

Making Sense of wash water analysis - Part 1

Analysis of wash water during a tank cleaning operation is undertaken for a number of cargoes with the main objective of decreasing the need for tank entry after a cleaning to perform a wall wash test*.

Tank entry (or any so called confined space entry) is an operation involving serious risks. When safety is concerned, new technologies to lessen this dangerous operation should be embraced. But is this feasible?

The analysis of wash water samples is performed with an UV/VIS spectrophotometer. In short, this device makes scans of wash water in visible and ultraviolet light.

Organic substances absorb light at a specific wave length and thus organic substances can be detected in for instance - water. The wash water scan with the UV/VIS spectrophotometer is compared with existing reference scans of the substance, to determine if the wash cycle is complete or washing needs to be continued. Using this method, could reduce the use of water, resulting in less fuel consumption and prevent over-cleaning, thus also saving time.

There is a relation between a certain substance or molecule and the amount of absorbance at a particular wave length. This is the so called molar extinction coefficient. The beauty of this physical fact is that it can be used to determine substance concentrations. This is why the UV/VIS device is so widely used for the analysis of watery samples in so many industries.

The fact that this substance molar extinction coefficient is a physical constant for each substance, therefore the UV/VIS device is not part of the equation. So each UV/VIS device should give the same result, provided other parameters are the same. Therefore, it is important that procedures for taking and handling of samples, including other parameters that can influence a measurement, such as temperature and soluble medium, should be known.

To correctly compare the wash water UV/VIS scans with the substances' reference scans, it is important these scans are made according to laboratory standard practice. As physics shows, substance UV/VIS reference scans should be able to be exactly reproduced on any UV/VIS spectrophotometer, given all the parameters are known.

This ability to be reproduced is one of the pillars of the scientific method and important to make judgements of observations. The scientific



A UV/VIS spectrophotometer

hypothesis is verifiable and can be used as a theory until proven and verified otherwise.

Now here lies the crux of the matter. Trying to duplicate existing market reference UV/VIS scans of certain substances gave different results, hence the scans could not be verified. One of the problems is the fact reference UV/VIS scans exist of substances that are not or very poorly water soluble. Nonetheless reference scans can be found of non-water soluble substances, for instance Octene, up to 200 ppm, while the maximum solubility of the substance Octene is less than 6 ppm at ambient temperature.

When trying to dissolve a substance above this maximum solubility value, it tends to float on water, due to its specific gravity, being lower than water, resulting in a solution with maximum dissolved substance and probably some unknown amount of dispersed or suspended substance.

Cloudy solution

Another problem found was that some substances form a cloudy mixture in water. Measuring a cloudy solution is unreliable, as it will both absorb light and also scatters light, thus turbidity is measured instead of absorbance. This last example of forming turbidity is especially seen in vegetable and mineral oil substances and product mixtures.

We question how these standards are set? The standard should be based on the scientific method, as consensus is just an agreement.

Further questions arise, what is the cleaning standard in relation to wash water analysis and who is setting it:

-Sample preparations and parameters, or better

said the analytical protocol?

-Up to which concentration measured on the UV/VIS scan of the wash water of a certain substance, the tank cleaning is completed and proven as 'clean', and how does the UV/VIS Scan relate to wall wash analysis results?

-Should standard cleaning procedures and analytical methods per substance, in accordance with the wash water analysis procedure, be available and transparent for the market to follow, given the incentive of creating a safer process for crew and inspections by means of fewer tank entries?

- Which type of tank material/coating qualifies for the applied method? Coatings tend to retain cargo residues, possibly influencing the wash water measurements.

Wash water analysis can be shrouded in mystery. For instance, as the cleaning standard or consented methodology is missing, interpretation of the UV/VIS scan is done randomly and some scan conclusions are resulting in insufficient cleaning.

Looking at the above, a clear separation should be made in two types of substances (or cargoes) and the use of the UV/VIS Spectrophotometer in wash water analysis.



