RESPONSIBLE CARGO TANK CLEANING – WASHING WATER ANALYSIS

Introduction

From January 1st 2016 the new industry rules on the inerting of chemical (and gas) tankers with nitrogen were implemented. This will undoubtedly eliminate the risk of explosion during the discharging, (loading) and cleaning from flammable chemical cargoes, but the introduction of nitrogen gas brings its own risks that are well documented and understood:

- **Colourless / Invisible**
- **Odourless**
- **Asphyxiant**
- **Often called the "silent killer"**

Moreover, if we now have a mixture of nitrogen gas and the previous cargo vapour inside the atmosphere of the cargo tanks of chemical tankers during cargo tank cleaning, it has to be recognised that there is a particularly increased risk related to confined space entry (CSE) to seafarers each time they have to go inside the cargo tanks.

In a paper to the IMO in 2008, the Marine Accident Investigators' International Forum (MAIIF) reported that more than 1000 deaths related to CSE were feared in the 20 years leading up to the publication of this report. Between 1998 and 2008, 93 CSE fatalities were reported in chemical tankers alone. But perhaps the most chilling fact was noted in the conclusion of report, which left the readers asking whether this data was actually the "tip of the iceberg?" on account of the fact that less than 15% of the flag states approached had actually responded, meaning these figures could be significantly higher.

All chemical and oil majors have rigorous CSE procedures, and any one of these procedures could be used to make this point stronger, but actually, the example chosen is from the UK Health and Safety Executive (HSE) – Confined Spaces Regulations 1997 # 1713, which simply and concisely encourages all workers to:

"avoid entry to confined spaces, e.g. by doing the work from the outside"

The ONLY reason for multiple cargo tank entry during tank cleaning operations on board a tanker is to monitor the tank cleaning in order to ensure compliance with the pre-loading inspection specifications for the next nominated cargo. Regardless of whether these requirements are visual inspection or wall wash, the cargo tanks still have to be effectively cleaned and monitored, in order to ensure that they are ready for the next cargo to be loaded.

Washing Water Analysis

There is an alternative which all but eliminates confined space entry during tank cleaning operations, and that is WASHING WATER ANALYSIS, utilising a UV / Visible spectrophotometer.

A growing number of chemical tanker owners and operators are now using washing water analysis to monitor all tank cleaning operations and have reported:

- **A significant reduction in CSE**
- **A real reduction in tank cleaning time and therefore far fewer cases of "over-cleaning"**
- **Reduced bunker consumption**
- **Optimised cleaning chemical consumption**

The process allows any vessel to ensure that cargo tanks and lines are free from previous cargo by measuring the quality of the washing water, <u>during</u> tank cleaning. All parts of the cargo tank (and lines) have to be clean, not just the lower visible parts of the tank where a wall wash inspection might take place.

Essentially, when the washing water is clean, this is the point at which routine tank cleaning can stop. It should be noted that this does not necessarily mean that the cargo tank is ready for loading the next nominated cargo at this time, indeed, consideration has to be given to any specific quality requirements of that cargo, but very often the amount of additional cleaning work is minimal, when it is accepted that the previous cargo has been completely removed from all parts of the cargo system on board the vessel.

So the key question is this; if vessels are able to successfully use washing water analysis to determine that their cargo tanks (and lines) are clean and free from the last cargo, can the same method be used instead of the pre-loading inspection to determine cargo tank suitability prior to loading? In order to answer this question, the pros and cons of each process need to be carefully considered.

WALL WASH ANALYSIS

Presently the wall wash analysis is perceived to be the strictest pre-loading inspection. As in the picture below, solvent is splashed onto the bulkheads of the cargo tank and then tested to meet a series of pre-determined test specifications. But how reliable is this process and what information does it actually provide?

Firstly, and by design, the wall wash inspection is a random process, because it is impossible to write a procedure that exactly and precisely defines which places of a cargo tank should be "wall-washed"; particularly when no two cargo tanks are the same.

Secondly, the wall wash inspection is highly subjective. In other words, two different inspectors will always see the same cargo tank with very different eyes. Moreover, if a group of 10 inspectors were asked to wall wash one cargo tank, there would be 10 different wall wash samples to analyse. And which one would be correct? Each inspector would say their sample was the most representative, but it is just not quantifiable.

If the wall wash inspection is random and subjective, it follows that it is not reproducible, which now introduces a legal slant into the discussion. Indeed it is found that because the wall wash inspection is not reproducible, it actually has no legal value in the event of a cargo contamination claim, unless it can be proven that the inspector / surveyor acted negligently.

Random, subjective, non-reproducible, legally worthless, and what does it actually tell us?

The following two pictures show the same bulkhead of a chemical tanker; one without any markings and the other marked where a wall wash sample may typically be taken from:

What these pictures clearly highlight is the fact that a wall wash inspection is really only representative of random parts of the lower 2 – 3M of any cargo tank. At best this equates to 10 – 15% of the internal surface area of the tank, but in reality, in terms of how much of the cargo tank is really wall washed, <u>it is significantly less than 1% of the total internal surface area of the cargo tank.</u>

Yet "passing" this sample is what stands between a vessel loading and a vessel laying idle.

Furthermore, if less than 1% of the internal surface area of the cargo tank is actually wall washed, it follows that more than 99% of the cargo tank will remain untested; this portion of the cargo tank is therefore, by definition, an "unknown".

With greater than 99% of the cargo tank untested and potentially un-clean, one has to ask why there are not more off-specification cargoes?

The answer is <u>DILUTION EFFECTS</u> which is a quantification of the relationship between surface contamination and how this contamination becomes diluted into the fully loaded volume of cargo. Once this concept is recognised and understood, it becomes absolutely apparent that the wall wash inspection, really has no value nor place in determining whether a cargo tank is suitable for loading or not.

