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DETERMINATION OF THE TOTAL SULPHUR CONTENT OF OIL SHALE BY USING DIFFERENT ANALYTICAL METHODS

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Abstract. *This paper presents the results of determination of the total sulphur content of Estonian and Chinese oil shales (OS) by using different analytical methods – elemental analysis, quantitative chemical analysis and X-ray fluorescence spectroscopy (XRF). The different forms of sulphur and respective quantities were determined in order to offer a possible explanation to the discrepancy between the results. Thermogravimetric analysis coupled with mass spectrometry (TGA-MS) was used as an additional tool to verify the release of* SO_2 *and confirm the existence of sulphur in the organic and mineral parts of oil shale. Different analysis methods established different sulphur contents for the samples, showing a strong relationship between the sample composition and the analysis result. For both Estonian and Chinese oil shales the highest total sulphur content values, 1.53 and 2.23%, respectively, were determined using elemental analysis. As expected, the values were highly dependent on analysis conditions: the mass of sample and amount of catalyst used. The total sulphur contents of Estonian and Chinese oil shale samples as determined by the quantitative chemical analysis were 1.2 and 2.01%, respectively. Surprisingly, for Chinese oil shale the total sulphur content found by the quantitative chemical analysis was lower than that established by XRF. XRF determined the total sulphur contents of Estonian and Chinese oil shales to be 1.2 and 2.19%, respectively. These results suggest that elemental analysis should be the preferred method for the determination of total sulphur content.*

Keywords: *oil shale sulphur content, quantitative chemical analysis, X-ray fluorescence spectroscopy, elemental analysis.*

1. Introduction

Oil shale (OS) is a fossil fuel which is usually described as a complex material since it contains organics (kerogen) and a wide range of minerals

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[1–5]. Estonia is highly dependent on oil shale – 90% of electricity is produced from it [6]. China has the world's second largest resources of oil shale, which are estimated at 1600 million barrels [7]. As the reduction of sulphur emissions and sulphur content in shale oil are regulated by legislation and have therefore received considerable attention [8–10], the precise determination of sulphur content in the fuel used is of high importance worldwide. The properties of oil shales are highly dependent on their geographical location. For example, the ash content of Chinese Fushun and Huadian oil shales is 73.8 and 49.8%, respectively [11]. In addition, the sulphur content in their kerogen varies greatly, being 1.86% for Fushun OS and 2.54% for Huadian OS. According to some researchers, the total carbon content in oil shales may also differ largely: for example, the respective figures for Chinese Fushun and Huangxian oil shales are 13.8 and 30.7%, showing a major difference in their chemical composition [12]. For Estonian oil shale the ash content can be up to 57%, the total sulphur content is 1–2% and the organic matter amount ranges from 28 to 43% [13–14]. The advances of sulphur content determination go hand in hand with the development of analytical techniques. The correct determination of total sulphur content is a crucial part of quality control in refineries, laboratories, etc. Nowadays, time is a fundamental factor of a chemical analysis, being the most important component of its total cost. Elemental analysis is used in most laboratories due to providing quick and precise results. The analysis is usually performed according to the respective ISO or ASTM standards and parameters are not changed. This enables the comparison of the results with little effort. The methods described in the standards have been developed almost to perfection, yet sometimes debatable results are obtained. Therefore, a question arose whether changing some parameters would give different results. Due to the relatively easy sample preparation and elemental analysis procedure, time-consuming quantitative chemical analysis methods are used more and more rarely. Yet there is a price to pay for having results of the same (or even higher) quality in a much shorter time. Each method has its own advantages and disadvantages. X-ray fluorescence spectroscopy (XRF), the fastest of the abovementioned analytical methods, has the greatest advantage of being a non-destructive technique. Elemental analysis is known to provide highly precise results when it comes to pure organic substances, but this might not be the case with non-homogeneous samples that contain a lot of different minerals. As oil shale is a complex material that contains, for example, sulphur and carbon in both the organic and the mineral part, the precise determination of its elements content is of high importance. In this paper, we elucidate which of the analytical methods used provides the most precise total sulphur contents for Estonian and Chinese oil shales. In case of elemental analysis, the effect of sample mass and catalyst amount on the results is investigated. Additionally, a correlation between the sample composition and the analytical method result is established.

