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ANALYSIS OF MARINE FUEL OIL PURIFIER EFFICIENCY, CHEMICAL ELEMENTS AND COMPOUNDS FOUND IN THEM

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ABSTRACT

Ensuring the proper operation of a ship's propulsion system necessitates the use of high-quality fuels. Several factors contribute to fuel quality, including the source of origin crude oil, refining methods, blending processes, and the quality of storage and distribution. Marine fuels must adhere to international standards such as ISO standards to be suitable for consumption on ships.

This article presents an analysis of over 6000 fuel samples obtained from two sample points within a purification system, conducted by independent laboratories. While all samples must meet the ISO 8217:2017 Standard for marine residual fuel before bunkering, this analysis focuses on elements with potentially harmful effects on marine engine systems. A comprehensive examination will be conducted, employing an inductive method to draw general conclusions about the current levels of abrasive impurities and other detrimental elements in fuels post-purification.

Specific attention will be given to elements like aluminium, silicon, vanadium, calcium, magnesium, lead, nickel, potassium, sodium, zinc, and phosphorus present in residual fuel oils. These elements, in certain forms or concentrations, pose challenges to marine engines. Testing conducted according to the IP 501 standard, utilizing inductively coupled plasma emission spectrometry, is essential to ensuring smooth engine operation and mitigating damages and associated costs caused by abrasive fines in the fuel oil.

Keywords: fuel treatment, fuel quality, abrasive fines, ISO standard.

INTRODUCTION

Fuel represents one of the most significant cost factors in operating a ship and is also the source of numerous operational issues, both direct and indirect. Several reasons contribute to this situation: the fluctuating cost of fuel due to geopolitical events, supply and demand dynamics, and regulatory changes; stringent environmental regulations dictating the permissible types of fuel, particularly concerning sulphur content and other requirements; technical challenges associated with the diverse properties and requirements of different fuels regarding storage, handling, and combustion; the imperative to improve fuel efficiency due to both cost and environmental concerns; and the risks inherent in the fuel supply chain, especially in high-risk areas where delays or interruptions in fuel delivery can impact ship schedules and incur additional costs.

In light of these factors, shipowners and operators continuously seek ways to mitigate the impact of fuel-related challenges through fuel management strategies, the adoption of new technologies, education, and regulatory compliance measures. Issues such as fuel contamination, compatibility, stability, and quality can lead to operational problems including engine failures, increased maintenance (and it costs), and reduced efficiency. A major concern among ship operators is the quality of fuel delivered to their vessels. Off-specification bunkers can lead to commercial losses and further costs if such fuels damage engines and their components.

Ensuring the efficiency of marine fuel purification requires proper sampling and detailed analyses of each element in the fuel.

MATERIAL AND METHODS OF WORK

The ISO 8217 (Vermeire, 2021) standard specifies the requirements (maximum or minimum limits) for petroleum fuels used in marine diesel engines and boilers before appropriate treatment onboard. It defines several categories of distillate fuels and residual fuels.

The primary objective of ship purification processes is the removal of contaminants such as water, impurities (sediment, rust, particles, etc.), and microbial agents from the fuel. To achieve this, methods including centrifugal separation, filtration, and settling are employed. The separator's effective throughput should match the diesel engine's maximum consumption, with an additional margin of approximately 18% (Latarche, 2021, p. 145). This ensures that the separated fuel oil can flow back from the daily tank to the settling tank. When properly treated, centrifugal separation is the most effective method for extracting these impurities from the fuel. When operating at optimal efficiency, ship purifiers can remove particles larger than 5 microns. Solid contaminants in marine fuels, such as aluminium and silicon, originate primarily from the cracking process in refineries (Fisher, & Meech, 2013).

The current ISO 8217:2017 standard introduced additional grades and reduced some limitations. This standard specifies fuel characteristic limits such as viscosity, density, cetane index/CCAI, sulphur, flash point, hydrogen sulphide, acid number, total sediment, carbon residue, cloud point, pour point, cold filter plugging point, appearance, water, ash, lubricity, vanadium, sodium, aluminium plus silicon (cat fines), calcium, and zinc (Chybowski, Myśków, & Kowalak, 2023). The focus of this article will be on these latter elements as they can damage the engine or reduce its efficiency.

There are numerous methods to detect elements in fuel, such as Particle Sizing using Scanning Electron Microscope (SEM) in conjunction with Energy Dispersive X-Ray Analysis (EDX). These methods are employed to check the size of different particles present in tested marine fuels. Depending on the laboratory, two different IP methods (IP 501 and IP 470) are commonly used (Khayal, 2019). Both methods are used to determine elements like aluminium, silicon, vanadium, nickel, iron, sodium, calcium, and zinc in residual fuel oil by ashing. IP 501 utilises fusion and inductively coupled plasma emission spectrometry (ICP-OES) and can determine an additional element, phosphorus. IP 470 uses fusion and atomic absorption spectrometry (AAS). The testing results are presented in Table 1.

