Application Note

030/2010

SpeedDigester K-436, K-439 / KjelFlex K-360

Nitrogen Determination in Lubricating Oils according to the Kjeldahl Method

SHORT NOTE

Nitrogen Determination in Lubricating Oils according to the Kjeldahl Method

A simple and fast procedure for nitrogen determination in lubricating oils according to the Kjeldahl method, as described in the ASTM designation D 3228 - 05, is introduced below. The sample is digested with sulfuric acid using the SpeedDigester K-436 or K-439, followed by distillation and titration with the KjelFlex K-360. There are no differences between the results obtained with the K-436 and the K-439 respectively. The determined nitrogen contents are reliable and reproducible with low relative standard deviations.

Introduction

If lubricating oil is used in the motor for cooling and lubrication it produces insoluble oxidation products when in use. This leads to the production of deposits which harm the motor. Low nitrogen contents in lubricating oils are important to avoid these deposits.

The samples require digestion with sulfuric acid to convert nitrogen into ammonium sulfate. After conversion to ammonia through the alkalinization with sodium hydroxide, the sample is distilled into a boric acid receiver by steam distillation, followed by a titration with sulfuric acid solution.

Experimental

Instrumentation: SpeedDigester K-436, K-439, KjelFlex K-360

Samples: Lubricating oil 5W40 and 75W-90R

Figure 1: Lubricating oil 5W40 (left) and 75W-90R (right).

Determination: 1.0 g of the samples were added directly into a sample tube. A portion of 30 ml of sulfuric acid and 2 Kjeldahl tablets were added, and the digestion was performed using the the parameters specified in Table 1. After digestion the ammonia of the sample was distilled into a boric acid solution by steam distillation and titrated with sulfuric acid (Table 2).

The method was verified by using 5 ml glycine solution (0.6008 g/500 ml) as the reference substance.

Table 1: Temperature profile for digestion with the K-436, K-439

	K-439		K-436	
Step	Temp. [°C]	Time [min]	Level	Time [min]
Preheat	350	-	6.0	10
1	350	20	6.0	20
2	550	25	9.5	25
3	490	75	8.5	75
Cooling	-	30	-	30

Table 2: Parameters for distillation with the KjelFlex K-360 and titration

KjelFlex K-360		Schott TitroLine easy	
Water	80 ml	Titration Solution	H_2SO_4 0.005 mol/l
NaOH	110 ml	Internal Method	pH fast strong
Boric acid 2 %	50 ml	Endpoint	pH 4.6
Reaction Time	5 s		
Steam Power	100 %		
Dist. Time	240 s		
Titration Start	240 s		
Titration Type	Boric Acid		
Stirrer Sp. Dist.	5		
Stirrer Sp. Titr.	7		

Results

The glycine recoveries (n=4) were 100.0 %, rsd 0.67 % (K-439) and 99.6 %, rsd 0.49 % (K-436).

The determined nitrogen contents are presented in Table 3.

Table 3: Determined nitrogen contents in lubricating oils (relative standard deviation in brackets, n=4)

	Nitrogen content K-439 [ppm]	Nitrogen content K-436 [ppm]
Lubricating oil 5W40	726 (0.75 %)	726 (0.83 %)
Lubricating oil 75W-90R	1009 (0.92 %)	1012 (0.79 %)

Conclusion

The determination of nitrogen content in lubricating oils according to Kjeldahl using SpeedDigester K-436, K-439, and KjelFlex K-360 provides reliable and reproducible results with low relative standard deviations.

References

ASTM Designation: D 3228 – 05: Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method

Operation manual SpeedDigester K-425 / K-436
Operation manual SpeedDigester K-439
Operation manual KjelFlex K-360

For more detailed information please refer to Application Note 030/2010

1 Introduction

If lubricating oil is used in the motor for cooling and lubrication it produces insoluble oxidation products when in use. This leads to the production of deposits which harm the motor. Low nitrogen contents in lubricating oils are important to avoid these deposits.
An easy and reliable method for the determination of total nitrogen in lubricating oils according to the Kjeldahl method, as described in the designation: ASTM D 3228-05, is introduced below. The samples are digested using the SpeedDigester K-436 and K-439. The distillation and boric acid titration is performed with the KjelFlex K-360 and Schott TitroLine easy.

2 Equipment

- SpeedDigester K-436, K-439 (the parameters used for K-436 are also valid for Büchi SpeedDigester K-425)
- Scrubber B-414 with condenser
- KjelFlex K-360 with titration set (or any other Büchi Kjeldahl distillation unit)
- TitroLine easy (Schott)
- Connecting cable from titrator to K-360 (Büchi No. 043618)
- Analytical balance (accuracy ± 0.1 mg)

3 Chemicals and Materials

- Sulfuric acid conc 98 %, Fluka (84727)
- Catalyst, Hg/Se-free, 5 g/tabl., Büchi (028765)
- Sodium hydroxide 32 %, Brenntag (81980-452)
- Boric acid 2 %, 100 g boric acid, Brenntag (80948-155) diluted to 5 l with deionized water + KCl 3 g/l, pH adjusted to 4.65
- Sulfuric acid 0.005 mol/l (50 ml sulfuric acid 0.1 mol/l, Fluka (35357) standard solution diluted to 1000 ml with deionized water)
- 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, Fluka (93680; assay: 99.7 %)
- Glycine solution (0.6008 g glycine / 500 ml)

4 Samples

- Motor Oil 5W40
- Motor Oil 75W-90R

The samples were purchased at a local garage.
The oil samples were homogenized by shaking.

