

Sulfur Concentration Analysis of Marine Fuel Oil with SLFA Series

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Following The Paris Agreement (2015) by United Nations Framework Convention on Climate Change, new regulation of sulfur concentration of marine fuel oil will be applied from 2020, and existing vessels will have to change their fuel oil from normal type to expensive low sulfur type before entering the regulated marine area properly. The continuous monitoring of sulfur concentration of inlet fuel oil will be also indispensable, where X-ray fluorescence method is most simple and accurate for this application, so our SLFA-60M sulfur-in-oil analyzer is introduced in this article.

Overview

The Conference of the Parties to the United Nations Framework Convention on Climate Change (COPs: Conference of the parties abbreviations) was held annually by the United Nations Framework Convention on Climate Change (United Nations Framework Convention on Climate Change abbreviations: UNFCCC), which began in 1992. The Kyoto Protocol was adopted in 1997, and the Paris Agreement was adopted in 2015. The Paris Agreement aims to reduce greenhouse gas emissions to the level that forests can absorb them in the second half of the 21st century in order to suppress global average temperature rise, and measures to deal with environmental issues are beginning to be strengthened worldwide. This trend is the same in the ship industry, and particularly in the regulation on sulfur concentration in marine oil which started from 2020, the regulation on sulfur concentration has changed drastically so that the ship industry is also making a great move toward the reduction of the emission amount. This regulation aims to reduce the amount of sulfur oxides emission into the environment, but there are three main methods for reducing the amount of sulfur oxides discharged.

- (1) Use conventional heavy oil and install exhaust gas treatment equipment.
 - (2) Switching to natural gas (LNG) engines
 - (3) Use of low sulfur fuel
- (1) or (2) is mainly applied for new ship building because large-scale modification is necessary for existing ships. Although (3) can be dealt with only by replacing fuel/lubricating oil in existing, it is necessary to switch fuel between the sea area where air pollutants are regulated (ECA sea area) and the normal sea area. Especially, when a ship enters the ECA sea area from the normal sea area,

since the fuel is switched from the high sulfur concentration fuel to the low sulfur concentration fuel, it must be confirmed whether or not the fuel switching has been completed correctly, and it is necessary to analyze the fuel before the fuel is supplied to the engines. It is also possible to switch fuels from several ten hours before entering the ECA sea area in order to reduce the risk of inadequate switching, but it is also useful to measure the sulfur concentration in order to reduce the consumption of expensive low sulfur fuels.

The concentrations of sulfur in fuels have long been measured, and methods of measuring sulfur in fuels have been defined by ISO/ASTM/JIS and the like. X-ray fluorescence analysis is the simplest way for measuring the sulfur concentration in fuels, and it is used in places where fuels are refined and consumed, such as pipelines, petroleum refineries, and power plants. X-ray fluorescence analyzers are capable of non-destructive measurement, so that samples are held, and detailed analysis after X-ray analysis is possible, and they are widely used for screening analysis in various fields. Especially for the analysis of sulfur in the fuel in a ship, the analysis operation of X-ray fluorescence analysis is required to be simple because the crew member who is not an expert in the analysis performs the analysis of sulfur in fuel as part of daily work.

Measurement of Sulfur in Oil by X-ray Fluorescence Analysis

X-ray fluorescence generated by irradiating primary X-ray to a sample and detected by X-ray detector. Since the energy of the generated fluorescent X-rays differs depending on the element contained in the sample, an

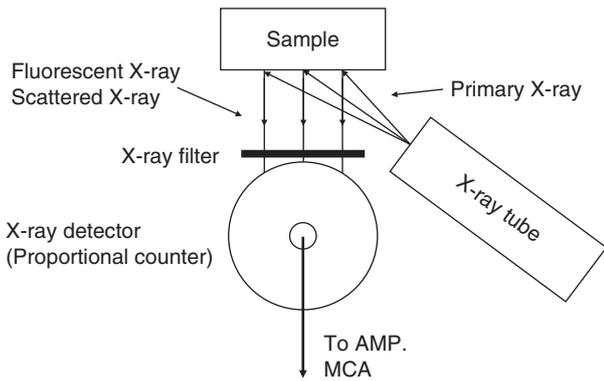


Figure 1 System out line



Figure 2 Outside appearance of instrument

energy spectrum can be obtained. By observing peak energy and its intensity of each element, qualitative and quantitative analysis can be performed. In analyzing the sulfur in the fuel, when the fuel serving as the sample is irradiated with primary X-rays, fluorescent X-rays corresponding to elements contained in the sample (2.3 keV in the case of sulfur) are generated. Some of the irradiated X-rays are scattered by the sample and become scattered X-rays. Figure 1 shows schematic diagram of SLFA-series and Figure 2 shows outside appearance of SLFA-60M.

If the intensity of the irradiated X-rays is constant, the fluorescent X-rays intensity of sulfur can be correlated with the concentration of the sulfur contained in the sample and the intensity of the scattered X-rays, so that the calibration curve can be determined by measuring a plurality of standard samples having known sulfur concentrations in advance.

X-ray signal detection processing

In this apparatus, the fluorescent X-rays and the scattered X-rays emitted from the sample enter a proportional counter tube, and an electric charge proportional to the energy of the X-rays is generated.