Table1. Tested element and their range (IP 501 and IP 470)

Element	**Range (mg/kg)**
aluminium	5 to 150
silicon	10 to 250
vanadium	1 to 400
nickel	1 to 100
iron	2 to 60
sodium	1 to 100
calcium	3 to 100
zinc	1 to 70
phosphorus	1 to 60

Aluminium and silicon

Aluminium and silicon are typically found in residual fuel due to catalytic cracking during the crude oil refining process (Latarche, 2021). Commonly referred to as *cat fines*, these particles are very sharp, hard, and abrasive, posing significant risks to the main engine and its components. Cat fines can cause substantial damage to sensitive engine parts, such as fuel pumps, fuel injectors, cylinder liners, and piston rings (Vukičević, 2022). If excessive amounts of these abrasive impurities enter the engine, they can even lead to total engine failure. Major manufacturers of main engines recommend that cat fines be kept within a range of up to 10 mg/kg. If the concentration reaches 15 mg/kg, it is considered a warning level. The maximum permissible concentration of catalytic fines according to ISO standard 8217 (Draffin, 2012) is 60 mg/kg, so it is crucial for marine crews to reduce this value to below 10 mg/kg.

What is meaning in terms of a good fuel?

- It must not contain components which leave deposits that can affect the proper operation of the fuel treatment and injection system.
- The fuel must maintain stability under various operating conditions.
- It should atomize consistently, producing droplets of nearly uniform size.
- It must have predictable ignition and burning characteristics, particularly regarding pre-ignition and stable burning performance.
- The fuel must completely combust before the exhaust phase of the cycle begins.
- It should not contain corrosive elements that exceed the tolerance levels of the engine materials.
- It must be free from abrasive particles in amounts exceeding the engine manufacturer's specifications, even after treatment.

Ash

Ash content in fuel represents the quantity of inorganic, non-combustible material present. While certain ash-forming components exist naturally in crude oil, others result from refining processes or contamination during storage and distribution. For instance, vanadium occurs in crude oil and can reach concentrations of approximately 400 mg/kg in residual fuels. Other elements such as sodium, iron, and calcium are found in low concentrations in crude oil and refined residual fuel. However, elevated levels of these elements detected during marine fuel analysis typically indicate contamination (Fisher, & Meech, 2013).

Fuel contamination during storage and distribution can increase ash levels, with sodium potentially originating from seawater, iron from pipeline and tank rust, or from dust, dirt, and careless or intentional mixing with other substances. High ash content in fuel can cause post-combustion fouling of marine boilers and engines. Certain ash components, like vanadium and sodium, are corrosive and can damage engine exhaust valves, turbochargers, and boiler tubes through the formation of corrosive deposits.

Ash tends to adhere to piston rings and accumulate in piston ring grooves within the piston crown. This can cause the rings to seize, leading to excessive wear of both the rings and cylinder liners, and gas blow-by, resulting in scavenge fires. Ash accumulation on turbochargers can reduce their efficiency, and insufficient charge air results in poor combustion, generating additional carbon deposits that exacerbate the problem.

The presence of phosphorus, calcium, and zinc in fuels often signifies contamination with waste lubricating oils, particularly when these elements are detected together. However, if any of these elements are found in isolation in bunker fuel, it could indicate a different form of contamination. When vanadium is present alongside these elements in a non-particulate form, it cannot be reduced through mechanical treatment onboard. Consequently, if these elements are present in high concentrations in the fuel upon delivery, they will persist in the fuel even after combustion.

Water

Water is introduced into marine fuels usually due to poor housekeeping. The challenges faced by a ship’s crew when receiving fuel deliveries with increased water levels are multifaceted and encompass various issues. These problems can include the formation of sludge in fuel tanks, blockage of filters, corrosion of fuel injection equipment, corrosion of exhaust valves, and fouling of turbochargers (ExxonMobil, 2017). The severity of these issues is influenced by factors such as the type of water present (seawater or freshwater), the design and heating capabilities of storage tanks, and the design and operation of onboard purifiers. Additionally, the density and viscosity of the fuel impact the effectiveness of settling tanks and purifiers in removing water. These challenges require careful consideration of multiple variables and may necessitate proactive measures to mitigate potential damage and disruptions to ship operations.

Ships equipped with properly designed settling tanks and well-maintained and operated separators can typically reduce water content to satisfactory levels before fuel injection into the main engine, even when the initial water content is as high as 3%.

