

New Test Method for Measurement of Water-Soluble Corrosion Inhibitor Residual in Oil Samples for Low Water-Cut Oil Systems

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ABSTRACT

Organic corrosion inhibitors protect the metal by forming a hydrophobic film on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. To sustain the protective film, a certain minimum inhibitor concentration should be maintained in the solution, usually designated as corrosion inhibitor residual. If the residual falls below the minimum concentration, then the adsorbed layer will start to degrade leaving the carbon steel surface unprotected. Globally, water-soluble corrosion inhibitor residuals are measured from water sample. For low water-cut oil systems, collecting a water sample is difficult, especially considering the safety concerns related to Bottom of Line (BOL) traps. A review held during 2017 within Petroleum Development Oman (PDO) Company, led to the suspension of BOL activities because of HSE risk, which impacted the residual monitoring in low water-cut system.

This paper explains the developed method which is a modified version of the industrial standard methyl-orange colorimetric titration method¹. It is based on the extraction of a water-soluble corrosion inhibitor from an oil sample by further methyl-orange titration of cation-active component. The test method has been successfully applied with a minimum root mean square error (R^2) value of 0.93.

Key words: Corrosion monitoring, Corrosion control, Chemical treatment, Water-soluble Corrosion inhibitors, Corrosion Inhibitor Residual, Low water-cut system, colorimetric/spectrophotometric titration method

INTRODUCTION

Corrosion Inhibitor (CI) Residual is part of corrosion monitoring to confirm availability of chemical in the pipeline. The difficulties to monitor CI concentration in low water-cut oil systems is well-known. Several research efforts have been conducted to develop methods for different field conditions and different type of fluids.

The most common method used in the oil and gas industry, is methyl-orange colorimetric titration, which is applied for water samples. Historically, several attempts were conducted to measure the CI residual using a spectrophotometer, utilizing ultraviolet (UV) and wave length concepts.^{1,2}

An innovative method, which uses a voltametric measurement with specific solid electrodes was patented;^{3,4} however, it can only be applied to water or conductive electrolytes samples, e.g. rich glycol. A similar method is based on utilizing solid phase extraction (SPE) which allows for exchanging solvent system while the active components are retained on the extraction media. This method eliminates background interference and loss of active components to sample containers, however, it is for water samples only.⁵

Another technique used is Liquid Chromatography – Mass Spectrometry (LC-MS), mainly within the investigation field for synthetic fluids to determine residual in Mono-Ethylene Glycol (MEG) samples.⁶

Oil and gas operators are facing the difficulty to sample water in low-water cut oil systems in order to monitor residual for water-soluble corrosion inhibitors. In that sense, the above described techniques are unsuitable for oil samples. Therefore, this work focused on developing a method for oil samples which considers eliminating the interference of background substances by extracting dispersed product residual from the sample collected.

This paper describes the technique, which is a modified version of the industry standard methyl-orange colorimetric titration method used for water sample, as well as, the field results.

The new procedure has the following considerations;

- Water-soluble corrosion inhibitor with amine as active component
- Sampling upstream and downstream corrosion inhibitor injection point to eliminate background interference
- Use of brine water for extraction of the residual corrosion inhibitor to increase the water content sufficiently to allow for colorimetric analysis.
- Implementation of the Quantitative Standard Addition technique⁷ to determine the levels of inhibitor concentration within a sample whilst ensuring any interferences are compensated by the inherent calibration within the sample being analyzed.
- Calculation of corrosion inhibitor residual by calibration curves interpolation.

EXPERIMENTAL PROCEDURE

Elimination of Background Interference

One of the focus areas when developing the procedure was to eliminate the background interference which can be caused by several substances such as minerals, salts, upstream injected chemicals (biocide, emulsion breakers, scale inhibitors, etc.). This interference can cause misleading readings when monitoring corrosion inhibitor residuals, resulting in a higher value than actual.

In order to eliminate the interference, two samples were collected at the same day: i) a sample collected from upstream the corrosion inhibitor injection point and ii) a sample collected from downstream of the corrosion inhibitor injection point. The test does not require separate calibration; the calibration is inherent within each of the samples being analyzed.

Wash Extraction

The low-water cut oil pipelines were grouped as per Total Dissolved Solids (TDS) concentrations and classified into three (3) main groups within the fields as low, medium and high TDS. Table 1 shows the average values from results obtained from January, 2016 to December, 2018.

Table 1
TDS Classification for Low-water Cut Oil Pipelines

Field Name	TDS, kg/m ³	Group classification, kg/m ³
A	4.8	Low TDS 5-20
B	7.8	
C	9.5	
D	21	Medium TDS 21-100
E	39	
F	82	
G	127	High TDS >100
H	160	
I	178	
J	192	
K	193	
L	236	

One location from each group was selected to represent high, medium and low TDS water samples, as shown below:

Field C - 9.5 kg/m³
Field E - 39 kg/m³
Field J - 192 kg/m³

Three (3) concentrations of brines, as per above TDS values, were prepared to extract the water-soluble chemical from the oil samples as part of the first stage of the method.

Quantitative Standard Addition Technique

Oil samples were collected before corrosion inhibitor injection point from Fields C, E and J. The samples were treated with the corrosion inhibitor at different dosages; 5, 10, 25 and 50 parts per million (ppm); and corrosion inhibitor was extracted to the water phase using the wash extraction method.