A dilution factor can be calculated for any particular cargo tank as follows:

- **Let us say that a cargo tank has dimensions of 10M x 10M x 10M, giving it a total internal surface area of 600M^2 and a fully loaded volume of 1000M^3**

- **If it was then possible to wall wash <u>each</u> square metre of this tank with 0.5L of methanol, the total volume of the wall wash sample would be 600 x 0.5L = 300L = 0.3M^3.**

- **If this wall wash sample was then diluted into the fully loaded tank, the <u>dilution factor</u> for the cargo tank would be 600 / 0.5 = 3333 times**

Now consider the following export specification for a typical water white chemical cargo:

Colour	5 APHA maximum
Chloride	1ppm maximum
Hydrocarbon	Pass (ASTM D 1722) or 1 FTU*
Previous Cargo	0.5ppm maximum

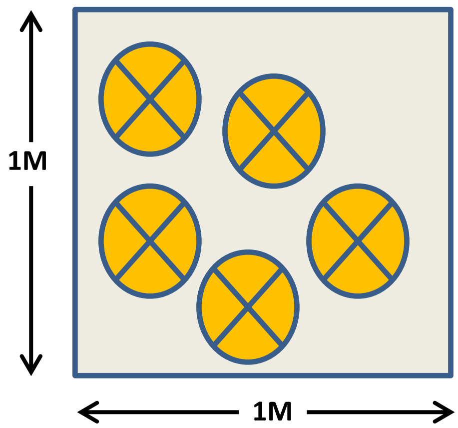
* (assuming that 1 FTU passes ASTM D 1722)

By applying the dilution factor to the above specification, it is absolutely feasible that the wall wash sample could contain the following level of contamination:

Colour	16,665 APHA
Chloride	3,333ppm maximum
Hydrocarbon	3,333 FTU*
Previous Cargo	1,665ppm maximum

And the cargo could be successfully loaded. Such a level of contamination in a wall wash sample is for all intents and purposes impossible to achieve, but it needs to be acknowledged that such extreme levels of contamination would not impact the quality of the fully loaded cargo.

Furthermore, in the absence of an industrywide "accepted" wall wash procedure, the "unwritten" rule is that any wall wash sample should represent a surface area of approximately $1M^2$ of the cargo tank, and this area of cargo tank should be wall washed with 500ml – 1L of methanol. The number and site of spots to be wall washed is as discussed earlier, arbitrary and subjective, but it is assumed that the total surface area is one square metre.



Let the above schematic represent one square metre of a cargo tank from which the wall wash sample is taken, with the yellow circles representative of the contamination on the surface of the cargo tank which will be completely removed during the wall washing process.

The contamination could be anything, but for the sake of this discussion, let us say that it is inorganic chlorides, at a concentration of 10mg, within the square metre.

If the volume of solvent collected during the wall wash inspection was 2.5L of methanol, all of the inorganic chlorides would become dissolved in 2.5L of methanol, meaning the final wall wash sample would contain 10mg/2.5L or 4mg/L of inorganic chloride.

Reducing the volume of collected methanol to 1L, reduces the volume into which the inorganic chlorides can become dissolved. Accordingly, the concentration of inorganic chlorides in the final wall wash sample would be 10mg of inorganic chloride in 1 L of methanol

= 10mg / L or 10ppm

Reducing the volume of collected methanol to 250ml and the inorganic chlorides content of the final wall wash sample would now be 10mg of inorganic chloride in 250ml of methanol

= 40mg / L or 40ppm

Even though there is a fixed and finite concentration of inorganic chlorides on the surface of the cargo tank. The only factor that has changed, is the volume of wall wash solvent that has been collected and where in the inspection process does it say how much solvent should be collected?

Which answer is correct? 4ppm? 10ppm? 40ppm?

Or put another way, is the cargo tank suitable for loading or not?

Wall wash inspections are imposed for one reason only and that is to provide reassurance to cargo interests that any particular cargo tank is suitable to load the next nominated cargo. But actually, this is just not achievable, because the final result is so skewed, it could basically be manipulated to mean almost anything. Passing the wall wash inspection does not guarantee that the next cargo can be loaded successfully and actually, if the cargo does become contaminated, the owner / operator of the vessel is always legally responsible, providing the quality of the cargo loaded onto the vessel is confirmed as being within specification.

Consider further that the vast majority of wall wash samples are tested for non-specific contaminants, for example hydrocarbons, permanganate time test and colour. An acceptable inspection result implies that the cargo tank is free from discolouration, has "no" hydrocarbons and contains no contamination that could be oxidised by potassium permanganate. Whilst this is absolutely true, it does not mean that the cargo tank is free from the previous cargo. The most common group of cargoes that will slip though the wall wash test are aromatics and these are generally the most unwanted contaminants in "non-aromatic" chemical cargoes.

To say it again, passing the wall wash inspection does not provide cargo interests with the one piece of information that they require, and that is a guarantee that the nominated cargo can be loaded without risk of contamination. The dilution effect is what "allows" chemical cargoes to be loaded without them becoming contaminated, not the wall wash specification and in the future, vessels can focus on removing the previous cargo during tank cleaning and not just trying to pass the wall wash inspection.

Perhaps more significant, cargo interests need to recognise prior cargo history and accept that in some cases, vessels (specifically coated vessels) just cannot clean sufficiently to remove the risk of contaminating the next cargo. In such cases, imposing the most stringent wall wash specifications will never make the vessel more suitable to load and the only way of ensuring the quality of the loaded cargo is for example, to not load methanol into a vessel with organic cargo tank coatings that have carried toluene as last cargo.

