

**The Overview of Scale Inhibitor Residual Detection Methods  
for Both Downstream and Upstream Applications**

Haiping Lu  
Baker Hughes  
12645 W. Airport Blvd.  
Sugar Land, TX 77478  
USA

Kristen Curry  
Baker Hughes  
12645 W. Airport Blvd.  
Sugar Land, TX 77478  
USA

Sankaran Murugesan  
Baker Hughes  
12645 W. Airport Blvd.  
Sugar Land, TX 77478  
USA

Chelsea Eaton  
Baker Hughes  
12645 W. Airport Blvd.  
Sugar Land, TX 77478  
USA

Ya Liu  
Baker Hughes  
12645 W. Airport Blvd.  
Sugar Land, TX 77478  
USA

**ABSTRACT**

Scale formation is a very troublesome issue for oil and gas industry, and chemical treatment is a cost effective approach for solving scale formation prevention and control. Monitoring scale inhibitor residual is very critical for inhibitor dosage control on both downstream and upstream applications.

Currently, there are several major testing methods for scale inhibitor detection down to part per million (ppm) levels, including 1. Inductively coupled plasma (ICP) and wet chemistry method for phosphorous containing inhibitors; 2. Hyamine turbidity method; 3. High performance liquid chromatography (HPLC) for certain types of polymer inhibitors, e.g. sulfonated copolymer inhibitor; 4. Fluorescence dye tracer, e.g., PTSA and fluorescein; 5. Colorimetric method for polymer residual detection; 6. Time Resolved Fluorescence (TRF) for both phosphonate and polymer inhibitors; 7. Surface Enhanced Raman Spectroscopy (SERS) for phosphonate inhibitors monitoring and differentiation; 8. An assay method for the detection of all scale inhibitors at extremely low concentration 9. Strip Immunoassay technique for tagged polymer inhibitors.

This paper summarizes scale inhibitor residual methods based on the testing results with synthetic waters, cooling waters, and produce waters, and presents laboratory and field testing data under different application conditions, including brine TDS, pH, etc. This paper gives the insight on selecting best-fit scale inhibitor monitoring methods for both downstream and upstream applications.

**Key words:** Scale Inhibitor, Residual Detection, Methods

## INTRODUCTION

Scale formation is a problematic issue for oil and gas production and industrial water treatment. Scale deposits may block pipelines, damage equipment, reduce the heat exchanger efficiency, etc. Scale prevention through chemical inhibition is a preferred method, and the implementation of a suitable scale management strategy is critical for continual and safe operation of the asset.

When optimizing a scale treatment dosage, the accurate detection of the scale inhibitors in the brines is essential. The development of offshore drilling for upstream operation or automation for downstream applications post an urgent need for the detection methods with detection limit of the selected scale inhibitors to ppm (part per million) or sub-ppm level.<sup>1</sup> The operations of remote and complex fields or the applications of refinery automation have urged the development of techniques that can be used on-site to provide on-line data for making effective scale management decisions.

Various techniques for determining scale inhibitors residuals were reported. ICP, Ion Chromatography (IC), and TRF were studied for commingled samples containing a phosphonate, a polymeric inhibitor and a phosphate ester inhibitor.<sup>2-3</sup> HPLC and ICP detection techniques can achieved accurate measurements within a 5-10% error bar for P-tagged co-polymer type scale inhibitor. TRF method displays sub-ppm accuracy for various chemicals, and it can be set up in field on-site location.<sup>4-5</sup> HPLC and Liquid Chromatography Mass Spectroscopy (LCMS) were applied to analyze mixed polymeric scale inhibitors.<sup>6-8</sup> Hydrophilic interaction liquid chromatography (HILIC) coupled with mass spectrometry had been found to be promising for the detection and differentiation of two phosphonate scale inhibitors present in a sample.<sup>9</sup> The ability to detect both phosphonate and polymeric scale inhibitors at very low inhibitor level (<1ppm) has the potential for significantly extending scale squeeze lifetimes.<sup>10</sup>

The current techniques used for chemical analysis (colorimetric analysis, ICP, spectroscopy, UV spectrophotometry, hyamine method, IC, HPLC) often show some restrictions e.g. equipment setup, running costs, real-time monitoring, etc. Some of them even require time-consuming and complicated pre-treatment/purification stages for the separation of inhibitors chemicals from the interfering ions in the brines.<sup>11</sup> For example, for hyamine method, the quantification is time consuming, labor intensive and difficult to apply in real-time mode.

