Application Note No. 112/2013
Nitrogen & urea determination in cosmetics

KjelDigester K-449, KjelMaster K-375 with KjelSampler K-376:
Nitrogen and Urea Determination in Cosmetics according to the Kjeldahl Method

1 Introduction

An easy and reliable method for the determination of nitrogen and urea in cosmetics, is introduced below. Urea is widely used as an active ingredient in creams and lotions.The samples are digested using the KjelDigester K-449. The distillation and boric acid titration are performed with the KjelMaster K-375 with KjelSampler K-376. The combination of the new KjelDigester and the KjelMaster system K-375/K-376 increases the sample throughput.

2 Equipment

- KjelDigester K-449 (the parameters used are also valid for K-446)
- Scrubber K-415 TripleScrub ^{ECO}
- KjelMaster K-375 with KjelSampler K-376
- Analytical balance (accuracy ± 0.1 mg)

3 Chemicals and Materials

Chemicals:

- Sulfuric acid conc 98 %, Merck (1007482500)
- Titanium, BUCHI Kjeldahl Tablet (11057980)
- Sodium hydroxide 32 %, Brenntag (81980-452)
- Boric acid 4 %, 400 g boric acid, Brenntag (80948-155) diluted to 10 L with deionized water, pH adjusted to 4.65
- Sulfuric acid 0.1 mol/L, Fluka (35357)
- 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
- Glycine, assay 99.7 %, Merck (1.04201.0100)

For a safe handling please pay attention to all corresponding MSDS!

Samples:

- Face cream with a labelled urea content of 5 %
- Repair ointment with a labelled urea content of 10 %
- Foot cream with a labelled urea content of 18 %

The samples were purchased at a local drugstore.

4 Procedure

The determination of nitrogen and urea in cosmetics includes the following steps:

- Digestion of the sample, using K-449 (K-446 respectively)
- Distillation and titration of the sample, using KjelMaster system K-375/K-376

4.1 Digestion method – glycine (verification of the method)

1. Start the KjelDigester K-449 according to the parameters listed in Table 2
2. Place 0.1 g glycine in a 300 mL sample tube
3. Add 2 Titanium tablets and 15 mL of sulfuric acid (conc. 98 %)
4. Prepare additional blanks, chemicals without sample
5. Connect the Scrubber K-415 to the K-449 for absorbing the acid fumes created during digestion
6. Insert the rack with the samples into the cooling position and mount the suction module onto the samples, immediately start the digestion according to the parameters listed in Table 2.
7. Let the samples cool down when the digestion is completed.

4.2 Digestion method – samples

1. Start the KjelDigester K-449 according to the parameters listed in Table 2
2. Place each sample in a 300 mL sample tube as described in Table 1

Table 1: Weight for each sample

Sample	Weight [g]
Face cream	0.8
Repair ointment	0.6
Foot cream	0.4

3. Add 2 Titanium tablets and 15 mL of sulfuric acid (conc. 98%) to each tube
4. Prepare additional blanks, chemicals without sample
5. Connect the Scrubber K-415 to the K-449 for absorbing acid fumes created during digestion
6. Insert the rack with the samples into the cooling position and mount the suction module onto the samples, immediately start the digestion according to the parameters listed in Table 2.

Table 2: Temperature profile for digestion with the K-449

Step	Temperature [°C]	Time [min]
1	300	0
2	420	90
Cooling	–	35

NOTE: If the liquid inside the sample tube is not clear and blue-green, digest for additional 15 min at 420 °C.

7. Let the samples cool down when the digestion is completed.

4.3 Distillation and titration

Distill the samples according to the parameters listed in Table 3.

Table 3: Distillation and titration with the KjelMaster system K-375/K-376

Method parameters KjelMaster K-375

H_2O volume	50 mL	Titration solution	H_2SO_4 0.1 mol/L
NaOH volume	60 mL	Sensor type	Potentiometric
Reaction time	5 s	Titration mode	Online
Distillation mode	Fixed time	Titration start time	120 s
Distillation time	180 s	Measuring mode	Endpoint pH
Stirrer speed distillation	5	Endpoint pH	4.65
Steam output	100 %	Stirrer speed titration	7
Titration type	Boric acid	Titration start volume	0 mL
Receiving solution vol.	60 mL	Titration algorithm	Optimal

NOTE: The sample throughput for this application was increased by using the Titration mode “Online”.