This charge is converted to a voltage signal by a pre-amplifier and then stored in a multi-channel wave height

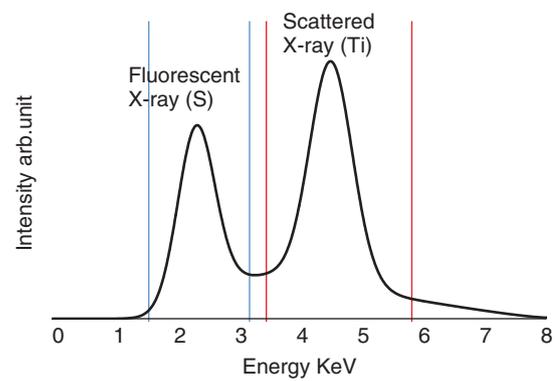


Figure 3 Measurement spectrum

analyzer through a spectrum processing circuit to obtain an energy spectrum. Figure 3 is a schematic diagram of spectra obtained when fluorescent X-rays and scattered X-rays of sulfur emitted from a sample are measured by a proportional counter tube. The matrix effect of the sample can be corrected by normalizing the area (S) of the region corresponding to the X-ray fluorescence of sulfur in this spectrum by the area (B) of the region corresponding to the X-ray scattering.

Quantitative analysis

Quantitative analysis can be performed by previously measuring heavy oil standard samples of multiple concentration levels to derive a relational expression between sulfur concentration and fluorescent X-ray intensity, and creating a calibration curve. In the concentration range of 1% to 10%, the relationship between the concentration and the X-ray intensity cannot be linearly approximated by the self-absorption effect of the fluorescent X-ray caused by the increase in the sulfur concentration, and therefore, the approximation by the quadratic expression is used.

Multiple calibration curves can be recorded, and the automatic selection function of the calibration curve which is automatically selected from three types of low, medium, and high concentration according to the sample is mounted. It is possible to automatically switch depending on the concentration of the measurement target, and it is possible to save the user from the time and labor of selecting the calibration curve. In the analysis of sulfur on board the ship, it is necessary to measure a low-concentration sulfur fuel of 0.1% from a high-concentration sulfur fuel of about 3%, and it is possible to perform an accurate analysis by preparing a calibration curve suitable for each concentration range in advance. The calibration curve using the heavy oil standard sample is shown in Figure 4, and the reproducibility of the measurement for the 0.2% sample is shown in Table 1.

Since we can get the reproducibility of the 0.0003% at 0.2%

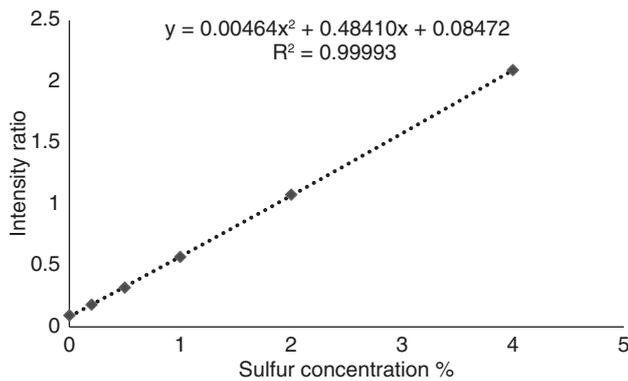


Figure 4 Calibration curve

Table 1 Result of repeatability test

Measurement number	Measurement value
1	0.1946
2	0.1949
3	0.1948
4	0.1950
5	0.1951
6	0.1956
7	0.1954
8	0.1950
9	0.1956
10	0.1951
Average	0.1951
Standard deviation	0.0003

samples*, considering reproducibility, safety thresholds be set as 0.0990 %. When sulfur content are lower than this safety thresholds, sulfur content are surely lower than 0.1%.

*When sample sulfur content is high, reproducibility becomes high. Usually, we define 3 times of reproducibility of 0% sample as detection limit.

Daily maintenance of devices

In the case of calibration curve quantitative, it is necessary to confirm whether the device is normal or not before analysis. However, solid confirmation samples can be substituted because it is difficult to manage a wide variety of standard samples on board the ship, and the standard samples are consumed entirely.

The solid confirmation sample is premeasured and labeled at a concentration equivalent to sulfur, and by analyzing this confirmation sample before the actual sample analysis, it is possible to judge whether or not the device is normal, abnormal, or contaminated.

Maintenance automation

Since the position of the peak of the X-ray spectra

changes depending on the use condition of the apparatus, it is necessary to perform energy calibration routinely. Energy calibration of a spectrum is usually performed by measuring a sample for energy calibration, calculating a difference between a peak position of a specific element and an actual peak position, and calculating a correction coefficient of a detector. When the energy position of the spectrum deviates, the SLFA-series automatically adjusts the compensation factor to perform the energy calibration process and automate the maintenance. As the fluctuation factors of the energy shift, there are a change in the peak value of the output pulse due to a change in the internal gas composition of the proportional counter tube and the like, and a change in the characteristics of the preamplifier and the analog-to-digital converter (ADC) due to a change in the ambient temperature and a change over time. When the energy shift of the spectrum occurs due to these factors, accurate measurement cannot be performed, so that the X-ray fluorescence peak of sulfur and the X-ray scattering peak of titanium obtained when the sample is measured are constantly monitored, and the energy calibration is automatically performed so that the peak position of sulfur or the peak position of the X-ray scattering of titanium becomes a predetermined energy. (The higher the intensity values of the sulfur and titanium peaks are used for calibration). This process makes it possible to make accurate measurements at all times even if energy shifts occur due to environmental changes during the measurement or due to aging of the proportional counter tube.

Summary

This paper briefly introduces the equipment outline, performance, and maintainability of the X-ray fluorescence sulfur in oil analyzer SLFA-60M. The onboard operator is not an analytical expert and is required to provide accurate values with minimal manipulation and care. Although the device requires routine measurement of a confirmation sample, no other maintenance is required, and data can be obtained by a simple analysis flow of sample preparation, set, and analysis.

* This content is based on our investigation at this publish unless otherwise stated.



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