5 Procedure

The determination of nitrogen in oils and fuel oils includes the following steps:

- Homogenization of the sample
- Digestion of the sample, using SpeedDigester K-436, K-439
- Distillation of the sample, using KjelFlex K-360
- Titration with Schott TitroLine easy

5.1 Digestion method - glycine (verification of the method)

- Place 1.0 g sucrose and 5.00 ml glycine solution (= 6.008 mg glycine) in a 300 ml sample tube
- Add 2 Kjeldahl tablets, and a portion of 30 ml[1)] of sulfuric acid (98 %)
- Prepare additional blanks, 1.0 g sucrose as sample, 2 Kjeldahl tablets and 20 ml sulfuric acid as described in the designation D 3228 – 05.
- Carefully suspend the sample by gently swirling the tube
- Connect the Scrubber B-414 to the SpeedDigester K-436 or K-439 for absorbing the acid fumes created during digestion
- Insert the rack containing the samples into the preheated unit
- Digest the samples according to the parameters listed in Table 1

5.2 Digestion method - samples

- Place approx. 1.0 g of the sample in a 300 ml sample tube
- Add 2 Kjeldahl tablets, and a portion of 30 ml[1)] of sulfuric acid (98 %)
- Prepare additional blanks, 1.0 g sucrose as sample, 2 Kjeldahl tablets and 20 ml sulfuric acid as described in the designation D 3228 – 05.
- Carefully suspend the sample by gently swirling the tube
- Connect the Scrubber B-414 to the SpeedDigester K-436 or K-439 for absorbing the acid fumes created during digestion
- Insert the rack containing the samples into the preheated unit
- Digest the samples according to the parameters listed in Table 1

Table 1: Temperature profile for digestion with the K-436, K-439

	K-439		K-436	
Step	Temperature [°C]	Time [min]	Heating Level	Time [min]
Preheating	350	-	6.0	10
1	350	20	6.0	20
2	550	25	9.5	25
3	490	75	8.5	75
Cooling	-	30	-	30

- If the liquid in the sample tube is not clear and blue-green, digest for an additional 30 min as described in step 2
- Let the samples cool down to ambient temperature

NOTE: When the samples are placed in the cooling position it takes approx. 30 min to cool them down; when they are left in the heating chamber it takes at least 60 min.

[1)] The lubricating oil consumes a lot of sulfuric acid during the digestion.

5.3 Distillation and titration

Distill the samples according to the parameters listed in Table 2. The determination was carried out with a KjelFlex K-360 connected to a Schott TitroLine easy.

Table 2: Distillation and titration parameters

KjelFlex K-360		Schott TitroLine easy	
Water	80 ml[1)]	Titration Solution	H_2SO_4 0.005 mol/l
Sodium Hydroxide	110 ml	Internal Method	pH fast strong
Boric Acid 2 %	50 ml	Endpoint	pH 4.6
Reaction Time	5 s		
Steam Power	100 %		
Distillation Time	240 s		
Titration Start	240 s		
Titration Type	Boric Acid		
Stirrer Speed Dist.	5		
Stirrer Speed Titr.	7		

[1)] Recovery of glycine: Due to heavy splashing during the reaction, add the water manually to the samples and distil them after they are cooled down. Set the Volume of water to 0 in the method.

5.4 Calculation

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

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

$$ppmN = w_N \cdot 1'000'000\ ppm \qquad (2)$$

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] (recovery: consider the assay of glycine)
1000	: conversion factor [ml/l]
ppmN	: percentage of weight of nitrogen [ppm]

6 Results

6.1 Digestion with SpeedDigester K-439

6.1.1 Recovery of glycine

The results of the nitrogen determination and recovery in glycine are presented in Table 3. The nominal value of glycine (assay glycine: 99.7 %) is 18.60 % nitrogen. The recoveries are within the specification of 98 – 102 % [1].

Table 3: Results for the recovery of nitrogen in glycine with K-439

Glycine	m_{Sample} [mg]	V_{Sample} [ml]	%N	Recovery [%]
Sample 1	6.008	9.03	18.54	99.6
Sample 2	6.008	9.11	18.72	100.6
Sample 3	6.008	9.10	18.70	100.5
Sample 4	6.008	9.00	18.47	99.3
Average	-	-	18.61	**100.0**
Rsd [%]	-	-	0.67	**0.67**

The mean blank volume for this sample was 1.080 ml (n = 2).

6.1.2 Nitrogen determination in lubricating oils and fuel oils

The results of the determination of nitrogen in lubricating oils are presented in Tables 4 - 5.

