# **Determination of Sulfur Content in Fuels**

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The sulfur content in fuels, Diesel fuels, and in the solutions of dibutylsulfide in a white oil was determined by various methods. The results obtained by elemental analysis have shown that the method is not advisable for the determination of sulfur in fuels. A good agreement was found by comparing the results in the determination of the sulfur content by Grote—Krekeler's and Hermann—Moritz's methods and by the energy-dispersive X-ray fluorescence analysis. The last method is the modern, comfortable, and timesaving method enabling the fast and precise determination of sulfur contents in the various types of samples.

The production of fuels has been adapted to a worldwide trend towards a decrease of harmful substances in combustion products. The diminishing of the sulfur content in fuels is one of the significant steps to the environmental protection. The determination of the sulfur content viewed from this aspect has assumed a great importance. The majority of methods for the determination of sulfur content are based on oxidation, sample combustion, and on the reactions of sulfur oxides with chemical agents [1-7]. Despite the fact that the principle of methods is similar, the great differences exist in individual procedures. The assessment of sulfur content in Diesel oils by the Slovak technical standard [8], which is identical to the European standard is followed by two prescribed methods: the determination of sulfur content according to Wickbold [1] and the X-ray fluorescence analysis [9]. Wickbold's method proved to be uncomfortable. It is based on sample combustion in the oxy-hydrogen flame and on the application of turbidimetric or thorin titration at its end. The X-ray fluorescence analysis is the up-todate, comfortable, and timesaving method. The comparability or correspondence of results obtained by the determination of the sulfur content applying various procedures are decisive factors for the choice of method.

#### EXPERIMENTAL

Five different methods were used for the sulfur content determination. There have been compared the results obtained by Grote—Krekeler's method (2), Hermann—Moritz's method (3), Dohrmann's method (4), and by the energy-dispersive X-ray fluorescence analysis (9). The apparatus and the conditions for the sulfur content determination are laid in the given prescriptions (2-4).

The determination of sulfur content by the energydispersive X-ray fluorescence analysis (5) was per-

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formed by means of the energy-dispersive X-ray fluorescence analyzer LAB-X 3000. The 25 kV X-ray tube with a palladium cathode and a proportional argon detector is built in the apparatus. Dúring the analyses, the apparatus was calibrated up to the sulfur content of 0.2 %. Instruments of the last generation permit the determination of samples containing a very low and a very high amount of sulfur. The calibration of the instrument LAB-X 3000 is usually practiced within the range  $w_S$  of 0.05—5 % for samples containing a high amount of sulfur (*e.g.* fuel oils) and for those containing a low amount of sulfur either within the range  $w_S$ of 10—1000 ppm or 10—5000 ppm, for instance for Diesel fuels.

As the model samples of the high sulfur content, fuel oils and the solvents of dibutylsulfide in the white oil were used. Table 1 presents the standard methods results [10-13] of Diesel oil samples with the low sulfur content.

Diesel oil samples were distilled according to the standard method (13) and in the distillation fractions there was determined their sulfur content. Properties of the fractions obtained by distillation are presented in Table 2.

#### **RESULTS AND DISCUSSION**

In choosing the method for determination of the sulfur content in fuels there exist many possibilities of standardized procedures which are recommended or applicable to individual fuel grades. As an example of the analysis of fuels by a nonstandardized procedure can serve the elemental analysis. The verification of the correspondence or comparability of results obtained by determining the sulfur content on the basis of some standardized methods and the elemental analysis is shown in Table 3.

