days.

4. Check the parameters of the DuMaster D-480; all parameters (temperature, flow, pressure) must be green colored.
5. Run three blanks (empty position), use the key word “Blnk” with the method “Blank with O₂” to check the purity of the gases and the performance of the instrument.
6. Run one “RunIn” with the daily factor reference (typically 200-250 mg aspartic acid) as conditioning using the method “250mgStandard”.
7. Run minimum two daily factor references each, 200-250 mg aspartic acid by using a keyword “aspartic acid”.
8. Run the samples using the method “250mgStandard”.

NOTE: The blank area should be <100.

NOTE: The daily factor should be within 0.9 - 1.1 for aspartic acid.

6. Results

The results of the determination of total Kjeldahl nitrogen, ammonium and nitrate in fly ash are presented in tables 7, 8 and 9, respectively. Table 11 shows the summary of all determinations and the calculations of the different nitrogen sources measured with KjelMaster K-375.

6.1. Total Kjeldahl nitrogen

In the following table 7 the values, mean value and relative standard deviation (Rsd) of the total Kjeldahl nitrogen determination are listed. The mean blank volume (V_{Blank}) was 0.119 mL ($n = 3$).

Table 7: Results of the total Kjeldahl nitrogen determination.

Kjeldahl method	m_{Sample} [g]	V_{Sample} [mL]	N [%]
Sample 1	0.5782	5.356	6.344
Sample 2	0.5690	5.158	6.203
Sample 3	0.5756	5.243	6.235
Sample 4	0.6094	5.576	6.272
Average [%]	–	–	6.263
Rsd [%]	–	–	0.839

For the total Kjeldahl nitrogen the mean value of four sample determinations was 6.26 % (0.84 % Rsd).

The digestion step before distillation, converts nitrogen from organic origin to ammonium. As the analyzed fly ash sample contained also ammonium of inorganic origin, e.g. ammonium nitrate, both, ammonium from organic and inorganic origin are co-distilled by the total Kjeldahl nitrogen method.

To determine the inorganic ammonium only, a further ammonium determination without digestion is necessary. Hence, the difference between total Kjeldahl nitrogen and directly distilled ammonium will be the organic sourced nitrogen of the sample (e.g. glycine).

6.2. Total inorganic nitrogen

Tables 8 and 9 present the values, mean values and Rsd of the direct ammonium and nitrate determination. The mean blank volume (V_{Blank}) for ammonium analysis was 0.087 mL ($n = 3$), for nitrate (V_{Blank}) was 0.136 mL ($n = 3$).

Table 8: Results of the ammonium nitrogen determination.

Ammonium	m_{Sample} [g]	V_{Sample} [mL]	N [%]
Sample 1	0.8205	5.651	4.749
Sample 2	0.8588	5.932	4.766
Sample 3	0.8173	5.586	4.712
Sample 4	0.8789	6.140	4.823
Average [%]	–	–	4.762
Rsd [%]	–	–	0.842

Table 9: Results of the nitrate nitrogen determination.

Devarda after ammonium	m_{Sample} [g]	V_{Sample} [mL]	N [%]
Sample 1	0.8205	3.165	2.585
Sample 2	0.8588	3.346	2.618
Sample 3	0.8173	3.228	2.650
Sample 4	0.8789	3.495	2.677
Average [%]	–	–	2.632
Rsd [%]	–	–	1.298

6.3. Total nitrogen determination according to Dumas method

Table 10 shows the values, mean values and Rsd of the total nitrogen determination according to Dumas.

Table 10: Results of the total nitrogen determination in fly ash according to the combustion method (dumas).

Total Nitrogen (DuMaster)	m_{Sample} [g]	N [%]
Sample 1	0.0947	9.516
Sample 2	0.0849	9.429
Sample 3	0.0954	9.725
Sample 4	0.1072	9.953
Average [%]	-	9.656
Rsd [%]	-	2.422

6.4. Summary of results

The following table 11 shows the summary of the nitrogen determination using Kjeldahl and Dumas equipment.

