WILSON ANALYTICAL

Wilson Analytical Services Inc., #2075, 61 Broadway Boulevard, Sherwood Park, AB T8H 2C1

Tel: (780) 702-0610
Fax: (780) 998-5327
Toll free: 1-866-3wilson (394-5766)
Email: info@wilsonanalytical.com
Website:www.wilsonanalytical.com

Corrosion Inhibitor Residual Measurements

Continuously applied oilfield corrosion inhibitors are designed to adsorb spontaneously on the surface of carbon steel equipment, such as tubulars and flowlines, to form a hydrophobic, water-impermeable barrier between the steel and the produced fluids. These types of corrosion inhibitor are generally water-soluble or highly water dispersible in nature. The formation of the adsorbed layer requires a certain minimum concentration of inhibitor to be maintained in solution, the so-called residual level. Should the residual level fall below a minimum effective value (usually defined in the corrosion mitigation program for the facility) the adsorbed layer will start to degrade, as inhibitor molecules migrate away from the surface layer back into solution. The maintenance of an effective inhibitor film therefore requires that the amount of inhibitor in the produced water exceeds a certain minimum concentration. This important operational requirement means that the actual inhibitor level must be monitored frequently, via an appropriate analytical technique. There are three main methods currently in widespread use.

1. Chloroform Extraction

The most common methods of determining corrosion residuals are based on solvent extraction, the so-called 'wet' methods. The basic technique is to add an organic solvent (usually chloroform) to a fixed volume of the produced water sample being analyzed. The premise is that the active inhibitor species in the water will partition, or preferentially dissolve in, the organic phase. Sometimes an ion-pairing agent, such as a sulphonic acid, is added to the water to improve selectivity and efficiency. The amount of inhibitor is then determined colorimetrically, using a "Spec 20" or similar spectrophotometer. The organic solvent may or may not be 'back-extracted' into a clean water phase, and various reagents may be employed to enhance the color change in either the organic or 'clean' water phases.

The method works best when a single operator establishes her or his own technique, and rigidly follows the same protocol. Under these conditions, some level of repeatability can be obtained, sufficient to determine any significant upward or downward trends in the residual level. In practice, the technique suffers from a number of practical drawbacks:

- Variability due to different operators
- Cumulative experimental errors from a multi-stage process (liquid transfers, volume measurements, etc.)
- Significant interferences from any other chemicals or substances in the water - the selectivity of the method is based only on preferential solubility in the organic solvent.

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2. High Performance Liquid Chromatography

The HPLC method was developed by Travis Chemicals in the early nineties, and has been used by them ever since. Any quaternized nitrogen ("quat") components in the water sample are retained on an HPLC column, being separated and finally eluted by pumping a solvent through the column whose polarity changes with time. Detection of the quat 'peaks' is done typically by monitoring the differential change in refractive index of the eluting solvent.

The method has many advantages over chloroform extraction. Accuracy is far higher, as the experimental variables such as injection volumes, solvent flow rates and peak measurement can all be automated. In addition, there are almost no interferences, as the chromatography procedure can be made selective to not just the quats in general, but to a particular molecular type within the quat inhibitor intermediate itself. But therein lies the greatest drawback of the method.

It should be appreciated that alkyl pyridine quat (APQ) intermediates are in fact mixtures of dozens, or even hundreds of individual molecular species. During manufacture, an alkyl pyridine feedstock is "quaternized" by heating under pressure with a quaternizing agent such as benzyl chloride. But the reaction by no means goes to completion, and typically 30% or more of the starting material remains unquaternized. The HPLC method discriminates between the different quat molecules present on the basis of their water solubility (polarity), it is important to realize that this isn't the same thing as their effective contribution to corrosion inhibition. The HPLC method does not quantify unquaternized material, or quaternized material that is relatively water insoluble (due to long alkyl chain lengths), even though these species make a significant, perhaps dominant contribution to the effectiveness of the overall inhibitor product.

A crucial assumption is made when the HPLC data is converted into a "PPM" value, and reported to the customer. It is that is all of the active inhibitor intermediates are present in the water in the same proportion as they are in the initial product. In other words, although it is only the most strongly water soluble component of the inhibitor that is detected by HPLC, the less soluble and non-quaternized portions are assumed to be present by multiplying the concentration of the detected component by a certain product-dependent adjustment factor.

This assumption has great implications if the inhibitor is actually being used in a system containing liquid hydrocarbon, because the partitioning of the inhibitor package between the water and the non-aqueous phases must then be considered. It is quite possible for the less hydrophilic components of an inhibitor to partition into an oil or condensate phase, if one is present, leaving behind the highly water soluble species, such as short chain length quats. If this water is then sampled and analyzed by HPLC, a higher than appropriate "PPM" value may be reported as the loss of active material to partitioning effects has not been detected.

One final drawback to the HPLC method is that not all "quat" type intermediates give a viable HPLC signal. By relying on the HPLC method for residual determination, the range of available intermediates is necessarily limited.

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3. Fluorescence

The fluorescence method relies on an inherent property of "quat" type inhibitor intermediates, i.e. their ability to absorb certain frequencies of light and re-emit that light in a characteristic and detectable way. The emitted light is called fluorescence, and the amount of the light emitted is directly proportional to the concentration of the species in solution that is causing the fluorescence.

Fluorescence does not therefore rely on detection of one specific species of "quat" in the same way as HPLC. All active material in the water sample will be quantified by the method, so there is no concern about unquaternized species, or material that has borderline water solubility. The method is extremely sensitive (sub-ppm detection limits are usually possible), and highly selective. Many oilfield chemicals have no fluorescence properties, and therefore do not interfere with the method. Those that do exhibit some degree of fluorescence will do so at a wavelength that is a function of the particular molecule in question. As different chemicals have active species that are chemically distinct (otherwise they would be the same chemical) they will have a different fluorescence signature.

Fluorescence therefore combines the high accuracy of an instrumental method (such as HPLC) with the ability to detect all the active species in the water (like the chloroform extraction method), but in a selective manner. The technique correctly accounts for partitioning effects, and in this respect offers a significant technical advantage.

Wilson Analytical therefore offers its clients a calibration service, whereby standard samples, containing the inhibitor product in question, are made with and without the appropriate amount of any hydrocarbon phase that is actually present in the system. The calibration carried out in water only corresponds to the value that is normally measured and reported. But wherever possible, we prepare a second calibration curve, where the inhibitor is partitioned between produced water and produced hydrocarbon. When the 'unknown' samples are analyzed, we can report ppm residuals as per usual, using the water only calibration chart. But if desired by the client, we can also 'factor in' the partitioning effects, based on the known water/oil ratio and the experimental calibration.

Comparing Methods for Analyzing Corrosion Inhibitor Residuals in Oilfield Waters

	Chloroform Extraction	HPLC	Fluorescence (Lab-based)	QuatBox (Field-based)
Turnaround Time after Field Sampling	Slow	Slow	Slow	Fast
Accuracy	Poor	Good	Good	Good
Sample Integrety at Time of Analysis[1]	Poor	Poor	Poor	Good
Field-Friendly Analysis Technique?	Difficult	No	No	Yes
Free of Hazardous Solvents?	No	No	Yes	Yes
Cost per Analysis[2]	High	High	High	Low

Notes

1 Sample must be transported to Lab, slowing analysis further.

2 Sample must be transported to Lab and stored. Sample and solvents must be disposed of.