In this paper, the common detection methods available in the industry or have been published are discussed: 1. Inductively coupled plasma (ICP) and wet chemistry method for phosphorous containing inhibitors; 2. Hyamine turbidity method; 3. High performance liquid chromatography (HPLC), IC, LCMS, etc. for certain types of polymer inhibitors, e.g. sulfonated copolymer inhibitor; 4. Florescence dye tracer, e.g., PTSA and fluorescein; 5. Colorimetric method for polymer residual detection; 6. Time Resolved Florescence (TRF) for both phosphonate and polymer inhibitors; 7. Surface Enhanced Raman Spectroscopy (SERS) for differentiating phosphonate inhibitors; 8. An assay method for the detection of all scale inhibitors at extremely low concentration 9. Strip Immunoassay technique for tagged polymer inhibitors.

This paper reviews each type of scale inhibitor residual detection methods, and compares their pros and cons, and limitations of these techniques for both phosphonate and polymeric scale inhibitors. In addition, testing results with synthetic waters, cooling waters, and produce waters are presents under different application conditions, including brine TDS, pH, etc.

## Inductively Coupled Plasma (ICP) and Wet Chemistry Method for Phosphorous Containing Inhibitors

The most common technique for phosphonate scale inhibitor residual determination is inductively coupled plasma optical-emission spectrometry (ICP-OES). Inductively coupled plasma-mass spectrometry (ICP-MS) is also used for low concentration analysis.<sup>1, 12</sup> Phosphorus based scale inhibitors such as phosphonates, phosphate-esters and phosphorus-tagged polymer scale inhibitors can be analyzed by ICP-OES with quantification routinely to sub ppm concentrations.<sup>13-15</sup>

However, the major limitation of ICP is that no speciation information of different types of phosphorous can be obtained. It breaks down molecules and measures the total phosphorus, and it can only give the total phosphorus concentration of all components present in the sample. Therefore it is not able to separate different types of phosphonates or differentiate phosphonate from P-containing polymers. For example, this method cannot be used under multipart circumstances where phosphorus-containing inhibitors are applied in several wells or downhole/topside of the same oil platform.

In addition to ICP analysis on phosphorus concentration, there have been many studies on phosphorous analysis.<sup>16-21</sup> A wet chemical method based on Colorimetry (of strongly absorbing phosphor-molybdate complexes) is frequently used and generally based on the HACH method for quantification of residual phosphonate concentration. The method gives speciation information by discriminating between organically bound phosphorus and inorganic phosphate. Orthophosphate concentration can be detected directly by following HACH procedure, and organic phosphonate need to be digested before the analysis. Although reliable, the method can be time consuming. It is also sensitive to interferences from strontium, barium or Sulphur present in the produced water, although there are various steps can be taken to remove these.

Table 1 shows a comparison of ICP and wet chemistry method on a phosphonate inhibitor. During the analysis, the accuracy of the ICP and wet chemistry method were validated with a set of phosphoric acid and phosphonate inhibitor solutions. The wet chemistry method used in this test is by forming phosphor-molybdate complex and then reducing to molybdenum blue complex with ascorbic acid. The color changes shown as absorbance is proportional to  $\text{PO}_4$  concentrations. The total phosphorus concentration of a phosphonate inhibitor was analyzed by ICP and compared to the wet chemistry method to confirm the completeness of UV/persulfate digestion. The total and free phosphate (inorganic phosphate) concentration in scale inhibitor was analyzed by the wet chemistry method using the HACH PhosVer 3 method after UV digestion to determine the phosphonate concentration in inhibitor. Twelve samples were analyzed by both methods. Comparing of  $\text{PO}_4$  concentration and total  $\text{PO}_4$  from wet chemistry method, the testing results show that, both ICP and wet chemistry methods can detect to sub-ppm level of phosphorous, and they agree with each other within 10% if the analysis was properly done.

