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RGB histograms as a reliable tool for the evaluation of fuel oils stability

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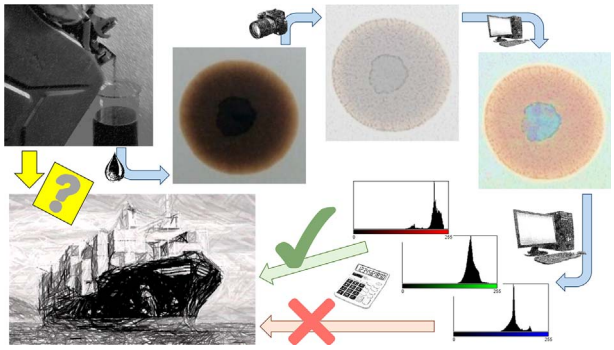
GRAPHICAL ABSTRACT



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ABSTRACT

The stability of fuel oils could be affected by sediments and sludge, which may block filters and lines in the feeding pipes and engines. The development of a reliable method for the fuel oil stability assessment is still a hot topic. The presented method is based on the Spot test according to ASTM D 4740 but the spot is visualized, modified by software and converted into RGB histograms. The histograms provide the parameters necessary for the calculation of the V-value. This parameter was effectively correlated with the frequently used Total Sediment Accelerated and with other properties for the evaluation of the fuel oil quality and stability.

1. Introduction

Fuel oils are very often used as marine fuel according to the ISO 8217. Depending on the total sulphur content [1], they can be used as marine fuels or fuel for other purposes. Marine fuel must meet the specific quality parameters according to the standard ISO 8217 [2]. Density as well as viscosity are important parameters for the basic characterization or categorization of such products into the individual classes (Table 1).

The stability of marine fuel is a very important and frequently discussed parameter. Fuel oils can contain a significant amount of asphaltenes which could have a tendency to aggregate [3] and produce sediments and sludge. Thus, the main problem is their formation, which consists of precipitation followed by sedimentation of certain solids in the liquid [4], subsequent settling to the bottom of the storage vessel. The standardised method for stability testing is the Total Sediment according to ISO 10307 [5,6]. This method can have some specific pitfalls, such as sticking or even damage to the glass filter, which may affect the test assessment or even make it impossible [7–9]. Moreover, it is a quite complicated and time consuming method of analysis. Therefore, simplified methods for the stability assessing are being used. For example, drop tests (Spot test [10], Oliensis test [11]) and/or other different solubility tests (heptane insolubles, toluene insolubles [12]). Drop tests have a considerable disadvantage, which is subjective evaluation potentially resulting in inaccurate results. There are various commercial kits for performing the Spot Test available on the market,

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Table 1
The list of the individual categories according to the ISO 8217.

Viscosity at 50 °C [$mm^2 \cdot s^{-1}$], max.	Density at 15 °C [$kg \cdot m^{-3}$], max.	Category ISO-F-
10.0	920.0	RMA 10
30.0	960.0	RMB 30
80.0	975.0	RMD 80
180.0	991.0	RME 180
180.0	991.0	RMG 180
380.0	991.0	RMG 380
500.0	991.0	RMG 500
700.0	991.0	RMG 700
380.0	1010.0	RMK 380
500.0	1010.0	RMK 500
700.0	1010.0	RMK 700

but it is still a subjective type of evaluation.

The stability of fuel oils can also be measured by trans-illumination with a light source. The sample is dissolved in a relevant diluent and a drop of the mixture is placed on a filter paper. The light beam passes through the sample and goes to a photodetector [13], where absorbance is measured. It is also possible to backlight the fuel oil with the solvent placed in a measuring cell so that the light source can be compared with the light beam passing through the detector [14]. However, the mentioned method needs appropriate instrumentation.

Another possibility is the assessment of the composition of the oils, especially the content of saturates, aromatics, resins and asphaltenes (SARA) [15] followed by calculation of the Colloidal Instability Index (CII) [16]. The disadvantage consists in the relatively expensive equipment required for this SARA analysis.

The alternative solution could be Spot Test, which is a fast and very simple method. The article deals with optimization and verification of the new method based on visualisation of the Spot Test followed by transformation to RGB histograms. Then V-value is calculated from the information obtained from the histograms. The laboratory results showed very good correlation between the V-value and the total sediments (TS and TSA) parameter.

2. Experimental

2.1. Materials and methods

The samples of fuel oils were prepared using a heavy residue and a relevant diluent. All the components were preheated and carefully homogenized. The residual fraction was heated to 160 °C and weighted, and then the required amount of the diluent component was added. The mixture was homogenized using a glass rod at 80 °C. The fuel oils were categorised as RMD 80 (according to ISO 8217, see Table 1) with respect to their density as well as kinematic viscosity.