2. Experimental

2.1. Materials

For analysis Estonian and Chinese oil shale samples were used. The Estonian OS sample was obtained from the Estonia underground mine, Estonia. A more detailed analysis of this energetic sample can be found in our previous publication [15]. The Chinese OS sample was from the Maoming mine, Guangdong Province, Southwest China, with the local classification C. Prior to analysis, the samples were dried and crushed to less than 1 mm and a mean sample was taken. The sample particles median diameter (dm) was 180 µm. These samples were chosen in order to have oil shales of different composition and geological origin.

2.2. Methods and apparatus

Elemental analysis was performed on a Vario MACRO CHNS analyser. The effect of sample mass and catalyst amount on total sulphur content was investigated. Four parallel measurements were run for each varied parameter. Blind reference runs were done to verify the quality of the obtained results. Being a regular catalyst for reactions of sulphates-containing compounds, tungsten trioxide (WO_3) was used as a catalyst also in this work. The samples were packed in tin leafs, thereby locally increasing the combustion temperature in the analyser in order to ensure complete combustion. In order to see the effect on the analysis results, the sample amount and catalyst ratio were varied. Since the mass uncertainties for a 6-digit balance for sample masses of 20 and 50 mg were negligible, 0.0089 and 0.002%, respectively, these were not taken into account. XRF analysis was done using a Rigaku WD-XRF spectrometer. The sample was simply pressed together, no binding agents were used. Quantitative chemical analysis was performed according to ISO 334:2013 and EVS 664-1995 using gravimetric analysis [16, 17]. In order to investigate the emission of the different forms of sulphur, thermal analysis was used. This enabled us to distinguish which part of the sulphur moved to the gas phase depending on the temperature, which resulted in the appearance of SO_2 in the flue gas (in case of combustion), or the sulphur in pyrolysis process products. Thermal analysis was done employing a NETZSCH STA 449 F3 Jupiter® TG-DSC apparatus coupled with a NETZSCH QMS Aëolos® mass spectrometer. A heating rate of 20 °C/min was used in all experiments. A protective gas (high purity nitrogen (5.0)) flow rate of 50 mL/min was used. The samples were analysed in Pt/Rh alloy crucibles with removable thin-walled liners of Al_2O_3. In order to eliminate buoyancy effects, correction runs with empty crucibles were carried out and results subtracted from the measurement data. The proximate analysis results for OS samples studied are presented in Table 1.

Table 1. The results of proximate analysis of oil shale samples

Sample	Ash_{815}, wt%	Moisture, wt%	Volatile matter, wt%	Fixed carbon, wt%	Higher heating value, MJ/kg
Estonian oil shale	51.3	0.5	47.5	1.3	9.85
Chinese oil shale	61.7	3.0	24.7	13.6	8.12

3. Results and discussion

Sulphur in oil shale is present in both the inorganic compounds and the organic matrix, its total content amounts typically to 3%, depending on the origin [18, 19]. To be more precise, it exists in the form of sulphide, sulphate and organic sulphur and the organic sulphur content is usually calculated by difference between the total sulphur content and those of sulphide and sulphate forms [20, 21]. The results are presented in Table 2. It is important to note that the contents of nitrogen, carbon and hydrogen were determined using elemental analysis and the contents of total sulphur and different forms of sulphur were found using quantitative chemical analysis.