**Table 1**  
**ICP and Wet Chemistry for Phosphonate Inhibitor Analysis**

| Sample | ICP           |                           | Wet Chemistry             |                          | Ratio of ICP: Wet Chemistry method |
|--------|---------------|---------------------------|---------------------------|--------------------------|------------------------------------|
|        | P conc. (ppm) | $\text{PO}_4$ Conc. (ppm) | Total $\text{PO}_4$ (ppm) | Free $\text{PO}_4$ (ppm) |                                    |
| 1      | 1.22          | 3.74                      | 3.5                       | 0.02                     | 106.86%                            |
| 2      | 3.03          | 9.29                      | 9.37                      | 5.75                     | 99.15%                             |
| 3      | 2.26          | 6.92                      | 6.96                      | 5.65                     | 99.43%                             |
| 4      | 1.85          | 5.68                      | 5.71                      | 5.65                     | 100.53%                            |
| 5      | 2.1           | 6.42                      | 6.78                      | 5.79                     | 94.69%                             |
| 6      | 0.3           | 0.93                      | 0.96                      | 0.95                     | 96.88%                             |
| 7      | 0.56          | 1.73                      | 1.7                       | 0.97                     | 101.76%                            |
| 8      | 1.49          | 4.55                      | 4.99                      | 1.02                     | 91.18%                             |
| 9      | 0.79          | 2.42                      | 2.33                      | 1.0                      | 103.86%                            |

## Hyamine Method

The hyamine method is essentially a turbidity method, and used for detecting scale inhibitor residuals.<sup>1, 22</sup> The standard Hyamine 1622 method is using benzethonium chloride to form a complex with inhibitors, which develops turbidity over time proportional to the concentration of the scale inhibitor in solution.

During a test with standard Hyamine assay, a time of 40 minutes (from Hyamine addition to the prepared sample) to UV analysis is adopted. The time from Hyamine addition to analysis by UV was found to have a significant effect on the measured UV absorbance. The measured absorbance and corresponding inhibitor concentration reach a maximum after certain time, then decreases slowly. The time between Hyamine addition to UV analysis should be fixed and strictly adhered to. It has been observed that the Hyamine solution stratifies with time. It is recommended that the solution should be freshly prepared for each daily trial.

The accuracy of hyamine method is affected by many interferences. Therefore, the procedures include a pretreatment step for sample preparation. A cartridge is used to isolate the scale inhibitor before measurement. For current tests, a calibration curve was created using scale inhibitor in deionized water. An acceptable linear trend with concentration was observed. In order to verify the results, 6 fresh samples of a scale inhibitor in deionized water were made up and measured using the same procedure, and their concentrations were predicted using the trend generated in the calibration step. The scale inhibitor was accurately predicted down to 2 ppm in deionized water (Figure 1).

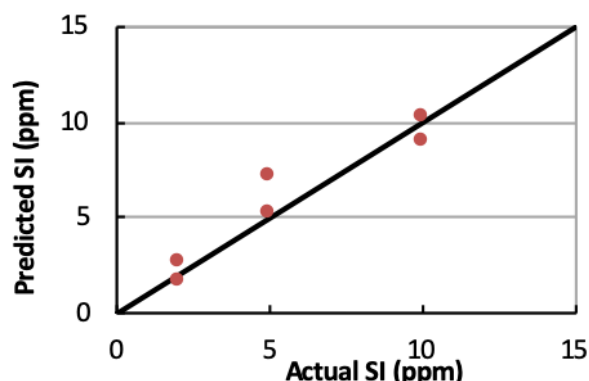


**Figure 1: Hyamine method quantification of SI in deionized water after pretreatment.**

However, with a high TDS (total dissolved solid) field sample, it was extremely difficult to obtain a reliable trend for concentration analysis. This is likely due to the high salt concentration in the produced water, particularly chloride, which is a well-known interference for this method. Therefore, extensive pretreatment procedure should be taken for high TDS brine or high potential contaminate brines.