Saltwater contamination can occur during fuel delivery due to several factors. These include contamination by the delivery barge (mixing seawater with the fuel during barge loading, barge voyage, or discharge), structural defects on the barge, or improper valve operations. Seawater can also enter ships’ storage tanks from a mixture of ballast water or ingress of the sea through defective hatch covers and small plate fractures. One common cause of ballast water entering ships’ fuel tanks is the corrosion of fuel tank sounding and vent pipes that pass-through ballast tanks. Seawater contamination of fuel raises significant concerns due to potential chemical reactions between sodium compounds in the water and vanadium compounds in the fuel during combustion. These reactions can result in the formation of corrosive ash, leading to high-temperature corrosion of exhaust valves. When vanadium and sodium oxidize during combustion, they tend to create semi-liquid, sticky salts with low melting points that adhere to exhaust valves. These sticky deposits not only corrode the valves and seats but also attract other combustion deposits, potentially causing mechanical damage.

To address this issue, engine manufacturers have introduced specialized alloys such as Nimonic steels with enhanced corrosion resistance. Additionally, they have designed exhaust valves to rotate, aiding in dislodging ash buildup and preventing repeated contact between the same valve and seat areas. Moreover, valve temperatures are carefully maintained below the threshold at which these ash compounds deposit. The sticking temperature of these corrosive ashes varies but is typically considered lowest when the ratio of vanadium to sodium is 3:1 (Fisher, & Meech, 2013).

Figure 1. Reconditioned exhaust valve (QuantiServ, 2024).

The metals in seawater contribute to the total ash content in fuel. High levels of sodium can form substantial amounts of ash on turbocharger grids and blades. If this ash is not removed by frequent water washing, the performance of the turbocharger will be impaired, leading to poor combustion and increased fouling. As mentioned earlier, saltwater contamination can be reduced by settling and centrifuging onboard. As a rough guide, 1% seawater contamination would contain approximately 100 mg/kg of sodium.

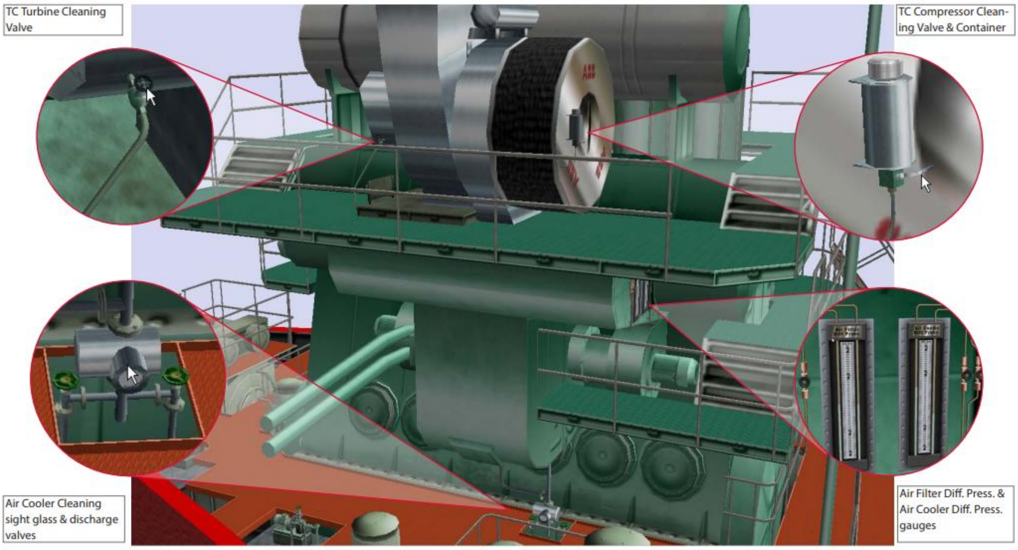


Figure 2. Turbocharger cleaning -compressor side (Transas Marine 2016 MAN B&W 6S60MC-C Diesel Engine – Tanker LCC. Trainee Manual pdf)

Freshwater infiltration into fuel systems on ships can occur through various scenarios, including delivery with fuel (bunkering), tank condensation, improper setting of purifiers, leaking steam heating coils, and rainwater ingress. While not as severe as seawater contamination, the presence of freshwater can still pose challenges. Emulsion formation and sludge issues may arise, potentially impacting fuel efficiency and system reliability. Regular monitoring and maintenance are crucial to mitigate these concerns and ensure optimal vessel performance.

Sulphur

Sulphur is naturally found in crude oils and, consequently, is present in residual fuels. Geographical variations in sulphur levels exist due to the diverse sulphur compositions in crude oils from different regions. Sulphur is associated with higher boiling point compounds and is therefore present at higher levels in residual fuel compared to distillates (Witherby, 2013).

During the combustion process, sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are generated. Under specific engine conditions, such as excess air, temperature, and pressure, these gases undergo partial conversion into sulphuric acid and sulphurous acid. This conversion typically occurs when the gases reach temperatures below their respective dew points.

Sulphurous acid forms within a temperature range of 50°C to 60°C, while sulphuric acid forms within a range of 110°C to 150°C. These acids pose a risk of corrosion, particularly in the cooler regions of engines and boilers. This phenomenon is commonly referred to as “cold end corrosion”.