As can be seen from Table 2, most of the sulphur in Estonian OS is in the form of sulphides. This is supported by the fact that there is up to 3.5% of pyrite in Estonian oil shale [22]. A significant amount of sulphur is also in the form of organics. Organic sulphur in oil shale usually occurs as part of aromatic rings or in aliphatic functional groups [23–26] but for Estonian oil shale there is little qualitative data and no quantitative results at all [27]. Only 0.07% of the total sulphur in the Estonian OS sample is in sulphate form. This may be indicative of the precision of the results of elemental analysis since sulphates are compounds that may not decompose totally during the analysis. The results of the thermal analysis of oil shale samples are shown in Figure. As can be seen from the figure, SO_2 (determined using mass-to-charge ratios of 64 and 48) was released from the Estonian OS sample in gaseous form during the decomposition of organic matter, in the temperature range of 300–640 °C. A sharper and more intense peak is noticeable in the temperature region of 460–640 °C. As mentioned above, Estonian oil shale contains pyrite which is known to decompose in the

Table 2. The results of elemental and quantitative chemical analyses of oil shale samples, wt%

Sample	N	C	H	S^{total}	$S_{sulphide}$	$S_{sulphate}$	$S_{organic}$
Estonian oil shale	0.1	27.3	2.7	1.52	0.96	0.07	0.49
Chinese oil shale	0.8	23.3	2.4	2.01	1.17	0.30	0.54

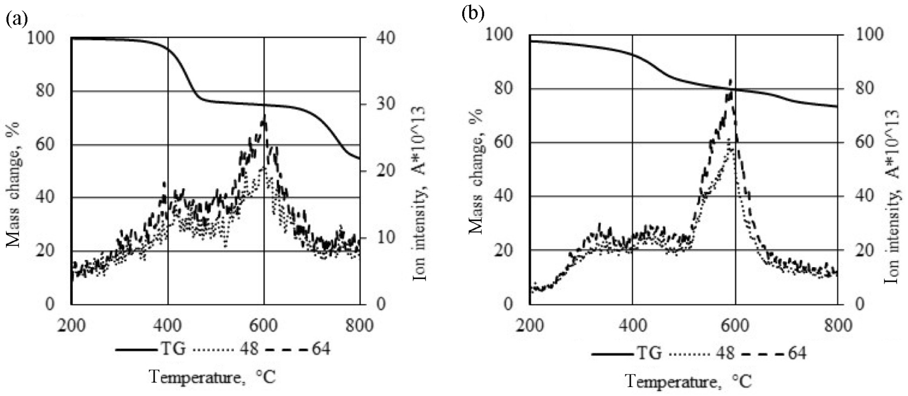

Fig. The release of SO_2 during thermal decomposition of samples: (a) Estonian oil shale, (b) Chinese oil shale.

temperature zone of 400–500 °C [28]. This means that the peak of pyrite decomposition overlaps with that of organic decomposition. As the content percentage of the sulphide form in the Estonian OS sample is greater than that of the organic form, the intense peak is most likely attributable to the decomposition of pyrite. For the Chinese OS sample, the pyrite release profile is a bit different: in the organic decomposition region its emission is lower than at the maximum organic decomposition, at about 600 °C. The maximal release of pyrite takes place in the temperature range of 500–660 °C. As the analysed OS samples contain a similar amount of organic sulphur, this difference is most likely due to the difference in their sulphide sulphur amount.

3.1. Analysis results for Estonian oil shale

So far there has been little discussion about the parameters of elemental analysis. There are several parameters which could alter the outcome: sample mass and homogeneity, the oxygen quantity used, sample to catalyst ratio, etc. As there are several parameters which can be varied for elemental analysis, the sample to catalyst ratio and sample mass were chosen as the research objects in this work as the most common ones. It was noticed that the elemental analysis results depended highly on the quantity of catalyst used, more specifically, the sample to catalyst ratio. For example, at a sample to catalyst ratio of 1:3 the total sulphur content was 1.38%, being 1.53% when this ratio was 1:10 (Table 3). This might be due to the non-homogeneity of the sample, a weak contact between the catalyst and the sample or incomplete combustion (due to minerals which were difficult to decompose), which affected the results and standard deviations. The highest total sulphur content, 1.53%, was determined at a 10:1 catalyst to sample ratio An important parameter to be observed in parallel measurements is the