The samples of oils with the sulfur content corresponding to a level used in the elemental analy-

Table 1. Physical and Qualitative Parameters of Analyzed Diesel Fuel Samples

Parameter	Ref.	MN-4	MN-22	MN-35	MN-CITY
Density at $20 ^{\circ}C/(kg m^{-3})$	[10]	836	834	825	839
Viscosity at $20 ^{\circ}C/(mm^2 s^{-1})$	[11]	4.501	4.228	3.026	5.143
Flash point/°C	[12]	75	65	56	76
Initial boiling point/°C	[13]	197	187	190	203
Final boiling point/°C	[13]	358	350	341	361
w(Sulfur)(9)/%	[ 9]	0.1425	0.1508	0.0911	0.0443

Table 2. Distillation Temperature and Densities of the Distillation Cuts

Distillation cuts $\varphi/vol.\%$	MN-4		MN-22		MN-35		MN-CITY	
	<i>θ</i> /°C	$d/(\mathrm{kg} \mathrm{m}^{-3})$						
010	221	809	216	805	207	801	227	827
10—20	231	816	229	812	215	805	238	829
20	243	820	241	818	223	808	250	828
30-40	256	825	251	824	234	812	263	831
4050	271	831	270	830	242	816	271	837
5060	287	837	284	- 835	241	820	291	840
60—70	304	842	301	841	263	826	306	843
7080	324	849	321	847	280	832	324	847
80—90	347	856	346	854	310	839	347	854
Residue		870		867		856		868

Table 3. Determination of Sulfur Content by Various Methods

<b>a</b> 1	$w(\mathrm{Sulfur})/\%$					
Sample	Method 1	Method 2	Method 3	Method 4	Method 5	
Oil 1		0.10	0.09	0.12	0.09	
Oil 2	2.67	1.43	1.47	1.77	1.45	
Oil 3	3.09	2.14	2.24	3.56	2.18	
Oil 4	2.99	2.11	2.26	2.86	2.16	

Method 1 - elemental analysis, method 2 - Grote-Krekeler, method 3 - Hermann-Moritz, method 4 - Dohrmann, method 5 - the energy-dispersive X-ray fluorescence analysis.

sis of organic compounds were for the comparison of the methods purposefully chosen. For these samples with a high sulfur content the results obtained by the elemental analysis and by the determination according to Dohrmann (4) were comparable. A very good agreement of the results of the determination was accomplished by Grote—Krekeler's (2) and Hermann— Moritz's (3) methods and by the energy-dispersive Xray fluorescence analysis (5). From the results of the analyses it followed that substantially different values were achieved using the nonstandardized methods 1 and 4 for the determination of sulfur content.

The precision of results was ascertained by estimating the sulfur content in samples of the known sulfur level. As a model compound for the preparation of those samples dibutylsulfide was used. The analytical results of the above-mentioned samples obtained by methods 2, 3, and 5 are presented in Table 4. The equational coefficients of linear dependences

Table 4. Comparison of Results Obtained by Various Methods

w(weighed)/%	Method 2	Method 3	Method 5
3.00	2.84	2.91	2.96
2.50	2.33	2.53	2.46
2.00	1.94	2.00	1.96
1.50	1.46	1.54	1.44
1.00	0.97	1.01	0.95
0.30	0.35	0.28	0.27
0.10	0.10	0.10	0.09

 $w_{\rm S}(\text{weighed}) = A_0 + A_1 \cdot w_{\rm S}(\exp)$  from the individual measurements are shown in Table 5.

On the basis of the equational coefficients of linear dependences (Table 5) and in virtue of the analytical results (Table 4) it is possible to deduce that sulfur determinations accomplished by methods 2, 3, and 5



Fig. 1. Determination of sulfur by elemental analysis.



Fig. 2. Dependence of detector response on the sulfur content.

Table 5. Coefficients of Linear Equations

Coefficients	Method 2	Method 3	Method 5
A <sub>0</sub>	-0.04532	-0.00117	0.02953
$A_1$	1.0728	1.0108	1.00526
R	0.9996	0.9999	0.9993

provide the results the agreement of which approaches the reproducibility stated by respective standardized methods.

Fig. 1 illustrates the sulfur content dependences derived from the elemental analysis carried out with the help of samples of the known sulfur content (the same samples were used as in the previous case).