Sodium, Iron, Nickel, Magnesium, Lead and Potassium

Sodium is a metal found in crude oil from certain geographical areas, such as western Venezuela. It remains in the fuel after refining and not only contributes to the ash content but also forms compounds that lower the melting point of ash in the exhaust when combined with any existing sodium.

Iron present in fuel oil originates from various sources, including iron particles from pipelines, valves, and worn metal components. Additionally, rust contributes to the iron content. Iron from engine wear can also be found in any waste lubricating oil added to the fuel.

Nickel, an element originating from crude oil, serves as a key component for identifying oil samples. Despite treatment efforts, the content of sulphur, vanadium, and nickel remains unaltered. Therefore, two samples purportedly from the same oil source will exhibit closely aligned levels of sulphur, vanadium, and nickel if indeed they are from the same oil (Fisher, & Meech, 2013).

Magnesium originates from salts present in seawater. The presence of magnesium allows the determination of the proportion of sodium attributable to seawater.

Lead can be present if waste lubricating oil from gasoline engines using leaded gasoline has been added to the fuel.

The elements of calcium, nickel, potassium, and zinc in small quantities can be used to indicate the presence of used lubricants in the fuel supply.

RESULTS AND DISCUSSION

This article presents an analysis of over 6000 fuel samples (with IP501 method) obtained from two sample points within a purification system, conducted by independent laboratories. While all samples must meet the ISO 8217:2017 Standard for marine residual fuel before bunkering, this analysis focuses on elements with potentially harmful effects on marine engine systems.

Fuel samples were analysed from two sample points within ships’ purification system, at the purifier inlet and outlet. Samples were analysed for 15 different elements and compounds. The elements tested were: aluminium (Al), silicon (Si), calcium (Ca), iron (Fe), lead (Pb), magnesium (Mg), nickel (Nc), phosphorus (P), potassium (K), sodium (Na), vanadium (V), and zinc (Zn), while the compounds were: aluminium-silicon alloy (AlSi), water (H_2O), and ash. There were 5667 measurements for each inlet and outlet, for each parameter.

Efficiency of purification was calculated using the formula:

$$1 - \frac{\text{Outlet measurement value}}{\text{Inlet measurement value}} \qquad (1)$$

Only positive efficiency values were taken into account for further analysis, i.e. negative efficiency values (where the value measured at the outlet were higher than those at the inlet) were discarded, along with any efficiency values equal to zero (0).

The resulting efficiency values for each measurement were then grouped into categories (by 0.1 or 10%), averaged, and plotted onto a graph to visually estimate the normality of distribution. Each parameter then had a linear trendline estimated, according to the formula:

$$y = a \cdot x + b \qquad (2)$$

The linear trendability (R^2) value was also estimated for each parameter and trendline, indicating how well the trendline fits the data.

The Spearman Correlation Coefficient was used to assess the significance of relationship between measured elements. This non-parametric measure does not assume normal distribution of the data. The correlation analysis was conducted using Python's pandas library, which provides a function corr(method='spearman') for calculating this statistic.

RESULTS

The original dataset had 5668 separate inlet and outlet measurements for each element. After calculating efficiency for each measurement, according to equation 1 above, it was decided to consider only the efficiency values greater than zero in further study. The descriptive statistics are given in Table 1.

Table 1. Descriptive statistics of purification efficiency of elements tested (No – number of valid measurements; Min – minimum efficiency value recorded; Max – maximum efficiency value recorded; Mean – arithmetical mean of measured efficiency values; StD – standard deviation of measured efficiency values; Median – median value of measured efficiency values); Var – variance of measured efficiency values)

	Al	**AlSi**	**Ash**	**Ca**	**Fe**	**Pb**	**Mg**	**Nc**	**P**	**K**	**Si**	**Na**	**V**	**H_2O**	**Zn**
No	5305	5476	4609	3999	4725	38	1275	2797	591	1342	5202	4336	2488	2087	1409
Min	0.024	0.013	0.011	0.007	0.014	0.200	0.125	0.013	0.006	0.040	0.014	0.015	0.003	0.029	0.028
Max	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mean	0.640	0.640	0.225	0.458	0.425	0.785	0.772	0.188	0.635	0.721	0.669	0.271	0.108	0.471	0.610
StD	0.234	0.238	0.178	0.293	0.233	0.266	0.282	0.160	0.351	0.308	0.246	0.200	0.166	0.254	0.333
Med	0.667	0.667	0.180	0.400	0.393	1.000	1.000	0.143	0.500	1.000	0.667	0.222	0.057	0.446	0.500
Var	0.055	0.057	0.032	0.086	0.054	0.071	0.079	0.025	0.123	0.095	0.061	0.040	0.027	0.065	0.111

Negative efficiency values resulted primarily when the outlet measurement value (i.e. value after purification) was greater than the inlet value (the value before purification), implying higher concentration of that element after purification. In situation when the inlet measurement value was equal to 0, the equation (1) retuned an error (division by zero), and such values were likewise discarded. When the calculated efficiency value was equal to zero, it implied that both inlet and outlet values were identical, in which case there was no purification. Figure below shows discarded efficiency values per parameter measured according to category.