Table 3. The effect of sample to catalyst ratio on the determination of total sulphur content in the 20 mg Estonian oil shale sample

Sample to catalyst ratio	S^{total}, %	Standard deviation, %	Relative standard deviation, %
1:1	1.39	0.11	8.19
1:3	1.38	0.04	3.17
1:6	1.45	0.06	4.41
1:10	1.53	0.01	0.64

relative standard deviation (RSD). In the current work, RSD was the lowest when the sample to catalyst ratio was the highest, which was indicative of complete combustion, as well as stable and near true results.

The effect of sample mass on the precision and stability of results was also investigated. To this end, a larger, 50 mg sample was used, the results are presented in Table 4.

As Table 4 reveals, the total sulphur contents determined in the 50 mg sample at sample to catalyst ratios of 1:1 and 1:10 were of the same magnitude as those of the 20 mg sample. As expected, RSD values for the 50 mg sample at sample to catalyst ratios equal to or higher than 1:3 were quite similar to those of the 20 mg sample. The S^{total} of the 50 mg sample at a 1:10 sample to catalyst ratio was the same as for the 20 mg sample but its RSD was higher. This also means a higher possibility of obtaining incorrect results. At lower sample to catalyst ratios the S^{total} values were much lower. This indicates that the sample mass used was too large: there was a poor contact between the catalyst and the sample, and the combustion of the sample was incomplete, probably due to the too low amount of the catalyst used. As expected, the S^{total} determined by XRF was the lowest, 1.2%, compared to elemental analysis and quantitative chemical analysis. This was due to that sulphur might have been shielded by the softer organic matter and clay or carbonaceous minerals. At the same time, the sulphur radiation emitted may be somewhat shielded and the resulting low total content of sulphur may prove incorrect. As the fused bead method is often used for XRD measurements, it can also be employed for S^{total} determination. However, the performance of this method will be a topic of future research. The use of high temperatures during fusion may lead to systematically lower

Table 4. The effect of sample to catalyst ratio on the determination of total sulphur content in the 50 mg Estonian oil shale sample

Sample to catalyst ratio	S^{total}, %	Standard deviation, %	Relative standard deviation, %
1:1	1.39	0.02	1.44
1:3	1.47	0.03	2.28
1:6	1.35	0.09	6.98
1:10	1.53	0.04	2.54

sulphur content values as part of the sulphur may evaporate at the melting temperature of the fusion agent. As the S^{total} determined by both the elemental analysis and the quantitative chemical analysis was similarly near 1.5 %, the value found by XRF, 1.2%, was considered inaccurate. Based on the above, elemental analysis represents the fastest and most flexible method for determination of total sulphur in oil shale. The 1.52% S^{total} found by the quantitative chemical analysis was chosen as a reference value. This was because quantitative chemical analysis, unlike the other two methods used in this work, enabled the determination of the different forms of sulphur present in the samples. Based on the above, the mass of 20 mg and sample to catalyst ratio of 1:10 were the most optimum for the determination of total sulphur content in oil shale.

3.2. Analysis results for Chinese oil shale

As can be seen from Tables 1 and 2, the Chinese OS sample has a higher total sulphur content than the Estonian OS sample. Moreover, its sulphate content is remarkably higher than that of the Estonian OS sample. As sulphates are known to inhibit total combustion, there might be differences in the analysis results. Tables 5 and 6 present total sulphur contents of Chinese OS samples determined by elemental analysis.