Table 11: Summary of all determinations and the calculations of the different nitrogen sources measured with KjelMaster K-375

Summary	N [%]	Rsd [%]
Total Kjeldahl nitrogen (organic nitrogen, NH_3)	6.263	0.839
Ammonium (NH_3)	4.762	0.842
Devarda after ammonium (NO_3)	2.632	1.298
Calculations		
Organic compound (Total Kjeldahl nitrogen - ammonium)	1.501	
Ammonium (NH_3)	4.762	0.842
Devarda after ammonium (NO_3)	2.632	1.298
Total nitrogen using Kjeldahl apparatus	8.895	
Total nitrogen according to Dumas method	9.656	2.422

For the determination of total Kjeldahl nitrogen a digestion step is necessary before distillation. The obtained result (6.263 % N) includes nitrogen from organic origin plus free inorganic nitrogen. For the determination of the organic sourced nitrogen only, the free ammonia amount must be determined by direct distillation in an additional step.

The difference between the total Kjeldahl nitrogen and ammonium determination is the real organic nitrogen content.

The nitrate determination (Devarda method) was performed after the ammonium distillation. In this case time and sample can be reduced.

The summary of the organic compound, ammonium and nitrate gives the result of the total nitrogen using Kjeldahl apparatus (8.90 % N). The total nitrogen according to Dumas method (9.66 % N) was slightly higher than the Kjeldahl result (+ 0.76 %).

The results from table 11 are shown as an overview in Figure 3. The total nitrogen content using the Kjeldahl apparatus (8.90 %) could be summarized from the individual compounds organic nitrogen (1.501 %), ammonium (4.762 %) and nitrate (2.632 %). With the DuMaster only the total nitrogen content could be determined (9.565 %).

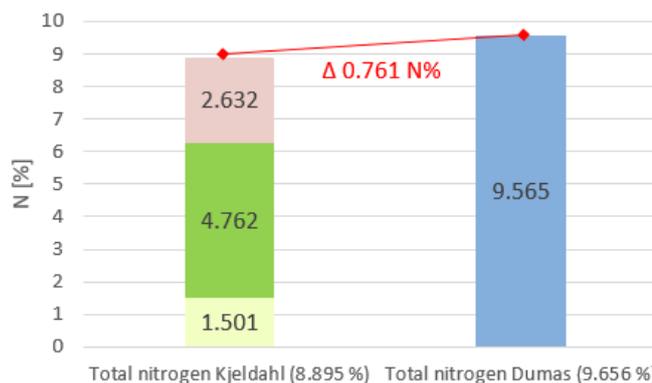


Figure 3: Summary of the nitrogen concentration measured in fly ash

7. Discussion

Regarding the total nitrogen measured by Kjeldahl (8.90 %) and Dumas (9.66 %) a difference of 0.76 % nitrogen between these two methods was detected. In most cases, results obtained by the Dumas method are slightly higher than those obtained by the Kjeldahl method [7, 8].

This is due to the fact that the Dumas method measures all nitrogen compounds, whereas the Kjeldahl method measures only a part of it (organic nitrogen, ammonium and nitrate).

With special applications using the Kjeldahl apparatus (Devarda method) also other inorganic compounds (nitrate) can be measured.

Hence, the difference of 0.76 % nitrogen indicates that further inorganic nitrogen compounds than ammonium and nitrate are contained.

8. Conclusion

Using the KjelMaster K-375 and applying a smart workflow, fly ash is analyzed for its nitrogenous compounds. Ammonium from organic and inorganic origin can be discriminated, nitrate is exactly determined, and the total nitrogen content analyzed.

Comparison of the determined total Kjeldahl nitrogen to the nitrogen content obtained using the DuMaster D-480 clearly shows that additional inorganic compounds are contained in the analyzed sample.

9. References

[1] DIN38406-E5-2: German standard methods for the examination of water, waste water and sludge; cations (group E); determination of ammonia-nitrogen (E 5)

[2] AOAC Official Method 892.01 Nitrogen (Ammoniacal and Nitrate) in Fertilizers

[3] DIN CEN/TS 15476:2006 Fertilizers- Determination of nitric and ammoniacal nitrogen according to Devarda (German version)

[4] Application Note No. 116 / 2013; Nitrogen determination in sodium nitrate

[5] <http://flyash.com/about-fly-ash/>

[6] KjelOptimizer App: <http://www.buchi.com/en/service-support/scientific-mobile-apps>

[7] ISO 14891:2002: Verbrennungsverfahren nach Dumas (Routineverfahren) (ISO 14891:2002)

[8] ISO 16634-1:2008 Bestimmung des Gehaltes an Gesamtstickstoff mit dem Verbrennungsverfahren nach Dumas und Berechnung des Gehaltes an Rohprotein – Teil 1: Ölsaatschrote und Futtermittel