For a vessel to achieve any wall wash standard, there are many consequences and repercussions, which have already been mentioned, but to summarise:

- **i.) Multiple cargo tank entry for the vessels crew and also the load port surveyors**
- **ii.) Potentially excessive CO_2 (greenhouse gas) emissions during tank cleaning**
- **iii.) Potentially excessive discharge of detergent based chemicals over-board**
- **iv.) Over-cleaning, particularly of cargo tank coatings, which is not only damaging to the coating, it can also skew the wall wash results even further**

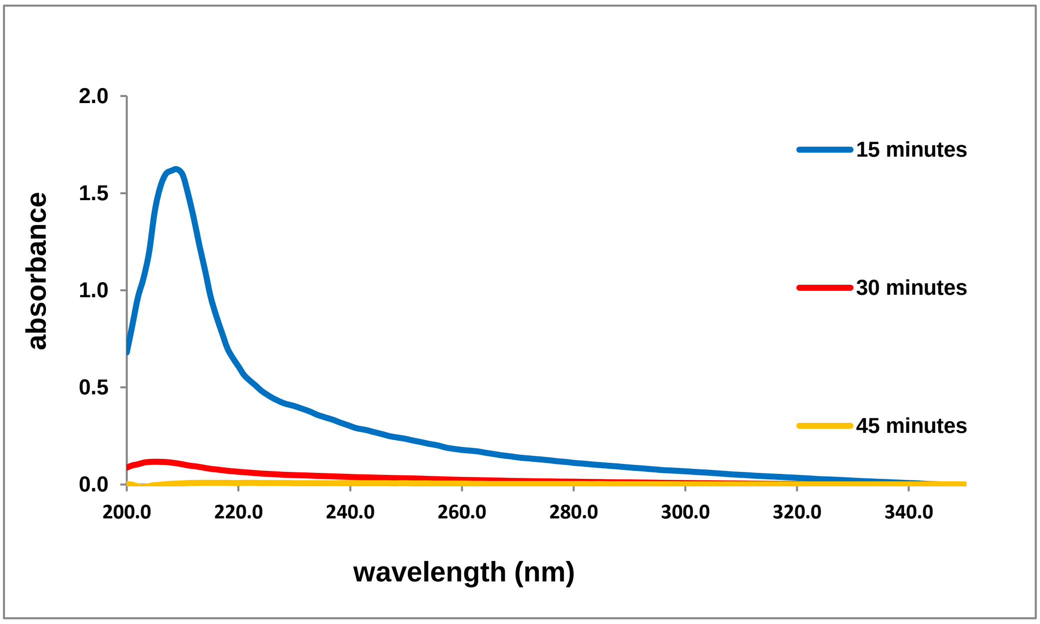
For cargo interests, passing a wall wash inspection really only has one consequence and that is to provide positive confirmation that a vessel is ready to load the next nominated cargo. But as demonstrated, this is not actually achievable, meaning the wall wash inspection is not only ineffective, time-consuming and expensive it is also dangerous in terms of the significantly increased incidences of confined space entry and also in terms of the false positive results it provides which may lead cargo interests to load a cargo that is bound to become contaminated.

An alternative inspection process is therefore clearly essential in order to provide far more reliable information that the cargo tank is suitable for loading the next nominated cargo.

WASHING WATER ANALYSIS

Washing water analysis is the complete opposite of wall wash analysis in so much that it is the identification of what is being removed from the cargo tanks / coating <u>during the tank cleaning process</u>, rather than finding out what is left behind after the tank cleaning is complete. Very simply, when there are no longer any traces of the previous cargo in the washing water, <u>tank cleaning can be stopped</u> as continued washing will not make the cargo tank any cleaner.

The following UV trace is typical of any tank cleaning operation. At this stage there is no need to know what the previous cargo is, or what the particular cleaning steps were, it simply shows what happens during tank cleaning:



- **After 15 minutes of cleaning, there is still a clear deviation in the graph which relates to the presence of previous cargo in the washing water.**
- **After 30 minutes, the deviation is significantly improved, which means the amount of previous cargo present in the washing water has been significantly reduced, but it is still present.**
- **After 45 minutes, the graph is almost a flat-line, meaning the quality of the water being discharged from the cargo tank is the same as the quality of water being pumped into the tank for cleaning purposes. In other words there is no longer any cleaning effect.**

This is a relatively simplified summary of washing water analysis, but the principle is the same for any tank cleaning operation on any vessel. The amount of residue remaining on or retained in the surface of the cargo tank after cleaning becomes far less relevant, because all of the cargo tank and the cargo lines must be free from previous cargo before the washing water samples are clean.

This is also the mechanism that vessels employ to monitor tank cleaning without cargo tank entry.

Consider that each step of any tank cleaning procedure needs to be confirmed as complete before the next step can commence. Without using washing water analysis and in the vast majority of cases, this confirmation requires at least one crew member to go inside the cargo tank, and a second, standing watch in accordance with confined space entry procedures.

Using washing water analysis, each step of the cleaning process can be monitored by looking at successive UV traces, which of course does not require any cargo tank entry and takes less than one minute per sample to analyse. When the graph becomes a "flat-line" or does not change between consecutive samples, this is the trigger that the cleaning step needs to be changed, or that tank cleaning can be stopped. If this trigger can be used to change a tank cleaning step early, because there is no longer any positive cleaning affect, there are significant time savings and also reduced environmental impacts to consider.

For example, each hour of hot water washing, consumes on average 0.6 metric tons (MT) per hour of HFO / MGO in the boiler and the auxiliary engines. Burning 1 MT of heavy fuel oil produces just under 3.2 MT of CO_2, meaning each hour of hot water washing on a chemical tanker will liberate just under 2 MT of CO_2 into the atmosphere.

