

WASHWATER MONITORS FOR MARINE SCRUBBER SYSTEMS: TECHNICAL CHALLENGES IN MEASURING PAH-VALUES

Scrubber systems produce washwater that can be discharged to sea. Before discharging, the scrubber washwater needs to meet certain environmental criteria. Therefore, washwater monitors are part of scrubber systems and pH-level, PAH (polycyclic aromatic hydrocarbon) concentration, turbidity and temperature are checked. Temperature, pH and turbidity measurements are well known and monitored according to international standards. However, less is known about PAH measurements.

PAH refers to a group of molecules with two or more fused aromatic rings. PAHs are a natural part of petroleum and, in addition, are formed as by-products of fuel combustion. Therefore, they are present in exhaust gases and can be transferred from the exhaust gas to the washwater in the scrubbing process. Since PAHs are known environmental contaminants, the PAH concentration in washwater needs to be monitored continuously and kept below specific limits before discharging washwater to sea. The limits are set by the International Maritime Organization (IMO) to ensure environmental protection of the sea.

Various techniques allow the determination of PAH concentration, the most precise method being gas chromatography (GC). While GC is a well-known laboratory method, it is not suitable for continuous online monitoring and, therefore, not an option for scrubber washwater monitors. However, optical techniques allow online monitoring and are therefore employed in scrubber washwater monitors. In most cases, PAH-monitors use ultraviolet (UV) fluorescence techniques, in which scrubber washwater is excited with UV light and resulting fluorescence from possible

contaminants is detected. For practical and cost reasons, the discrimination of different PAHs is not required. However, wavelength ranges for UV excitation and fluorescence detection are chosen such that they correspond well to absorption and fluorescence spectra of one specific PAH, namely phenanthrene (Fig. 1).

Phenanthrene is one of the most prevalent PAHs in exhaust gases and, therefore, the IMO decided to use it as an indicator PAH for the total amount of PAHs. Hence, IMO requires that PAH-monitors are calibrated with phenanthrene. The measured fluorescence signals are then indicated as phenanthrene-equivalent concentration values PAH_{phe} , and washwater discharge concentration limits are given by the IMO in PAH_{phe} .

It must be mentioned that even with phenanthrene-specific wavelength ranges for the excitation and fluorescence light, detected fluorescence signals originate not solely from phenanthrene, but can also have contributions from other

PAH compounds, such as naphthalene, dibenzothiophene, and so on, and derivatives thereof (Fig. 1).

Hence, with the definition of PAH_{phe} , the required optical monitors can indicate values that are different from the PAH concentrations measured with GC methods. The GC values are often taken for comparison with and verification of the PAH washwater monitors.

To understand the differences between the two techniques, a few aspects of the GC technique will be explained here. For accurate concentration measurements with GC, the GC instrument must be calibrated with the expected substances. Often, an international standard solution called 16 EPA-PAHs is used for PAH calibrations. Examples of the 16 PAHs in this standard solution include naphthalene, fluorene, phenanthrene, and so on, but no derivatives of these parent PAH substances. PAH derivatives such as methyl-phenanthrene or -naphthalene distinguish themselves from the parent