After plotting the efficiency values against the number of samples, it was apparent that the parameters could be grouped into four distinct groups according to the shape of the curve formed as well as general trendline equation and R^2 values. Figures 4 to 8 show the groups.

Group 1 includes aluminium (Al), aluminium-silicon alloy (AlSi), and silicon (Si). This group is characterised by an upward slope of the trendline and the relatively high to high R^2 values (ranging from 0.69 to 0.82) (Figure 4). These elements show the best purification results. Their mean and median efficiency values are fairly close together and relatively high (Table 1). They also had the lowest number of discarded efficiency values (Fig. 3).

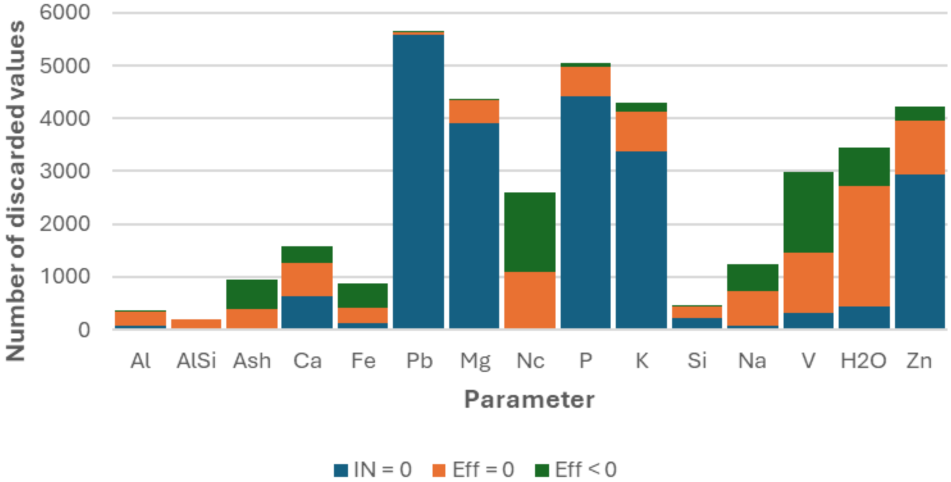


Figure 3. Representation of discarded efficiency values (IN = 0 – measurement at the inlet was equal to zero; Eff < 0 – calculated efficiency value was negative; Eff = 0 – calculated efficiency value was equal to zero)

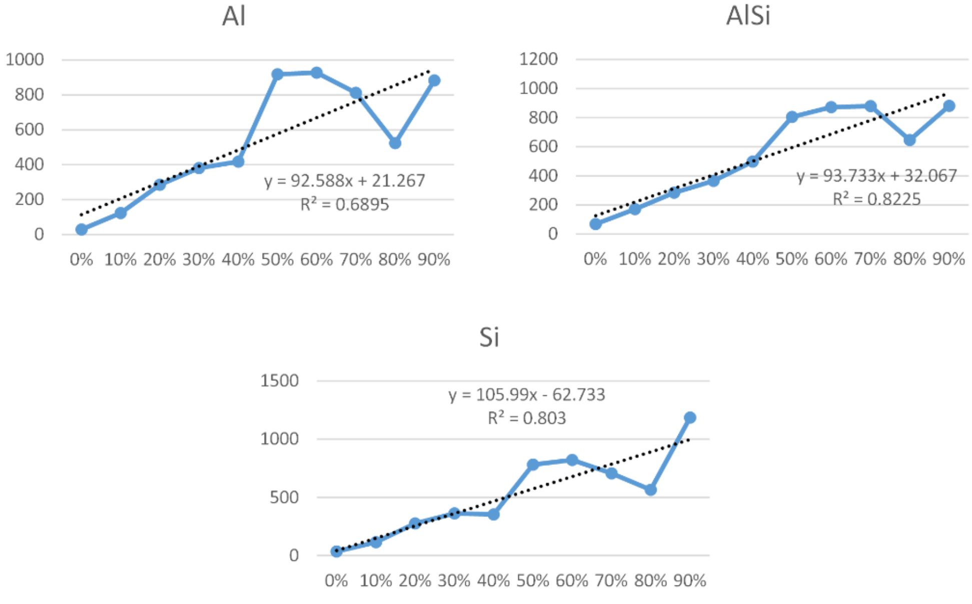


Figure 4. Parameters of Group 1 (X-axis – efficiency, Y-axis –number of samples)

Group 2 consists of Ash, sodium (Na), nickel (Nc), and vanadium (V), and the plots show a downward-sloping trendline and R^2 values lower than those of Group 1 (0.43 to 0.81). These elements had the highest number of measurements below 20% and generally had very low number of measurements above 50% (Fig. 5).