If a vessel can save two hours of hot water washing per month, the annual HFO / MGO consumption of that vessel is reduced by 14.4MT, which directly equates to 45.6 MT of CO_2. Multiply this by the size of a modern chemical tanker fleet and the reduction in emissions will run into thousands of MT of carbon dioxide, just by having the capability of monitoring the cargo tank cleaning efficiently.

Recognising that the wall wash inspection does not actually provide charterers / commercial interests with the one piece of information that they demand from having this inspection, and it is in fact the dilution effect that enables vessels to load cargoes successfully, the emphasis on tank cleaning does now change to being able to successfully confirm that the cargo tanks and lines are free from the previous cargo. The following examples are all real cases where washing water analysis has been used in place of the load port inspection, or where a cargo has been loaded directly after a "banned" prior cargo

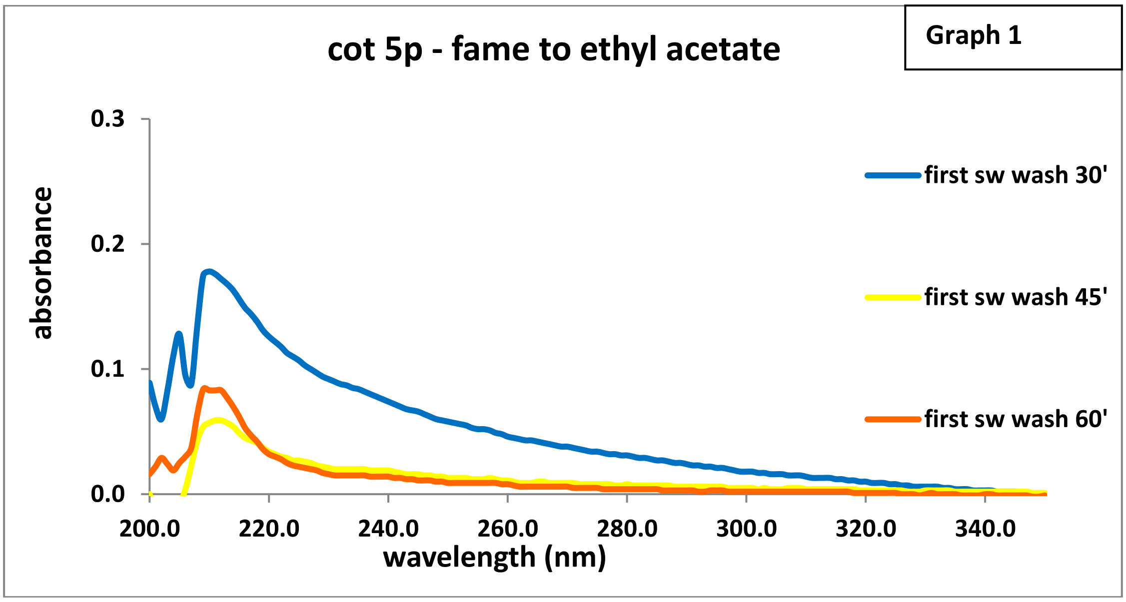
1. FAME to Ethyl Acetate

FAME was on the banned last cargo list for this particular charterer prior to loading ethyl acetate, but because of various circumstances and a willingness to co-operate with the washing water process, the vessel was accepted for loading, on the full responsibility of the owner. The cargo tank was epoxy phenolic coated.

It was agreed that the tank cleaning procedure would be based upon one of the industry accepted guidelines, as follows:

- **i.) 2 hours cleaning with seawater at 50°C**
- **ii.) 1 hour chemical recirculation**
- **iii.) 2 hours cleaning with hot seawater**

Graph 1 represents the washing with seawater at 50°C.



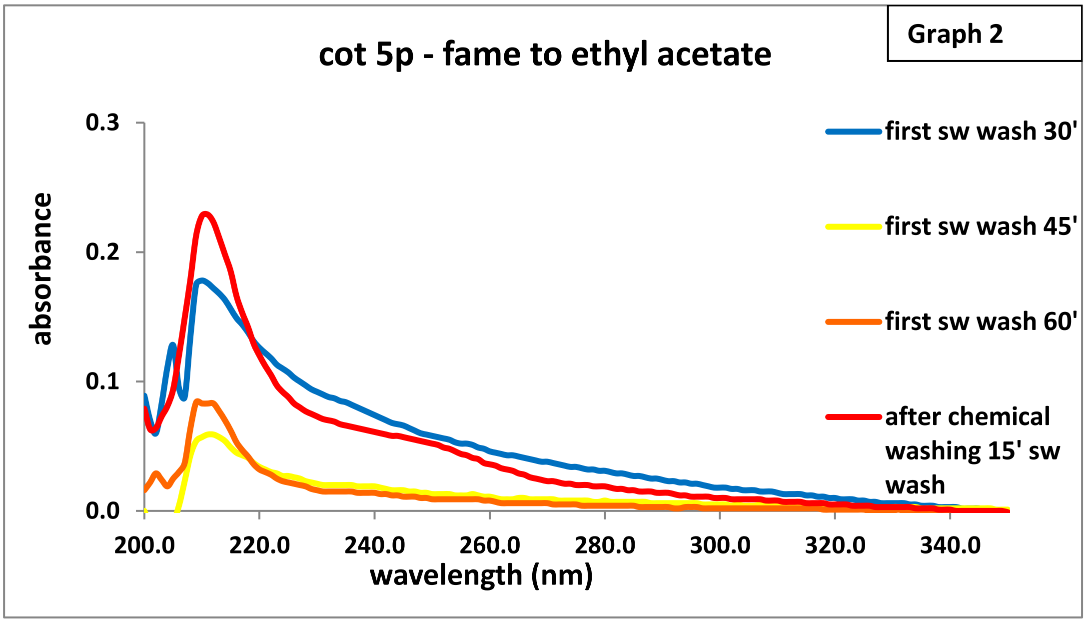
After 30 minutes of washing, there is still a clear deviation in the graph, meaning the washing is still removing traces of the previous cargo.