4.4 Calculation

The results are calculated as a percentage of nitrogen. In order to calculate the urea content of the sample, the nitrogen content is multiplied with a specific urea factor. The following equations (1), (2), and (3) are used to calculate the results. For the reference substance, the purity of the glycine is considered in equation (4).

$$w_N = \frac{(V_{Sample} - V_{Blank}) \cdot z \cdot c \cdot f \cdot M_N}{m_{Sample} \cdot 1000} \quad (1)$$

$$\%N = w_N \cdot 100\ \% \quad (2)$$

$$\%U = w_N \cdot UF \cdot 100\ \% \quad (3)$$

$$\%N_{Gly} = \frac{\%N \cdot 100}{P} \quad (4)$$

w_N : weight fraction of nitrogen

V_{Sample} : amount of titrant for the sample [mL]

V_{Blank} : mean amount of titrant for the blank [mL]

z : molar valence factor (1 for HCl, 2 for H_2SO_4)

c : titrant concentration [mol/L]

f : titrant factor (for commercial solutions normally 1.000)

M_N : molecular weight of nitrogen (14.007 g/mol)

m_{Sample} : sample weight [g]

1000 : conversion factor [mL/L]

%N : percentage of weight of nitrogen

$\%N_{Gly}$: percentage of weight of nitrogen corrected for the purity of reference substance glycine [%]

%U : percentage of weight of urea

P : purity of the reference substance glycine [%]

UF : specific urea factor (2.144 for urea)

5 Results

5.1. Recovery of glycine

The results of nitrogen determination and recovery for urea analysis (assay > 99.7 %) are presented in Table 4. The nominal value of glycine is 18.66 % nitrogen. The recoveries are within the specification of ≥ 98 %. [1]

Table 4: Results of the recovery of nitrogen in glycine

Glycine	m_{Sample} [g]	V_{Sample} [mL]	$\%N_{Gly}$	Recovery [%]
Sample 1	0.1113	7.563	18.62	99.8
Sample 2	0.1087	7.402	18.65	100.0
Sample 3	0.0995	6.807	18.70	100.2
Sample 4	0.0972	6.620	18.60	99.7
Average [%]	–	–	18.64	99.9
Rsd [%]	–	–	0.2	0.2

The mean blank volume (V_{Blank}) was 0.187 mL (n = 4).

5.2 Urea determination in cosmetics

The results of the determination of nitrogen and urea contents in cosmetics are presented in Table 5 – 7.

Table 5: Results of the determination of nitrogen and urea in face cream (urea content 5 %)

Face cream	m_{Sample} [g]	V_{Sample} [mL]	%N	%U
Sample 1	0.8096	7.251	2.444	5.24
Sample 2	0.8056	7.187	2.434	5.22
Sample 3	0.7697	6.936	2.457	5.27
Sample 4	0.7953	7.232	2.482	5.32
Average [%]	–	–	2.454	5.26
Rsd [%]	–	–	0.8	0.8

The mean blank volume (V_{Blank}) was 0.187 mL (n = 4).

Table 6: Results of the determination of nitrogen and urea in repair ointment (urea content 10 %)

Repair ointment	m_{Sample} [g]	V_{Sample} [mL]	%N	%P
Sample 1	0.5817	9.889	4.673	10.0
Sample 2	0.6032	10.263	4.680	10.0
Sample 3	0.6998	11.914	4.695	10.1
Sample 4	0.6319	10.719	4.669	10.0
Average [%]	–	–	4.679	10.0
Rsd [%]	–	–	0.2	0.2

The mean blank volume (V_{Blank}) was 0.187 mL (n = 4).

Table 7: Results of the determination of nitrogen and urea in foot cream (urea content 18 %)

Foot cream	m_{Sample} [g]	V_{Sample} [mL]	%N	%U
Sample 1	0.4138	12.894	8.603	18.4
Sample 2	0.4351	13.583	8.625	18.5
Sample 3	0.4056	12.722	8.658	18.6
Sample 4	0.4058	12.715	8.649	18.5
Average [%]	–	–	8.634	18.5
Rsd [%]	–	–	0.3	0.3

The mean blank volume (V_{Blank}) was 0.187 mL (n = 4).

6 Conclusion

The determination of nitrogen and urea in cosmetics using the KjelDigester K-449 and KjelMaster system K-375/K-376 provides reliable and reproducible results. These results correspond well to the labelled values of the different creams with low relative standard deviation (rsd). The recovery with glycine was 99.9 % (rsd = 0.2 %), which was within the specification of ≥ 98 % [1].
With the KjelDigester K-449 the digestion process (including preheating, digestion and cooling) is very fast and is fully automated. Together with the fully-automatic KjelMaster system K-375/K-376, the time to result is ignificantly reduced and it offers fully walk-away convenience.

7 References

[1] Application Note 100/2013, Nitrogen Determination in Reference Substances – Operational Quality Check Procedure

Kjeldahl Calculator App

Operation Manual of KjelDigester K-446/K-449
Operation Manual of Scrubber K-415
Operation Manual of KjelMaster system K-375/K376