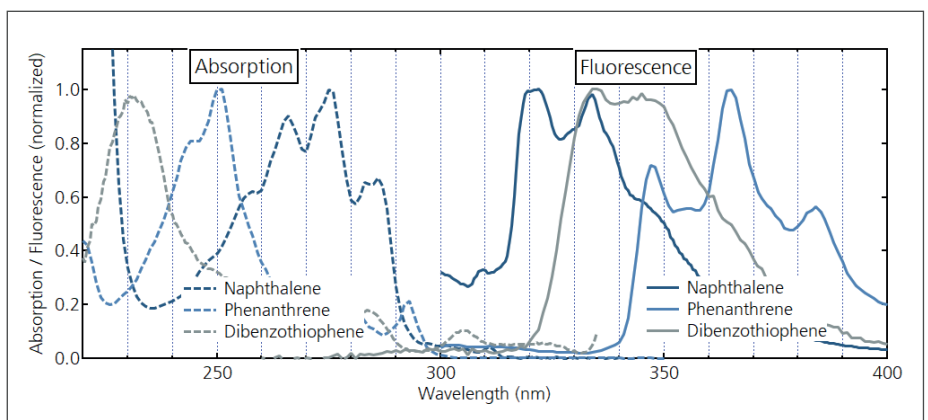


Fig. 1: Normalised absorption (dashed lines) and fluorescence (solid lines) spectra of naphthalene (dark blue), phenanthrene (light blue), and dibenzothiophene (grey). Since the absorption and fluorescence spectra of phenanthrene overlap partly with those of other substances (naphthalene and dibenzothiophene spectra are shown here exemplarily), measured fluorescence signals always contain contributions from non-phenanthrene substances. Therefore, PAH-monitors do not display phenanthrene concentrations but phenanthrene-equivalent concentrations PAH_{phe} .

compound by one or more methyl groups. Such derivatives are present in similar concentrations as their parent compounds in fuels and exhaust gases and, therefore, in scrubber washwaters. Although GC can discriminate derivatives from parent compounds, they are often not quantified in GC laboratory reports, since the instrument is not calibrated for these substances.

In contrast, fluorescence techniques employed in washwater monitors cannot distinguish derivatives from their parent compounds because their optical properties are very similar to the parent compounds. Hence, washwater monitors record fluorescence signals from phenanthrene and all its derivatives and indicate these signals as PAH_{phe} concentrations. As a result, PAH_{phe} values of PAH washwater monitors are generally higher than phenanthrene concentrations in washwater samples measured by GC.

It must be noted that the IMO has defined limits for PAH_{phe} values and not for phenanthrene concentrations. The gap between online measurements of PAH washwater monitors and laboratory measurements by GC methods can be even larger, because GC measurements are not online, but washwater samples must be taken on board the ship and transported to laboratories for GC analysis. In this process, PAH concentrations in the washwater samples can decrease when water samples are not stored properly and not measured within a few days. After all, IMO guidelines require PAH measurements to be taken continuously and conducted with optical techniques and, therefore, PAH_{phe} values are the relevant values that must be within the IMO limits and not GC laboratory values of phenanthrene concentrations.

With the required optical techniques for online monitoring, several challenges arise for manufacturers of PAH washwater monitors. One general challenge for optical measurements of fluids is the contamination or fouling of optical elements that are in contact with the fluid. Such contamination can affect the optical measurements and either needs to be avoided or quantified. If contamination can be measured properly, then instruments can account for it. Most scrubber systems have two

monitors for washwater measurements: one before the water enters the scrubber and a second one after the scrubber process before discharge to sea. Since most scrubbers work with seawater, fouling of optical elements in contact with seawater is an issue for both washwater monitors.

In addition, contamination with additional substances from the scrubber process can occur when monitoring the washwater after the scrubber process. Optical windows that are often used to separate the measurement chamber with the washwater from other optical elements are prone to contaminate within days or weeks. As a result, the transmission of UV excitation light and the fluorescence of PAHs are reduced, and lower signals will be detected. Hence, if this window fouling is not quantified and taken into account properly, such monitors will display incorrect PAH_{phe} values that are too low.

Proper correction for optical window fouling can be challenging. Therefore, device designs that completely omit contact between washwater and optical elements are more reliable. For example, the washwater monitors of SIGRIST-PHOTOMETER AG apply a so-called non-contact free-fall technique, in which the washwater falls in a free jet through the instrument while measurements are taken (Fig. 2).

With this design fouling and contamination of optical elements is omitted and optical measurements are reliable over extended time periods. In addition, no regular cleaning of optical elements is necessary.