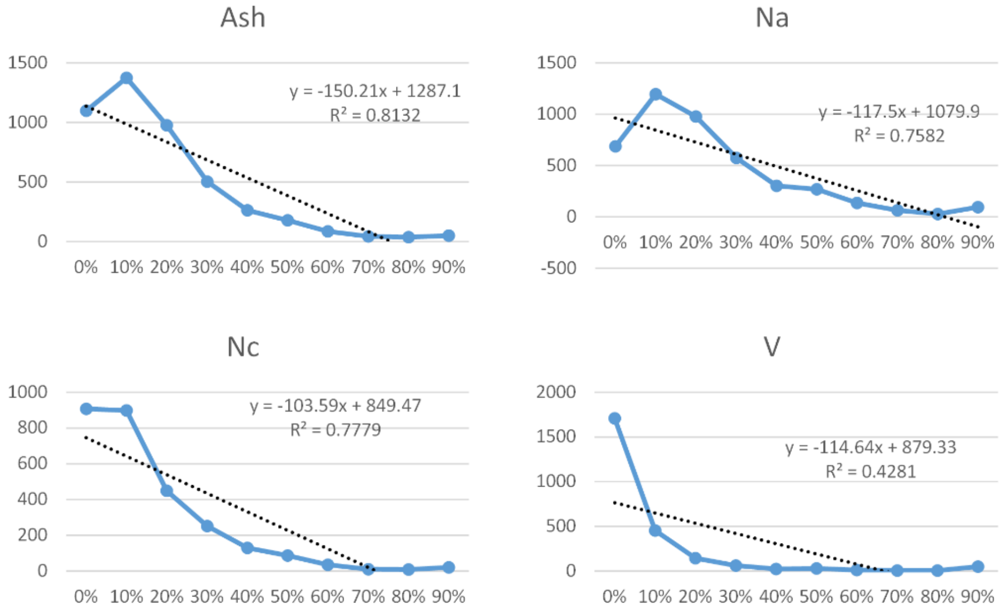


Figure 5. Parameters of Group 2 (X-axis – efficiency, Y-axis –number of samples)

Group 3 includes potassium (K), magnesium (Mg), phosphorus (P), lead (Pb), and zinc (Zn). The trendline has an upward slope, but not as pronounced as that of group 1, and R^2 values are in the low range (0.12 to 0.34). It is typical for this group to have evident peaks at 50% and 90% efficiency, with low values at 40% and 60 to 80% (Fig. 6). All elements of this group, apart from Zn, have the highest occurrence of efficiency values in the 90-100% range (which, in turn, increases the average and median efficiency values). They also had the highest number of discarded values, so that the efficiency calculation for lead (Pb) was done using just 38 valid entries (Table 1).

