Application Note No. 117 / 2013
Ammonia determination in hair dye

KjelMaster K-375 with KjelSampler K-376:
Ammonia determination in hair dye with direct distillation

1. Introduction

An easy and reliable method for the determination of nitrogen and ammonia in hair dye is described in this application note. The distillation and boric acid (2%) titration are performed with the KjelMaster K-375 with KjelSampler K-376.

2. Equipment

- KjelMaster K-375 and KjelSampler K-376
- Analytical balance (accuracy ± 0.1 mg)
- 300 mL glass tubes
- Devarda splash protector in case of foaming

3. Chemicals and Materials

Chemicals:

- Sulfuric acid 0.25 mol/L (0.5 N), Fluka (35355)
- Sulfuric acid 0.1 mol/L (0.2 N), Fluka (35357)
- Boric acid 2%, 100 g boric acid Brenntag (80948-155) diluted to 5 L with deionized water; Adjust the pH to 4.65 with 10% NaOH
- Sodium hydroxide, 32%, Brenntag (81980-452)
- Stearic acid in case of foaming, Fluka (85683)

Material:

- Plastic syringe 10 mL (BD Discartit II, VWR, 613-3952)

Samples:

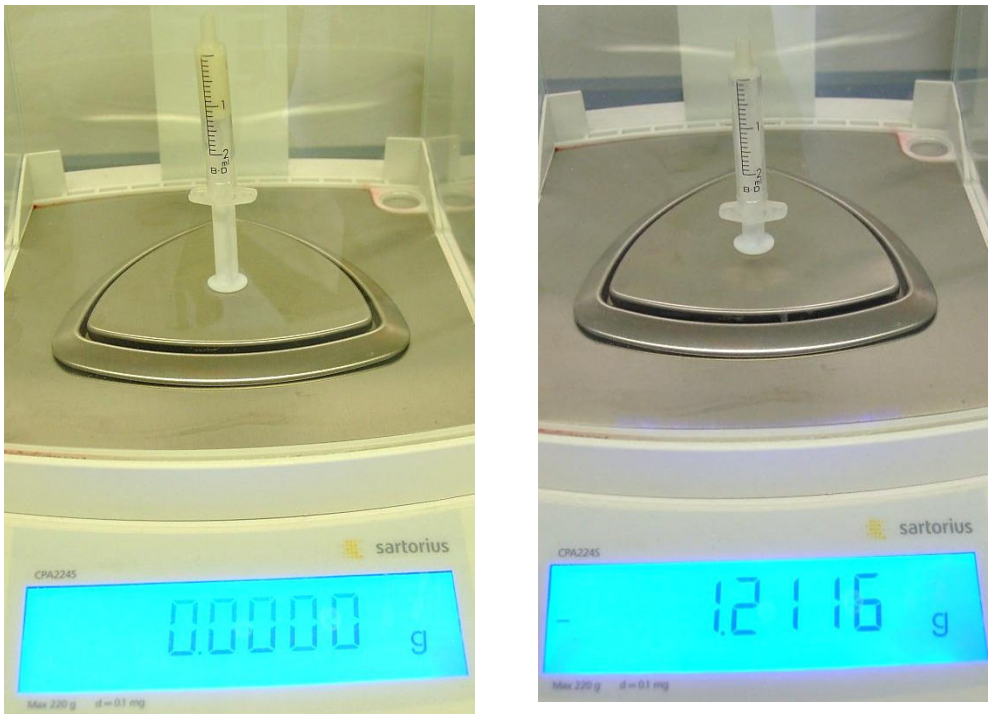
- Liquid coloration: Colorations-Shampoo, Preference 7.3 Floride Goldblonde from L`Òreal
- Cream coloration: Creme colorante nutritive, No 40 cacao brown, Nutrisse Creme from Garnier

Only the part of the hair dye that contains ammonia according to the declaration was used (color shampoo and cream). The sample was purchased at a local super market.

4. Procedure

4.1 Sample preparation:

- Each 300 mL glass tube was filled with 10 mL of 0.25 M H_2SO_4. The sample was uptaken into a syringe which was placed onto the balance and tared. About 1 - 1.5 g of sample was squeezed into each glass tube containing H_2SO_4 immediately to prevent NH_3 loss. The syringe including ALL remaining sample (don`t wipe it!) was weighed again and the mass was noted.
- The H_2SO_4 reacts with free NH_3 and $(NH_4)_2SO_4$ is formed. That helps to avoid NH_3 loss.



Picture 1: Left side: syringe is filled with sample, placed onto the balance and tared.
Right side: After transfering the sample into the glass tube the syringe with the remaining sample is weighed again and the weight is noted

4.2 Distillation and titration

Distill and titrate the samples according to the parameters listed in Table 1.
Additionally to ammonia steam volatile components, as for example fatty acids, essential oils and fatty alcohols, are distilled. These substances may lead to deposits on the steam inlet tube and on the condenser. The deposits don`t influence the results. To remove these residues it`s recommended to distill 30 mL ethanol before a new batch of samples is started. Therefore, a glass tube icluding 30 mL of Ethanol is placed into the autosampler after the last sample of one batch and distilled with a cleaning method which is mentioned in Tabel 2.