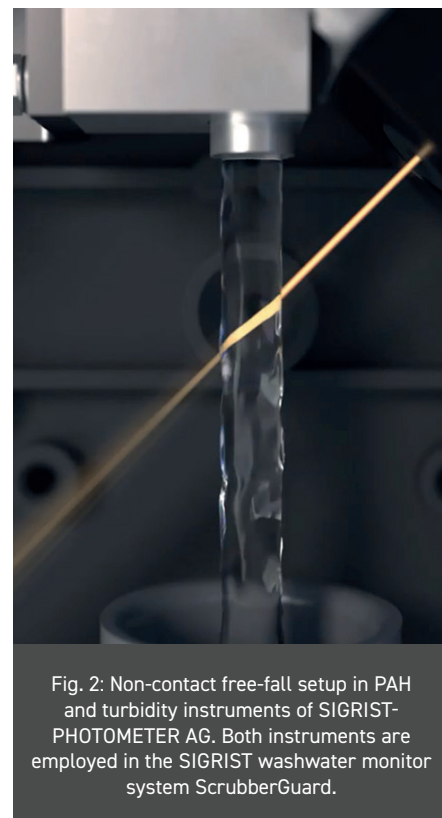


Fig. 2: Non-contact free-fall setup in PAH and turbidity instruments of SIGRIST-PHOTOMETER AG. Both instruments are employed in the SIGRIST washwater monitor system ScrubberGuard.

Another challenge with optical PAH measurements is optical absorption and scattering in scrubber washwater. Optical absorption and scattering can attenuate the UV light that excites PAH molecules in the washwater and reduce the detected fluorescence that results from these excited PAH molecules. Both effects lead to a lower detected optical signal. If not corrected properly, the indicated PAH_{phe} values will be lower than actual values. Whether absorption and scattering play a role depends on the concentrations of absorbing and scattering substances in the washwater and the optical path length L (Fig. 3).

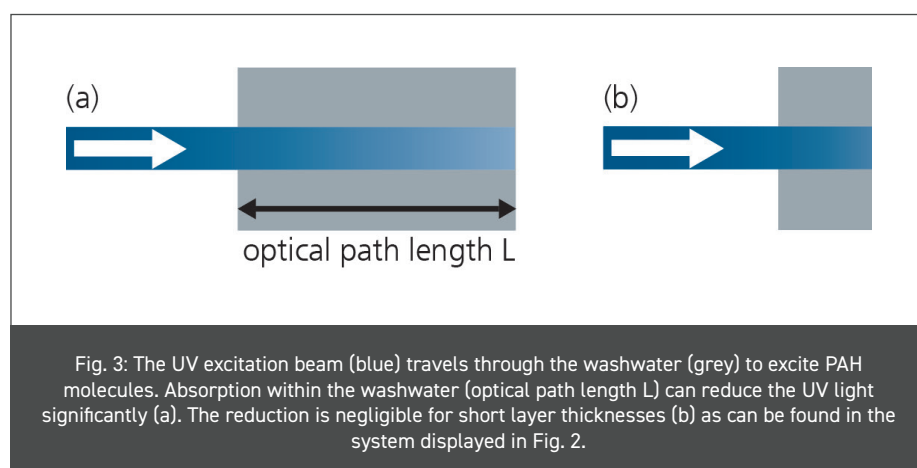


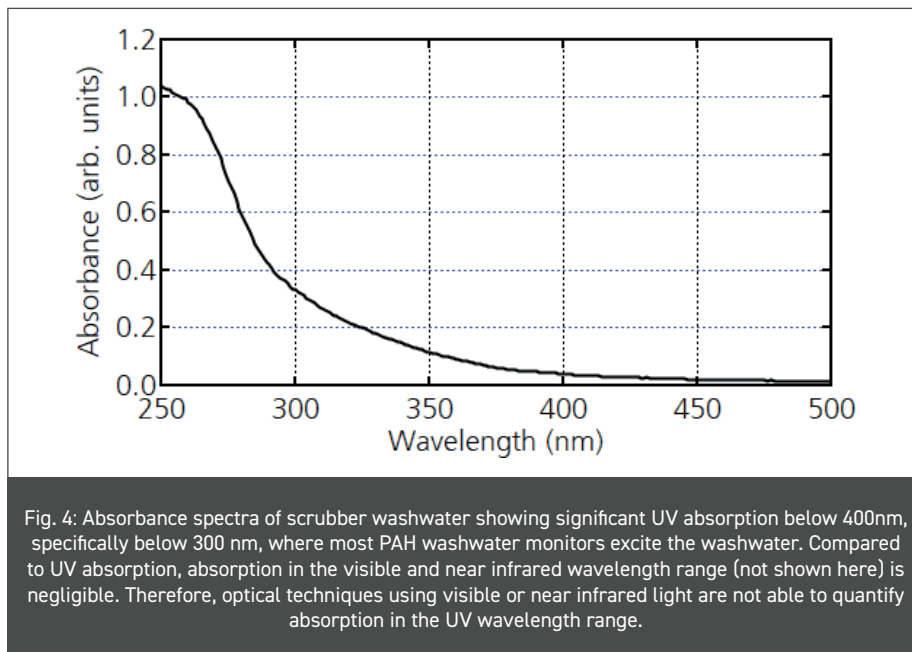
Fig. 3: The UV excitation beam (blue) travels through the washwater (grey) to excite PAH molecules. Absorption within the washwater (optical path length L) can reduce the UV light significantly (a). The reduction is negligible for short layer thicknesses (b) as can be found in the system displayed in Fig. 2.