## High Performance Liquid Chromatography (HPLC)/ Liquid Chromatography Mass Spectroscopy (LCMS)/Ion Chromatography (IC)

In recent years, much work has been done on the development of specialist scale inhibitor analysis techniques like High Performance Liquid Chromatography (HPLC) and Liquid Chromatography Mass Spectroscopy (LCMS) to push the boundaries of scale inhibitor detection.<sup>8, 23-25</sup>

Mass spectroscopy detection is sensitive and suitable for analysis of sub-ppm concentrations. It uses molecular fragments as fingerprints with functional groups used as molecular tracers for selective detection of inhibitors<sup>7</sup> Mass spectroscopy as a detection method has a number of advantages. It is selective for analysis with functional groups in polymers used as specific tracers i.e. cationic amine group can be used as a selective tracer to differentiate between different polymer types.<sup>6-8</sup> One example utilized the technique for analysis of samples from three subsea wells co-mingled in the same

flow-line for three different polymeric squeeze inhibitors (i.e. a P containing polyamine, a phosphorus-tagged quaternary amine Terpolymer and a P-tagged sulphonated copolymer) in the presence of a topside sulphonated carboxylate copolymer.<sup>7-8</sup> For quantification of chemicals in this complex mixture of production fluids, selective detection is essential which offers a significant challenge for conventional methods.

Like most methods, these technologies have some limitations: instrument costs are high and interpretation of results requires significant expertise. Matrix interferences, and the presence of many chemical species (in a complex produce water) can make quantification of residual chemical species still difficult. The assay can be limited to two or three SI's in the presence of each other. Mass spectroscopy detection methods also have issues with polymeric analyses as no single ion is generated, making "figure print" assay and interpretation difficult. Mass spectroscopy ionization can also be influenced by a number of factors including spectrometer voltages, flow rates, matrix and mobile phase effects.

The IC method incorporates a phosphor-molybdenum post column reaction. This methodology give speciation information allowing quantification of multiple phosphorous containing chemicals in a single sample. Successful separation of species is achieved using an ion-exchange column which is packed with a high capacity resin having a high affinity for phosphonates. A gradient of increasing nitric acid concentration causes elution of the phosphonate species in order of increasing charge and molecular weight. For example, DETPMP contains five phosphonate functional groups which results in a high affinity for the analytical column. Phosphonates with fewer functional groups have less affinity, do not retain as strongly and therefore elute at earlier retention times which allows differentiation.<sup>3, 16, 18</sup> IC with MS detection has been shown to be successful in quantifying a phosphonate squeeze inhibitor in the presence of phosphorus containing continuous injection scale inhibitors. This method shows promise in synthetic brine with the <0.25 mg/L quantifiable, although development is required due to the interferences at residual concentrations from high salinity, polymer preservatives, and suspended solid impurities.<sup>16</sup> IC-MS technique has been used for analysis of a scale inhibitor and corrosion inhibitor in a multi-component sample.<sup>18</sup> Inhibitors were successfully quantified to sub-ppm concentrations, highlighting the sensitivity. This technology allows individual inhibitor species to be successfully quantified in the presence of multiple production chemicals with succeeding quantification of all species.

### **Florescence-tagged Polymer Inhibitors**

Fluorescence techniques has been used on tagged-polymers for squeeze applications.<sup>26-27</sup> In general, fluorescent tags are inserted into the backbone of polymeric inhibitor. The tags are at ~1-2% content of the polymer, so they do not change the chemistry and performance of the untagged polymer. The technique allows discriminating detection of the specific polymers and shows the ability for these tagged polymers to be distinguished from the untagged polymer. The fluorescence tags are usually put on the backbone of those polymer inhibitors, which have extensive squeeze history, good brine compatibility, good environmental profile and established material compatibility data.

Fluorescence is the emission of photons by a substance that has absorbed electromagnetic radiation. Fluorescence can be used to detect different compounds in many applications because of its sensitivity, accuracy, and non-destruction on samples. Fluorescence spectrometry is based on radiation exposure of an analyte after excited by a light source with e.g. a xenon lamp or a laser having a very high luminous intensity. The light excites fluorescing molecules or atoms in the sample. The excited state in direct fluorescence exists for a finite time, normally 1–10 nanoseconds. When the excitation discharges the sample emits photons that can be measured with a specific detector. Fluorophores absorb and emit light at a specific wavelength, hence it is possible to distinguish fluorescent tags that have different excitation or emission wavelengths. A suitable fluorescent moiety can be selected based on the detection requirements to enable accurate monitoring of scale inhibitor concentrations and more details of the tagging procedure are given below.