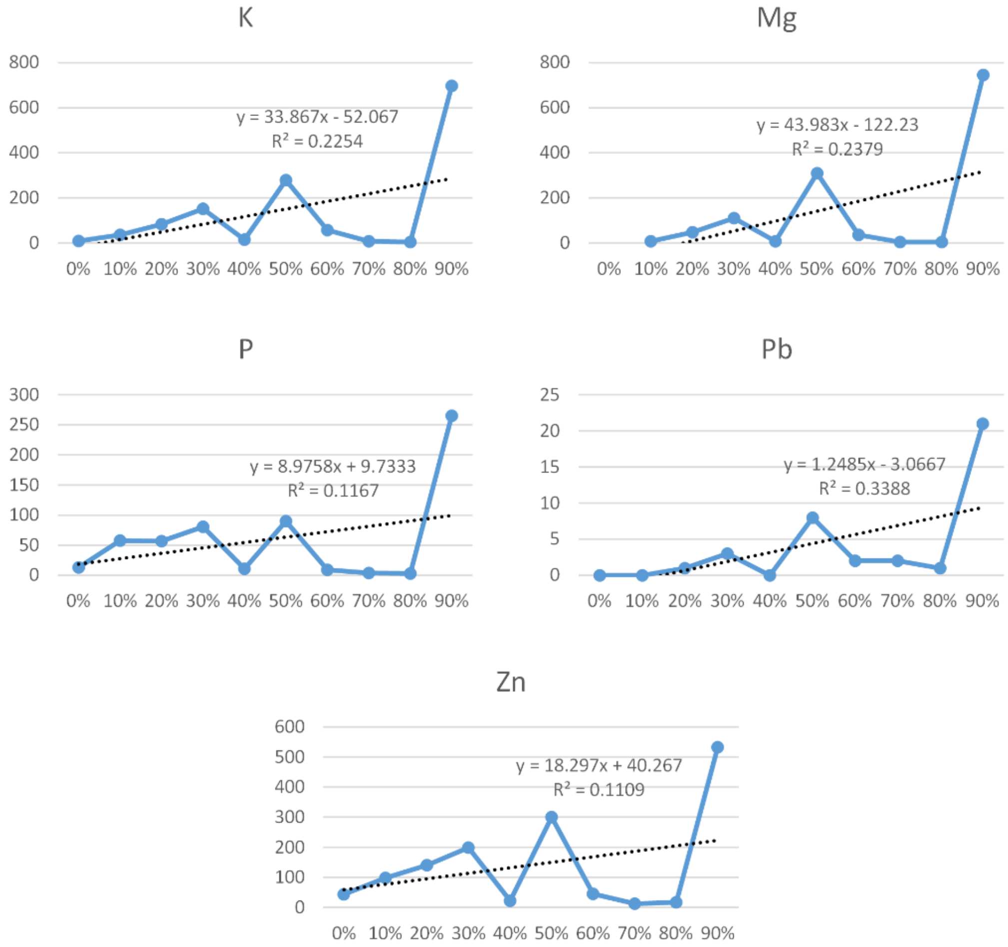


Figure 6. Parameters of Group 3 (X-axis – efficiency, Y-axis –number of samples)

Group 4 (calcium (Ca), iron (Fe), and water (H_2O)) shows a sharp increase in efficiency up to 20-30%, and pronounced reduction at 40%, with a sharp increase at 90%. This group has the lowest R^2 values (0.007 to 0.2), with downward sloping trendline.

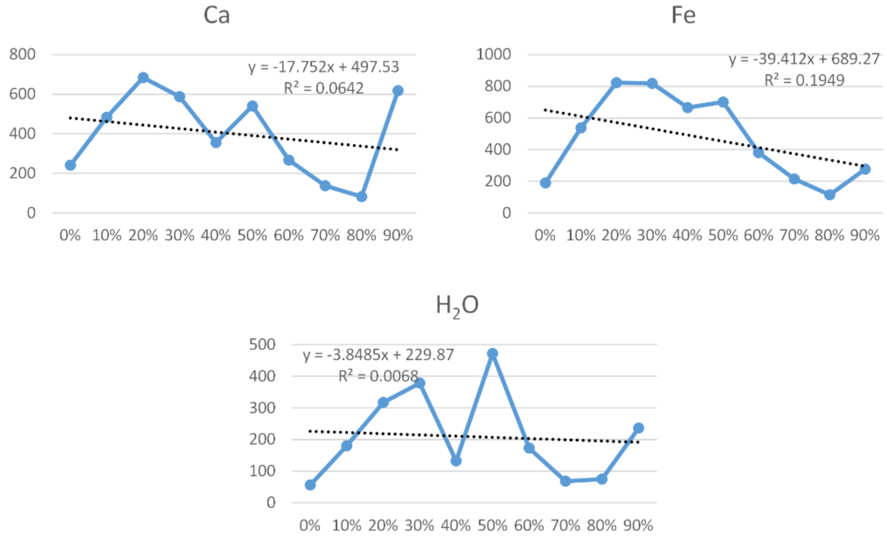
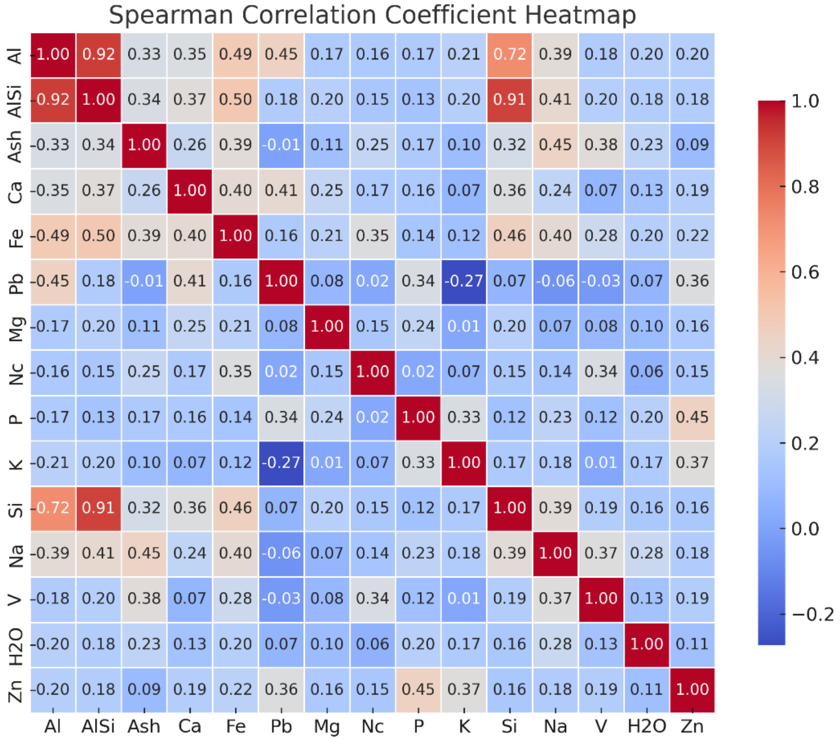


Figure 7. Parameters of Group 4 (X-axis – efficiency, Y-axis –number of samples)

Spearman Correlation Coefficient heatmap for the shows the strongest correlation between the group 1 elements (aluminium, silicon and aluminium-silicon alloy), ranging from 0.71 (Al-Si) to 0.92 (Al-AlSi) (Fig. 8).