After 45 minutes, there was an improvement from the 30 minute sample, but still evidence of previous cargo, so the cleaning continued.

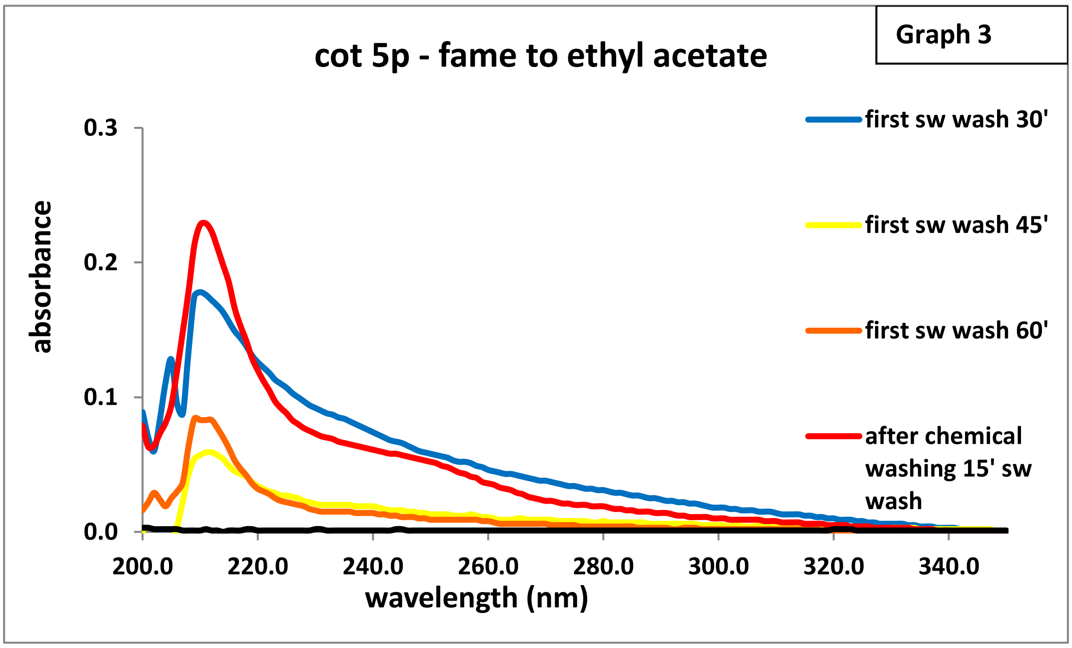
After 60 minutes, there was almost no difference between this sample and the sample taken at 45 minutes. In other words, the cleaning effect had stopped. There were still clearly traces of previous cargo in the water, but seawater washing alone at 50°C, could seemingly not remove any more of these residues.

In accordance with the tank cleaning plan, the vessel recirculated the cargo tank with a detergent based cleaning chemical for 1 hour at 50°C, before commencing hot seawater rinsing, planned for 2 hours.

Graph 2 shows the first sample of washing water taken 15 minutes into the hot seawater rinsing cycle and it is apparent that the quality of the washing water sample has deteriorated from the last sample taken at the end of the washing with seawater at 50°C. But actually, this is not unexpected, because the chemical recirculation was specifically carried out to remove the traces of FAME that could not be removed by using seawater on its own and indeed, this first rinsing sample is showing exactly that. It should also be noted that the samples taken during rinsing could also show up the presence of detergent in the washing water, if this was still present. In this case, the shape of the graph is characteristic of FAME which indicates that there are no traces of detergent present, but in cases where the detergent was used at too high a concentration and / or not successfully rinsed away, this would show up in the washing water samples.



Graph 3 shows the second sample of washing water, taken 30 minutes into the hot seawater rinsing cycle. The flat-line graph signifies that there are no longer any traces of FAME (or cleaning chemicals) in the washing water and accordingly, tank cleaning was stopped.



The cargo tank was then visually inspected by the crew, mopped, dried and successfully loaded with the nominated cargo of ethyl acetate. There was only one man entry per cargo tank during this cleaning operation, a reduction of 75% from the time previously when the vessel cleaned from FAME.

It should also be noted that the vessel saved one hour of seawater washing at 50°C and 1½ hours seawater washing at 75°C on the scheduled tank cleaning procedure, with absolutely no drop in cleaning efficiency.