From Fig. 1 it follows that the nonstandardized method for determining the sulfur content by the elemental analysis does not give results which could be used for the evaluation of fuels. It became apparent that this method differed considerably from the actual values gained also for fuels with  $w_{\rm S} = 2$  %. The evaluation of such fuel samples showed that the sulfur content estimated by this method was higher than that estimated by standardized methods. By analyz-

ing the samples of the known sulfur content the values acquired by this method were also different than it was expected. The method for the determination of sulfur content by the elemental analysis showed to be rather insensitive in the case of samples containing about 0.1 % of sulfur; for this reason the analysis was unsuitable for the determination in engine oils. A good agreement was found by comparing the results obtained in the determination of sulfur content by the Grote—Krekeler and Hermann—Moritz methods and by the energy-dispersive X-ray fluorescence analysis.

The sulfur content was determined in four different Diesel fuel samples. Table 1 presents the sulfur content and the fundamental physical and qualitative sample parameters. The calibration dependence is demonstrated in Fig. 2.

In Diesel fuels, the sulfur distribution was examined in distillation cuts performed according to ASTM D 86-67. From each sample, nine distillation fractions of the same volume together with the distillation residue were obtained. The mass of these distillation fractions was growing with increasing the density (Table 2). In Table 6, the sulfur contents determined by the energy-dispersive X-ray fluorescence analysis are incorporated.

Table 6. Distribution of Sulfur in Distillation Cuts. Method 5

Distillation cuts $arphi/ ext{vol.} \%$	w(Sulfur)/%					
	MN-4	MN-22	MN-35	MN-CITY		
0—10	0.0480	0.0508	0.0227	0.0086		
10—20	0.0594	0.0725	0.0290	0.0072		
20—30	0.0713	0.0864	0.0322	0.0099		
30—40	0.0874	0.1033	0.0359	0.0109		
4050	0.1059	0.1225	0.0416	0.0181		
5060	0.1253	0.1430	0.0506	0.0273		
60—70	0.1503	0.1645	0.0653	0.0402		
70—80	0.1832	0.1894	0.0917	0.0612		
80—90	0.2352	0.2315	0.1369	0.0925		
Residue	0.3217	0.3103	0.2605	0.1449		

The sulfur content established by the energydispersive X-ray fluorescence analysis in Diesel fuels was compared with the content calculated by summarizing the results from all fractions and from the residue. In all cases a good agreement of results obtained by the determination of sulfur content directly in Diesel fuels (Table 1) and the results calculated by the summation was evident. After summarizing, there was the following sulfur content in the samples: MN-4 0.140 %, MN-22 0.149 %, MN-35 0.078 %, and in the sample MN-CITY 0.0427 %, respectively. The sulfur content in distillation cuts was growing as the temperature of distillation was increasing. There remained 21 to 34 % from the total sulfur content in the distillation residue. The summarized sulfur contents in the last two fractions and in the distillation residue have represented 49 to 71 % of sulfur content in the samples. These results suggest that the majority of sulfur substances acquire the character of the higher-boiling compounds.

## DISCUSSION

By comparing the methods for the determination of sulfur contents the evaluation of their applicability to fuels containing 0.1 to 2.5 % of sulfur and to Diesel fuels containing 0.05 to 0.2 % of sulfur was accomplished. It became apparent that the determination of sulfur contents using the elemental analysis did not offer such results which would be comparable to standardized methods for the determination of sulfur contents. In the case of higher sulfur contents approx. 2 % of results obtained by this method were unexpectedly high, while in the case of low sulfur contents (round 0.1 %) the method was only slightly sensitive. Agreement of results ranging within the scope of values permitted by standards was achieved using Grote—Krekeler's and Hermann—Moritz's methods and applying the energy-dispersive X-ray fluorescence analysis. Advantages resulting from the determination of sulfur contents carried out by the above-mentioned analysis rest on the accuracy, quickness, simplicity, and on the undemanding operations performed during the routine analyses. This method is prospective and the most advantageous from among the applied standardized modes of determinations of the sulfur content in petroleum products.

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