Table 4: Results for the determination of nitrogen in lubricating oil 5W40 with K-439

Lubricating oil 5W40	m_{Sample} [g]	V_{Sample} [ml]	ppmN
Sample 1	1.0225	6.37	731
Sample 2	1.0102	6.30	730
Sample 3	1.0355	6.37	722
Sample 4	1.0469	6.42	721
Average	-	-	**726**
Rsd [%]	-	-	**0.75**

The mean blank volume for this sample was 1.033 ml (n = 4).

Table 5: Results for the determination of nitrogen in lubricating oil 75W-90R with K-439

Lubricating oil 75W-90R	m_{Sample} [g]	V_{Sample} [ml]	ppmN
Sample 1	1.0343	8.56	1019
Sample 2	1.0203	8.30	998
Sample 3	1.0451	8.59	1013
Sample 4	1.0393	8.50	1006
Average	-	-	**1009**
Rsd [%]	-	-	**0.92**

The mean blank volume for this sample was 1.033 ml (n = 4).

6.2 Digestion with SpeedDigester K-436

6.2.1 Recovery of glycine

The results of the nitrogen determination and recovery in glycine are presented in Table 6. The nominal value of glycine (assay glycine: 99.7 %) is 18.60 % nitrogen. The recoveries are within the specification of 98 – 102 % [1].

Table 6: Results for the recovery of nitrogen in glycine with K-439

Glycine	m_{Sample} [mg]	V_{Sample} [ml]	%N	Recovery [%]
Sample 1	6.008	9.04	18.64	100.2
Sample 2	6.008	8.95	18.43	99.1
Sample 3	6.008	8.98	18.50	99.5
Sample 4	6.008	9.01	18.57	99.8
Average	-	-	18.54	**99.6**
Rsd [%]	-	-	0.49	**0.49**

The mean blank volume for this sample was 1.045 ml (n = 2).

6.2.2 Nitrogen determination in lubricating oils and fuel oils

The results of the determination of nitrogen in lubricating oils are presented in Tables 7 - 8.

Table 7: Results for the determination of nitrogen in lubricating oil 5W40 with K-436

Lubricating oil 5W40	m_{Sample} [g]	V_{Sample} [ml]	ppmN
Sample 1	1.0399	6.38	730
Sample 2	1.0808	6.61	733
Sample 3	1.0329	6.27	720
Sample 4	1.0326	6.28	722
Average	-	-	**726**
Rsd [%]	-	-	**0.83**

The mean blank volume for this sample was 0.958 ml (n = 4).

Table 8: Results for the determination of nitrogen in lubricating oil 75W-90R with K-439

Lubricating oil 75W-90R	m_{Sample} [g]	V_{Sample} [ml]	ppmN
Sample 1	1.0060	8.32	1008
Sample 2	1.0155	8.49	1022
Sample 3	1.0260	8.49	1012
Sample 4	1.0207	8.39	1004
Average	-	-	**1012**
Rsd [%]	-	-	**0.79**

The mean blank volume for this sample was 1.078 ml (n = 4).

7 Comparison to Standard Methods

This application note is based on the standard method ASTM D 3228 - 05.

Table 9: Deviation to the standard method

	This application note	Standard method	Notes/Impact
Catalyst	10 g Tablets cont. - 47.7 % K_2SO_4 - 47.7 % Na_2SO_4 - 2.8 % TiO_2 - 1.8 % $CuSO_4$	Mixture of 9.9 g K_2SO_4 + 0.41 g HgO + 0.08 g $CuSO_4$	Easy to handle especially in routine analytics. The choice of catalyst does not influence the result. No mercury means less impact on environment.
Sulfuric acid	30 ml	20 ml + 5 – 15 ml addition during the digestion	No impact. The total volume of sulfuric acid is added at the beginning of the digestion so there is no need to open the equipment during the digestion.
Digestion end	45 min after the solution has cleared	2 h after the solution has cleared	2 hours are not necessary. To obtain results with good recovery a time of 45 min is sufficient. (Total time = 120 min)
Sodium hydroxide solution	80 ml NaOH (32 %)	75 ml NaOH (1000 g/l = 67 %)	No impact. The sample has to be strong alkaline and an amount of 80 ml sodium hydroxide solution is adequate.
Boric acid	50 ml boric acid 2 %	25 ml boric acid 4 %	No impact. Samples with low contents of nitrogen are preferably distilled in a receiver with low concentrated boric acid solution.
Sodium sulfit solution (addition after digestion)	No	25 ml	No impact. There is no Hg used so it's not necessary to percipate the Hg with sodium sulfit solution.

8 Conclusion

The determination of nitrogen in lubricating oils using the SpeedDigester K-436, K-439, and KjelFlex K-360 provides reliable and reproducible results with low relative standard deviations. There are no differences between the results obtained with the K-436 and the K-439 respectively. The recoveries with glycine were 100.0 % (K-439) and 99.6 % (K-436) respectively and are within the specification of 98 – 102 % [1].

9 References

[1] Application Note 001-437_370-03C: Operational Quality Check Procedure

ASTM Designation: D 3228 – 05: Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method

Operation manual of SpeedDigester K-425 / K-436
Operation manual of SpeedDigester K-439
Operation manual of KjelFlex K-360

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