Method parameters for Samples KjelMaster K-375			
H_2O volume	10 mL	Titration solution	H_2SO_4 0.1 mol/l
NaOH volume	10 mL	Sensor type	Potentiometric
Reaction time	5 s	Titration mode	Standard
Distillation mode	Fixed time	Measuring mode	Endpoint pH
Distillation time	240 s	Endpoint pH	4.65
Stirrer speed distillation	5	Stirrer speed titration	7
Steam output	100 %	Titration start volume	0 mL
Titration type	Boric acid	Titration algorithm	Optimal for liquid samples Slow for cream samples
Receiving solution vol.	60 mL		

Table 1: Distillation and titration parameters with the Kjeldahl sampler system K-375/K-376

Due to a higher amount of volatile compounds in cream hair dye the titration algorithm should be set to "slow".

H_2O volume	0 mL	Steam output	100 %
NaOH volume	0 mL	Distillation time	240 s
Reaction time	5 s	Stirrer speed distillation	5
Distillation mode	Fixed time	Titration type	None
Receiving solution vol.	60 mL		

Table 2:
Distillation and titration parameters for cleaning with the Kjeldahl sampler system K-375/K-376

4.3 Calculation

The results are calculated as a percentage of nitrogen and percentage of ammonia. The following equations (1), (2) and (3) are used to calculate the results.

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

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

$$\%NH_3 = \%N \cdot 1.2158875 \quad (3)$$

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
$\%NH_3$	: percentage of weight of ammonia, %N multiplied with conversion factor 1.216

5. Results

5.1 Blanks

For blank determination 10 mL of 0.25 M H_2SO_4 are prepared in 300 mL glass tubes.

Blank	V_{Blank} [mL]
Blank 1	0.053
Blank 2	0.055
Blank 3	0.053
Average [%]	0.054
SD	0.001
Rsd [%]	2.152

Table 3: Results of the blank determination

The mean blank volume (V_{Blank}) was 0.054 mL (n = 3).

5.2 Ammonia determination in hair dye

The results of the determination of nitrogen and ammonia contents in hair dye are presented in Table 4 and 5.

Liquid Coloration	m_{Sample} [g]	V_{Sample} [mL]	%N	$\%NH_3$
Liquid Coloration 1	1.1864	7.674	1.799	2.187
Liquid Coloration 2	1.1639	7.515	1.796	2.184
Liquid Coloration 3	1.2314	7.929	1.792	2.179
Liquid Coloration 4	1.2254	7.811	1.773	2.156
Average [%]	-	-	1.790	2.176
SD	-	-	0.012	0.014
Rsd [%]	-	-	0.653	0.653

Table 4: Results of the determination of nitrogen and ammonia in liquid coloration

The mean blank volume (V_{Blank}) was 0.054 mL (n = 3).

Cream Coloration	m_{Sample} [g]	V_{Sample} [mL]	%N	$\%NH_3$
Cream Coloration 1	1.2118	7.975	1.831	2.226
Cream Coloration 2	1.2878	8.513	1.84	2.237
Cream Coloration 3	1.5386	10.005	1.812	2.203
Cream Coloration 4	1.2928	8.518	1.834	2.230
Average [%]	-	-	1.829	2.224
SD	-	-	0.012	0.015
Rsd [%]	-	-	0.661	0.661

Table 5: Results of the determination of nitrogen and ammonia in cream coloration

The mean blank volume (V_{Blank}) was 0.054 mL (n = 3).

6. Comparison to standard methods 83/514/EEC and LFGB §64 L84.11 (EG)

The differences of this application note compared to the standard method 83/514/EEC are described in the table 6.

Parameter	Application note	Standard method	Notes / Impace
Liberation of ammonia salt	Addition of base (32 % NaOH)	Precipitation by addition of BaCl and methanol, storage at 5°C over night and filtration	Both methods lead to the liberation of ammonia. The automatic addition NaOH allows the automation and the reduction of analysis time.
Titration	Potentiometric titration with boric acid in the receiver vessel	Back titration with Tashiro indicator	Potentiometric measurement is more accurate than manual titration, there is no difference in accuracy between back- and boric acid titration

Table 6: Differences to 83/514/EEC and LFGB §65 L84.11 (EG); both methods are identical;

7. Conclusion

Two important characteristics of the latest version of the fully-automatic Kjeldahl sampler system, KjelMaster K-375 and KjelSampler K-376, are the short process time as well as reduced personnel time. The time needed for sample analysis is significantly reduced and therefore the throughput increased.

8. References

[1] Application Note K-370_K-371-008 V1.0 2008 Determination of ammonia in hair dye
[2] Standard method LFGB §64 L84.11 (EG)
[3] Standard method Commision Directive 83/514/EEC

Operation Manual of Kjeldahl sampler system K-375/K376