2. UAN to FAME

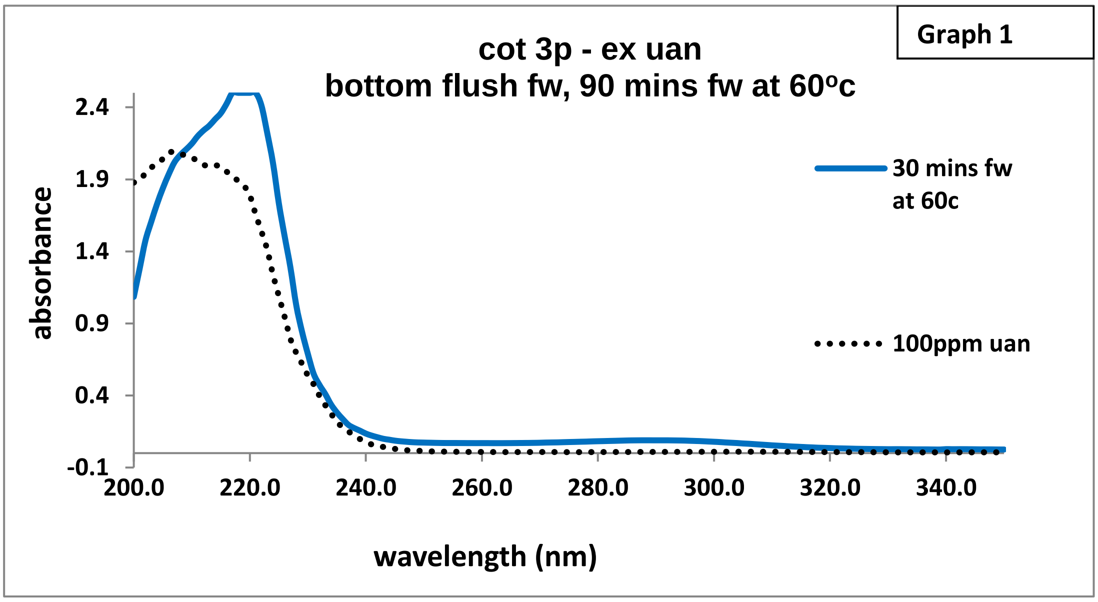
Again, the previous cargo was on the charterer's banned list prior to loading the nominated cargo of FAME.

The agreed tank cleaning procedure was as follows:

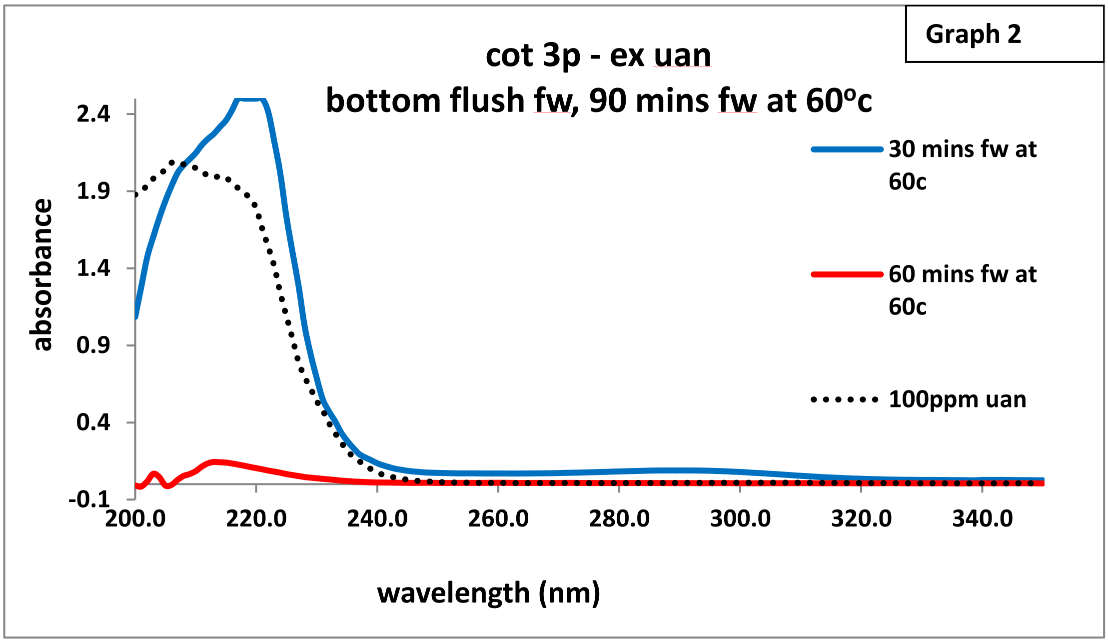
- **i.) Bottom flush with freshwater**
- **ii.) 90 minutes hot freshwater washing**

The vessel was scheduled to load in 8 cargo tanks. The following data only refers to only one tank, which was the first tank cleaned.

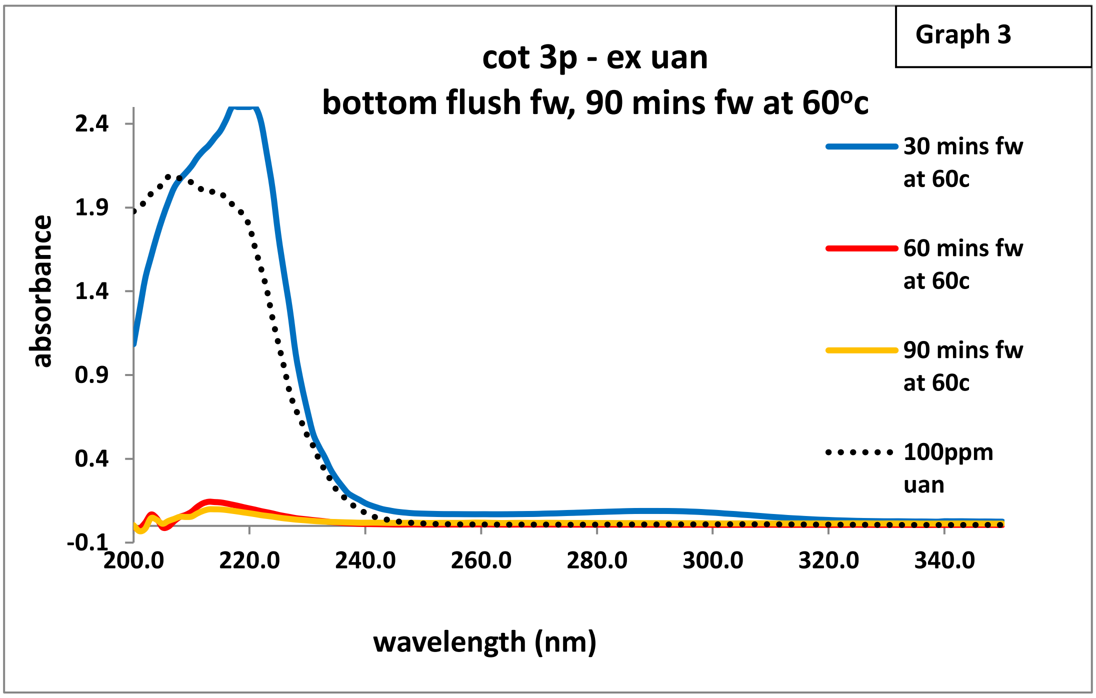
Graph 1 represents the first sample taken 30 minutes into the hot freshwater washing cycle. The graph also shows 100ppm UAN as a reference and it was apparent that at this stage of the cleaning, the washing water still contained more than 100ppm UAN.