Marine Care

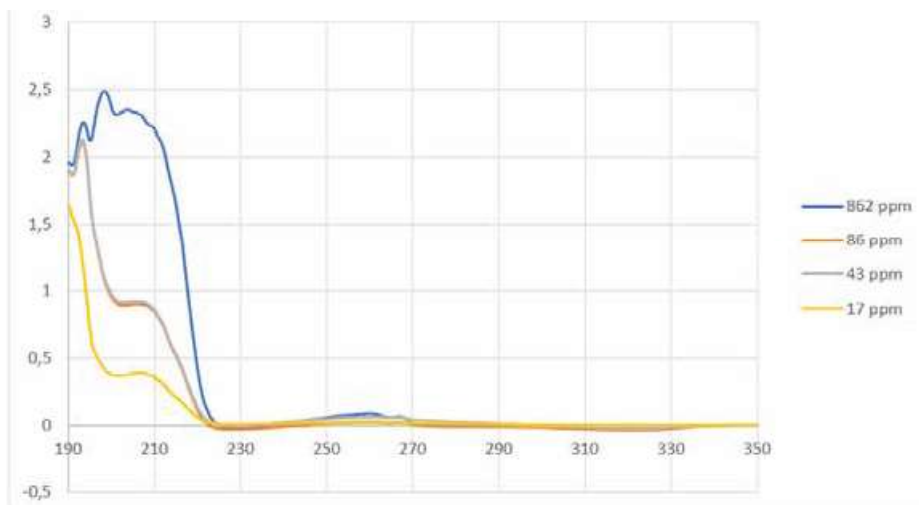
Founded in 1997, Marine Care is a privately owned company, specialising in cleaning solutions for bulkers and tankers.

For many years, the company has supplied the Caretech Spectroscan UV-Vis spectrophotometer to support hundreds of clients in both cleaning and wall wash testing challenges.

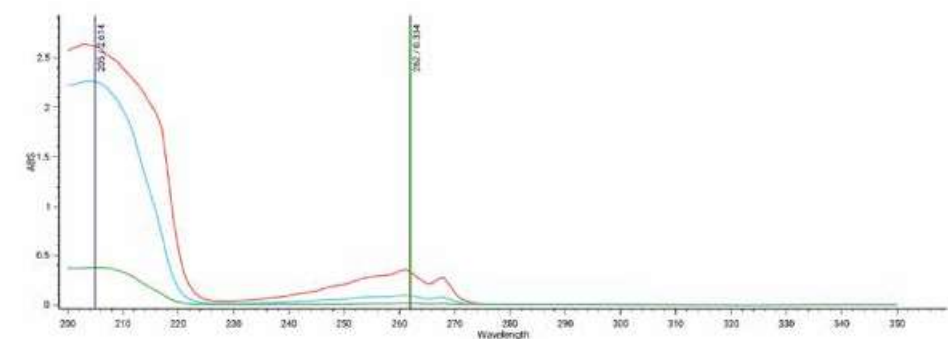
When discussions with customers started to develop on wash water testing the company sensed that a general scientific approach and understanding was missing.

With years of field experience, customer input and support for the latest development, the UV-Vis SmartLog, the company has investigated the sense and nonsense, which led to this paper.

TO



UV Scan Caretech Spectroscan UV-Vis Cumene in water 10mm cuvet



Sample	ABS(205)	ABS(262)
toluene 520 ppm	2.614	0.334
toluene 100 ppm	2.258	0.091
toluene 10 ppm	0.372	0.014

Tank cleaning toluene in water 10mm cell

- 1) Water soluble substances/cargoes.
- 2) Non- or poorly water soluble substances/cargoes.

For water soluble substances, the analysis of wash water can be used to determine if a tank is clean. This could save time, as over-cleaning is prevented by continuous monitoring of the process, by measuring the wash water with the UV/VIS spectrometer.

As water is the medium and the substance dissolves in water, the tank is clean when the measured substance/cargo is under a certain value. For this purpose, the wash water analysis and the UV/VIS graphs could be an excellent tool, although it is unclear what the certain value of acceptance of each substance is, as explained earlier.

Non-water soluble substances are less or not suitable to determine if a tank is clean with wash water analysis. The determination of the concentration of non-water soluble substances/cargoes is not accurately possible at concentrations higher than the maximum solubility in water.

In most cases, these kind of substances are generally not cleaned with water only, as a circulation wash with cleaning agents is

performed. In such cases, the wash water analysis could be of help to lower the use of water prior to the circulation cleaning. During this stage the water can dissolve as much as the maximum solubility of the substance/cargo.

Measuring wash water with an UV/VIS spectrophotometer will show a trend of the UV/ scans of the substance/cargo in the subsequent wash water samples.

When the analysis of this wash water shows no absorbance (a flat line) this pre-wash is complete. In this case the wash water analysis can shorten the cleaning time. It could also save fuel consumption, in case heated wash water is used and thus lowering the carbon footprint.

In conclusion, wash water analysis with an UV/VIS spectrophotometer can be a good tool for shortening water wash phases and thus saving time and energy. For water soluble substances this method could also be used to determine cleanliness of a tank and prevent tank entry to perform a wall wash test.

As questions remain, Marine Care, together with stakeholders, is undertaking further research.

**This is the first of two articles written by Thomas van Os, Research and Development Manager at Marine Care.*



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