The lowest correlation (−0,27) was found between lead (Pb) and potassium (K), with negative correlation also recorded for lead and sodium (−0,06), vanadium (−0,03), and ash (−0,01).



	Al	AlSi	Ash	Ca	Fe	Pb	Mg	Nc	P	K	Si	Na	V	H2O	Zn
Al	1.00	0.92	0.33	0.35	0.49	0.45	0.17	0.16	0.17	0.21	0.72	0.39	0.18	0.20	0.20
AlSi	0.92	1.00	0.34	0.37	0.50	0.18	0.20	0.15	0.13	0.20	0.91	0.41	0.20	0.18	0.18
Ash	0.33	0.34	1.00	0.26	0.39	-0.01	0.11	0.25	0.17	0.10	0.32	0.45	0.38	0.23	0.09
Ca	0.35	0.37	0.26	1.00	0.40	0.41	0.25	0.17	0.16	0.07	0.36	0.24	0.07	0.13	0.19
Fe	0.49	0.50	0.39	0.40	1.00	0.16	0.21	0.35	0.14	0.12	0.46	0.40	0.28	0.20	0.22
Pb	0.45	0.18	-0.01	0.41	0.16	1.00	0.08	0.02	0.34	-0.27	0.07	-0.06	-0.03	0.07	0.36
Mg	0.17	0.20	0.11	0.25	0.21	0.08	1.00	0.15	0.24	0.01	0.20	0.07	0.08	0.10	0.16
Nc	0.16	0.15	0.25	0.17	0.35	0.02	0.15	1.00	0.02	0.07	0.15	0.14	0.34	0.06	0.15
P	0.17	0.13	0.17	0.16	0.14	0.34	0.24	0.02	1.00	0.33	0.12	0.23	0.12	0.20	0.45
K	0.21	0.20	0.10	0.07	0.12	-0.27	0.01	0.07	0.33	1.00	0.17	0.18	0.01	0.17	0.37
Si	0.72	0.91	0.32	0.36	0.46	0.07	0.20	0.15	0.12	0.17	1.00	0.39	0.19	0.16	0.16
Na	0.39	0.41	0.45	0.24	0.40	-0.06	0.07	0.14	0.23	0.18	0.39	1.00	0.37	0.28	0.18
V	0.18	0.20	0.38	0.07	0.28	-0.03	0.08	0.34	0.12	0.01	0.19	0.37	1.00	0.13	0.19
H2O	0.20	0.18	0.23	0.13	0.20	0.07	0.10	0.06	0.20	0.17	0.16	0.28	0.13	1.00	0.11
Zn	0.20	0.18	0.09	0.19	0.22	0.36	0.16	0.15	0.45	0.37	0.16	0.18	0.19	0.11	1.00

Figure 8. Spearman Correlation Coefficient heatmap

CONCLUSIONS

Measuring fuel elements is crucial for ensuring the smooth operation and longevity of main engines. By monitoring fuel purifier efficiency and the quantity of different fuel elements, engineers can detect abnormalities and react preventively before they escalate into major engine troubles. In this study, an in-depth analysis of marine fuel composition was conducted, focusing on the presence of 15 distinct elements that serve as indicators of impurities.

The findings revealed abrasive elements, particularly aluminium (Al), silicon (Si), and their combination (Al+Si), across the samples examined. Notably, it was observed that in more than 50% of the samples, there was effective elimination of these impurities, signifying a high efficiency of the ship's fuel separator system. This underscores the importance of rigorous monitoring and efficient filtration processes in maritime operations to ensure the quality and integrity of the fuel used. This, in turn, contributes to the reliable and smooth functioning of marine engines while mitigating the risk of abrasive wear and related operational challenges.

Among the elements categorized in the second group, namely ash, sodium (Na), nickel (Ni), and vanadium (V), a concerning trend emerged. It was observed that these elements exhibited a higher prevalence of samples with low efficiency in elimination, with rates reaching up to 30%. Conversely, a significantly smaller proportion of samples demonstrated efficient elimination of these elements. This highlights a potential area of concern regarding the effectiveness of the ship's fuel separator system in addressing these specific impurities.

Although certain elements are not present in every sample (as indicated by the number of analysed samples, e.g., Pb, P, etc.), IP methods allow for the measurement of a large number of elements, which can be of great benefit to marine engineers and the preventive maintenance of systems. This proactive approach not only reduces the risk of unexpected breakdowns but also optimizes engine performance and extends its operational lifetime.

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