Table 5. The effect of sample to catalyst ratio on the determination of total sulphur content in the 20 mg Chinese oil shale sample

Sample to catalyst ratio	S^{total}, %	Standard deviation, %	Relative standard deviation, %
1:1	2.17	0.27	12.55
1:3	2.23	0.03	1.53
1:6	2.21	0.07	3.18
1:10	2.17	0.06	2.61

Table 6. The effect of sample to catalyst ratio on the determination of total sulphur content in the 50 mg Chinese oil shale sample

Sample to catalyst ratio	S^{total}, %	Standard deviation, %	Relative standard deviation, %
1:1	2.12	0.03	1.63
1:3	2.13	0.12	5.57
1:6	2.14	0.08	3.77
1:10	2.14	0.05	2.10

Table 5 gives the measured total sulphur contents for the Chinese OS samples of different sample to catalyst ratios to be around 2.2 %. The highest S^{total} was determined in the sample at a sample to catalyst ratio of 1:3, while its RSD was the lowest, 1.53%. When the sample to catalyst ratio was 1:6, the S^{total} of 2.21% and RSD of 3.18% recorded were also acceptable. As the obtained S^{total} values were similar, the samples with both ratios, 1:3 and 1:6, can be successfully used for the respective measurements, thereby maintaining low RSD values. The S^{total} determined for the samples of the ratios of 1:1 and 1:10 were lower. The RSD of 12.55% for the sample with a 1:1 sample to catalyst ratio indicated a high dispersion in and inaccuracy of the results. Therefore, the sample to catalyst ratio of 1:3 was optimal for total sulphur content determination.

The results obtained using a bigger, 50 mg oil shale sample are presented in Table 6. The table reveals that the measured S^{total} for the 50 mg sample are lower than those for the 20 mg one. At the same time, the average S^{total} figures are very similar irrespective of the different sample to catalyst ratios used. The RSD values lower than 6% are also acceptable. This is indicative of that although one might obtain acceptable and stable results, these may not be true ones.

As a reference, quantitative chemical analysis was used to determine the total sulphur content of the sample. The respective value was 2.01%. However, the S^{total} found by elemental analysis was higher than the one established by quantitative chemical analysis. Additionally, XRF was employed to find S^{total}, with the value of 2.19%. Interestingly, this figure proved to be higher than the value obtained by quantitative chemical analysis. This might be due to that the Chinese oil shale sample has quite high contents of ash and fixed carbon, and a low content of volatile matter, which somewhat differ from the respective figures of the Estonian OS sample (Table 1). The low volatile matter content of the Chinese OS sample may also account for the higher precision of its S^{total} measurements.

Based on the results obtained in this paper it may be said that the determination of the total sulphur content of OS samples was dependent on analysis conditions. In proper conditions, elemental analysis afforded the most reliable S^{total} figures. At the same time, without having results from any reference analytical method, one has to view the XRF-determined values with some caution as these, depending on sample composition, may not be reliable. For Estonian OS, quantitative chemical analysis provided also reliable results. However, with the latter method being highly time-consuming, one should prefer elemental analysis for S^{total} determination.

4. Conclusions

The results of determination of the total sulphur content of Estonian and Chinese oil shale samples by using elemental analysis, X-ray diffraction spectroscopy and quantitative chemical analysis have been presented. All the methods afforded somewhat different results. The highest sulphur content, 1.53%, was measured for the Estonian oil shale sample by employing quantitative chemical analysis. At the same time, the respective value obtained for the Chinese oil shale sample was the lowest and the method was therefore considered unreliable. The total sulphur determination by elemental analysis was highly dependent on the analysis conditions used. For the Estonian oil shale sample the respective measured value was 1.53%, and for the Chinese oil shale sample, 2.23%. X-ray diffraction spectroscopy also provided the lowest value for Estonian oil shale, 1.2% as against 2.19% for Chinese oil shale. As the exact S^{total} contents of the samples remained unknown, it is believed that these lie somewhere between the values measured by quantitative chemical analysis and elemental analysis. Thermogravimetry-mass spectrometry was used to determine the sulphur emission profile and forms of sulphur present in the samples. The findings of this paper should contribute to the precise determination of sulphur content in different oil shales.

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