Graph 2 represents the second sample taken 60 minutes into the hot freshwater washing cycle. The concentration of UAN in the water has now significantly dropped almost to nothing.



Graph 3 represents the second sample taken 90 minutes into the hot freshwater washing cycle. The concentration of UAN in the water is the same as it was after 60 minutes.



The cargo tank was gas freed, visually inspected and mopped dry, and was found to be perfectly clean. According to the data, the cargo tank was actually clean after 60 minutes of washing and in fact, all other cargo tanks were only cleaned for 60 minutes with hot freshwater which resulted in a saving of 3½ hours of hot water washing; equivalent to a reduction of 6.5 metric tons of carbon dioxide, just in one tank cleaning operation.

The vessel successfully loaded and discharged the FAME and whilst the charterers were completely against this fixture beforehand, they have since agreed to change their banned prior cargo list, on the proviso that the vessels use washing water analysis to confirm that the cargo tanks are suitable for loading.

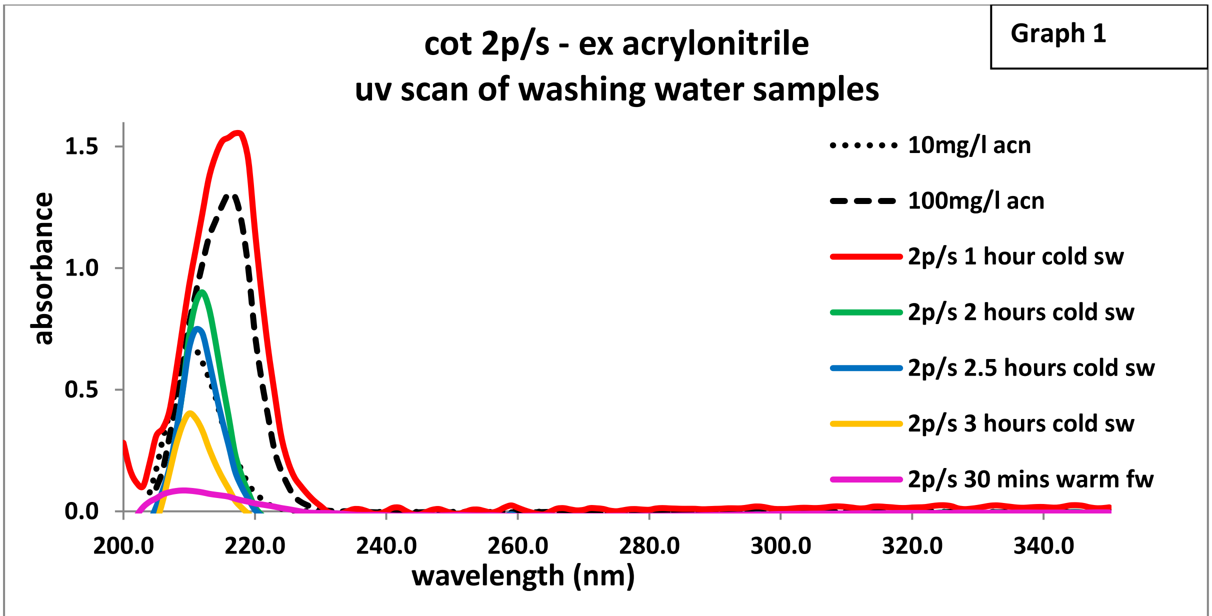
3. Acrylonitrile to MEG (fibre grade)

This is an example of loading directly after a banned prior cargo and also where there would normally be a wall wash inspection prior to loading. The charterer had a long standing relationship with the vessel's owner and accepted the vessel for loading, on the full responsibility of the owner, without even a wall wash inspection. The cargo was to be stowed in two stainless steel cargo tanks, COT 2P/S.