Total Sediment (TS) was assessed using hot filtration according to ISO 10307-1. The sample was filtered through a preheated apparatus (Setaclean Total Sediment Tester, STANHOPE-SETA, UK) at 100 °C. Then, the filter was washed by solvent and dried. The content of sediments was calculated by the difference in weight between the clean filter and the used filter after its drying. Glass microfiber filters were used (made from borosilicate glass, diameter 47 mm, GF/A grade: 1.6 μm, filtration velocity 62 s/100 ml, WHATMAN).

Total Sediment Accelerated (TSA) was carried out in accordance with ISO 10307-2 (Procedure B – chemical ageing). TSA was determined after accelerated ageing in which a sample of residual fuel oil was titrated with a specified amount of n-hexadecane (cetane) under carefully controlled conditions. The sample was then heated to 100 °C for 1 h, followed by hot filtration in accordance with ISO 10307-1.

Spot Test was performed according to ASTM D 4740. A drop of the preheated and thoroughly mixed fuel oil was put on a filtration paper (grade 391, diameter 125 mm, basis weight 84 $g \cdot m^{-2}$, filtration velocity 2500 s/100 ml, retention rate 2–3 μm, MUNKTELL) and placed in an oven at 100 °C. After 1 h the paper was removed from the oven and the resulting spot was examined for evidence of suspended solids. The spot was categorized into one of the five classes according to the standard ASTM D 4740.

Toluene insolubles were measured using ČSN 6,56,219. The principle of this testing method is the dissolution of the analyzed sample in toluene, followed with filtration, drying and weighing. Filter paper coded as MN 1640d was used (diameter 110 mm, filtration velocity 140 s/100 ml, MACHEREY-NAGEL).

Oliensis Test was performed in accordance with ASTM D 1370/D 1370 M. The method is based on the spot test (filter discs grade 389, diameter 70 mm, basis weight 84 $g \cdot m^{-2}$, filtration velocity 150 s/100 ml, retention rate 8–12 μm, MUNKTELL) where the sample is dissolved with known ratio of isooctane-xylene. The test results show the lowest concentration of xylene (Xylene Equivalent = XE) at which the spot is still homogenous.

Density was measured using DA 645 (KYOTO ELECTRONICS, JAPAN) according to ASTM D 4052. The principle is the electronically measured duration of oscillation from which the density is automatically calculated.

Simulated Distillation Curve was carried out according to ASTM D 7169 using gas chromatograph HP 7890 (Hewlett Packard, USA). This method is intended to determine the distribution of boiling points of petroleum fractions, and higher boiling product residues whose distillation end point may not be higher than 750 °C.

Determination of Carbon Residue (Micro Method) was performed according to ASTM D 4530 using MCRT-160 MICRO CARBON RESIDUE TESTER (PAC, USA).

Pour Point (PP) was determined in accordance with ISO 3016 by the fully automated pour point tester (NORMALAB NTE 450, France). The precision of the method is ± 3 °C.

Elemental Analysis (CHSN) was performed using the elemental analyzer Flash 2000 (Thermo Fisher Scientific, UK).

Metal Content was measured using Agilent 725 ICP OES spectrometer (Agilent Technologies, USA). The total content of metals in the solution was determined using a method of optical emission spectrometry with inductively coupled plasma followed by optical detection.

V-value was calculated from the RGB histograms, where the spot was visualized, modified by the relevant software, followed with the conversion into the RGB histograms. In this study, the ImageJ software was used, which is a public domain, Java-based image processing program (NIH, USA). V-value was calculated using two dimensional graphs (x, y), where y represents the percentage distribution of one of the three colors and x the code for the color shade (0–255 for RGB system) according to the Eq. (1).

$$V\text{–}value = B(\%) \cdot \frac{\frac{B(\max.y)(\%) \cdot B(max.y\ position)}{B(\max.x) - B(\min.x)}}{\frac{R(\max.y)(\%) \cdot R(\max.y\ position)}{R(\max.x) - R(\min.x)} + \frac{G(\max.y)(\%) \cdot G(\max.y\ position)}{G(\max.x) - G(\min.x)}} \quad (1)$$

where B (%) is the average total percent of blue colour intensity; B/R/G(max_y) (%) is the maximum contribution of blue/red/green colour; B/R/G(max_y position) is the value (0-255) of the blue/red/green peak maximum position; B/R/G(max_x)–B/R/G(min_x) represents blue/red/green dispersion (the first and last signals on the 0–255 scale).

3. Results and discussion

Eight samples of fuel oils were analysed by all the above mentioned methods and the correlation between them was evaluated. The prepared samples were sorted according to their TS value. The total sediments in two samples (coded as G and H) and the total sediments accelerated in six samples (coded as C-H) were too high and the value should be specified as > 0.50 wt% (Table 2) in accordance with the relevant standard.

The values of the Oliensis Test (XE) were generally > 80, therefore