The exciting UV light travels through a certain distance (layer thickness) within the washwater. If pollutants are present in the washwater the UV excitation light generates fluorescence light that itself has to travel through washwater before it reaches the optical detector. The shorter the involved path lengths of excitation and fluorescence lights, the smaller the signal reduction from absorption and scattering. Correcting the measured signal for absorption and scattering effects can be challenging.

Some washwater monitor systems use turbidity measurements to correct the detected signal for scattering effects. IMO guidelines require turbidity measurements using optical scattering methods according to ISO 7027. The applied scattering wavelength is 860nm, defined by the norm, which is very different from the UV fluorescence measurements at wavelengths below 400nm. Therefore, turbidity measurements can only provide an indication of light scattering in the washwater, however, precise correction of PAH_{phe} values for scattering effects in the UV wavelength range is not possible.

Turbidity measurements are even less suited to account for absorption effects. Molecular absorption occurs primarily in narrow wavelength ranges that are specific to the substances. Scrubber washwater often has pronounced absorption bands in the UV that can be associated with SO_x and PAHs from the scrubber process (Fig. 4). Such UV absorption that cannot be detected with turbidity monitors, leads to deviations (reductions) of the measured signals in PAH monitors.

Since absorption is governed by an exponential law, the deviation in percent is given by the formula $100 \cdot (1 - e^{-a \cdot L})$, in which a is the absorption coefficient and L is the thickness of the probed washwater layer. For small absorption coefficients the deviation is approximately $100 \cdot a \cdot L$, that is increases linearly with L . For example, an absorption coefficient of 1 1/m results in a reduction of the measured signal of 1% with a layer thickness



$L=0.01\text{m}=1\text{cm}$ and 5% with $L=5 \text{ cm}$. Therefore, PAH washwater monitors with a smaller L provide more accurate readings than such with larger L . This is particularly relevant for washwaters with high levels of SO_x and PAHs.

As shown in Fig. 2, the PAH monitor from SIGRIST-PHOTOMETER AG samples a washwater jet with a diameter of less than 1cm, which is distinctly less than other PAH-monitors with optical path lengths of more than 5cm. Therefore, the SIGRIST instruments indicate reliable PAH_{phe} values even at higher concentrations of washwater contaminants, in the range of IMO PAH_{phe} limits, where it is most relevant for seawater pollution prevention.

In conclusion, online washwater monitors that are part of exhaust gas cleaning systems or scrubbers are regulated by IMO guidelines and, therefore, PAH measurements have a specific meaning in the context of scrubber washwater monitoring. Online PAH washwater monitors that are compliant with IMO guidelines record so-called PAH_{phe} values that are different from PAH values measured with standard laboratory techniques such as gas chromatography.

It is the PAH_{phe} values which are relevant, and which must be within

the accepted limits in order to be compliant with IMO guidelines. Online measurements of PAH_{phe} values rely on optical techniques that bring along several challenges, for example fouling of optical elements or optical absorptions in the washwater. Employing proper engineering and system design ensure correct PAH_{phe} measurements and, therefore, contribute to the environmental protection of seawater.

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