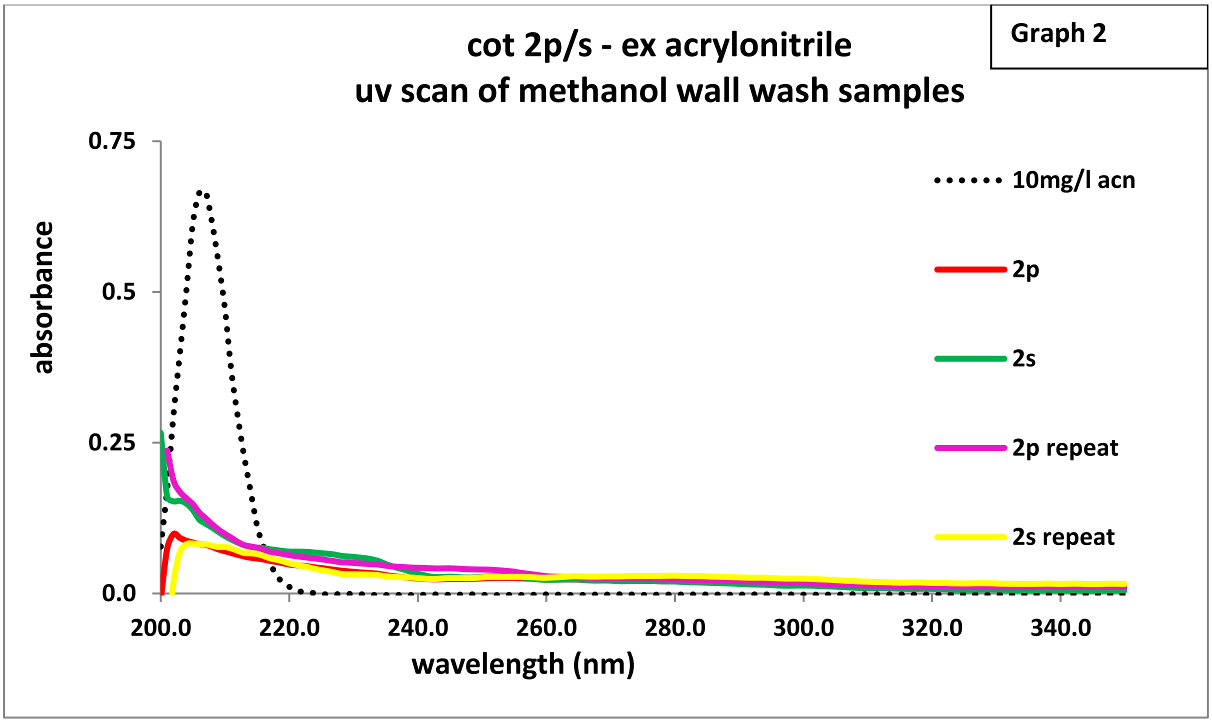
One of the leading tank cleaning guidelines simply recommends 40 – 60 minutes of ambient seawater washing, followed by steaming when switching from ACN to MEG and accordingly, the vessel started cleaning with ambient seawater. Both tanks were cleaned simultaneously and the washing water was sampled from the crossover valve on number 2 manifold.

Graph 1 shows very clearly that 40 – 60 minutes of ambient seawater washing was not sufficient to remove all of the previous cargo. Indeed, cleaning continued for 3 hours, until the concentration of acrylonitrile in the water had dropped to below 10ppm. At this point, the tanks were washed with technical grade freshwater at 60°C for a further 30 minutes, which reduced the acrylonitrile concentration in the water down to around 1ppm.

Graph 1



In view of the charterers normal requirements for a wall wash inspection, the vessel also carried out a methanol wall wash test from both cargo tanks and analysed them in the same way that the washing water samples were, to specifically look for the presence of acrylonitrile. Graph 2 clearly shows that there was no presence of acrylonitrile on the surface of the bulkheads.



The vessel successfully loaded and discharged the cargo of MEG fibre grade, without any incident.

<u>CONCLUSION</u>

If vessels now know that their cargo tanks and lines are completely free from previous cargo, by precise and accurate monitoring of the washing water, and it is recognised and accepted that the wall wash inspection is not only flawed, but does not actually provide reassurance to cargo interests that the nominated vessel is suitable to load, there is clearly no longer a need to pass a load port wall wash inspection prior to loading any cargo.

With this in mind, it is absolutely feasible for a vessel to complete tank cleaning in all cargo tanks, inert with nitrogen (providing the vessel is equipped with a nitrogen generator) and arrive fully load-ready at the load port.

The benefits are clear:

- **Significant reduction in confined space entry for vessels' crews during tank cleaning operation**
- **<u>No cargo tank entry</u> when the vessel is in port, which is in line with safety regulations at a growing number of chemical tanker terminals**
- **No pre-inspections at other / lay-by berths. This is unnecessary and only costs time and money**
- **Far enhanced safety for the cargo surveyors, because they are no longer required to go inside the cargo tanks. This does have insurance implications for the charterers who appoint the surveying companies.**
- **Much improved logistics for the cargo suppliers. When a vessel gives an eta at the load port, the shippers / suppliers / charterers know that the vessel is load ready. There is no risk of the cargo tanks being rejected alongside, which only creates "dead-time" alongside the loading jetty during which the cargo tanks are being re-inspected and / or manually cleaned prior to a re-inspection.**

- **Significant reduction in "time alongside" for the vessels. A vessel will berth, connect and start loading. Depending on the load port, the time for cargo tank inspection can be 12-24 hours, even if the vessel is accepted. This will be removed.**
- **Vessels equipped with a nitrogen generator that are nominated to load a flammable chemical cargo can inert all cargo tanks at sea, regardless of whether it is a mandatory requirement or not, which significantly enhances the safety of the loading operation for the vessel and the terminal. The current argument of there being "insufficient time" to carry out a pre-loading inspection prior to inerting, is no longer relevant, because the vessel will arrive alongside, fully inerted and ready to load.**

As also noted, in the future, vessels will be able to optimise their own tank cleaning procedures which significantly reduces carbon dioxide emissions and minimises the amount of cleaning chemicals that need to be pumped into the sea, which has huge environmental impacts at a time when the shipping industry is being so closely scrutinised.

We also often hear that safety has no price. Safety does have a price; it is the wall wash inspection and when one considers just how little the wall wash inspection actually provides, it is absolutely clear that the result does not justify the risk.

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