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Understanding Effective Corrosion Inhibitor Performance for Oil Pipeline Transport Using an Innovative Residual Analysis Technique

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ABSTRACT

Corrosion inhibitor (CI) residual measurements have been a decades-long source of frustration for chemical vendors and oilfield operators alike. These measurements are often expected to detect small amounts of CI in a complex matrix of interfering species. The authors have developed a new technique utilizing nanomaterials coupled with surface-enhanced Raman spectroscopy (SERS). This new SERS technique is capable of accurately and precisely detecting trace amounts of several corrosion inhibitors at sub ppm levels. A robust field protocol was developed for sample collection, sample preparation, and calibration to allow reliable field analysis.

In oil transport pipeline systems it is operationally important that small concentrations of CI are transported through the oil to the areas where low amounts of water may be present in the system. The residual technique discussed in this paper has shown that one CI is transported in sufficient quantity to

the areas where low amounts of water are collected. The new SERS technique is allowing operators to know with a high degree of certainty that the products selected for their pipelines are correct and effective. This residual technique in conjunction with corrosion monitoring empowers the operator to select a better performing product for a longer pipeline service life or to optimize the cost of treatment of their pipeline while still maintaining an optimal service life.

Key words: corrosion inhibitors, residual measurements, nanotechnology, Raman spectroscopy, SERS

INTRODUCTION

Low concentrations of corrosion inhibitors are used to prevent mild steel corrosion in acid gas environments. Residual measurements of corrosion inhibitor concentrations are used to monitor the availability of corrosion inhibitor and many techniques have been studied in the oil field.¹ Inhibitor loss to sample container surfaces can make dye transfer methods unreliable.² Solid phase extraction (SPE) has been used with techniques such as liquid chromatography ultraviolet-visible spectroscopy (LC-UV) to successfully eliminate some loss of inhibitor to container walls during sampling.³ However, there is still a technology gap for a precise and portable means to detect corrosion inhibitors at low concentrations. Raman scattering is the phenomenon that occurs when a photon interacts with a molecule and the photon's energy is converted to a weak fluorescence due to this interaction. Raman spectroscopy allows one to measure different vibrational states of the given molecule. While Raman signals are weak, they can be amplified when sub-monolayer assemblies of molecules absorb on roughened metal surfaces. The use of this technique to measure low concentrations of molecules is known as surface enhanced Raman spectroscopy (SERS).⁴ In earlier work, a SERS method for detecting several corrosion inhibitor formulations from field systems was described.⁵⁻⁷ The development of robust analytical techniques for field analysis is difficult. It requires procedures to prevent precipitates from forming in field samples. Precipitates like any solid surface act like sponges to parasitically remove surfactants. Method development requires techniques to account for different field brines. It also requires the ability of the technique to handle substances that might interfere with accurate detection. In this paper, earlier work is further advanced with the incorporation of updated procedures to create a robust and reliable analytical technique. This paper will explore the CI concentration and performance by using SERS to evaluate field samples, samples from partitioning experiments, samples from corrosion tests, as well as blind samples dosed by customers and sent to the authors' laboratories for analysis.

EXPERIMENTAL PROCEDURE

Produced water samples were gathered from appropriate sampling locations in the field. Care was taken to ensure the water sample was representative of the given system.

Colorimetric techniques were used to determine the sulfide content and pH of the brine. Sufficient water was collected to conduct a complete water analysis (CWA) of the brine. The positively charged ions were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Negatively charged ions were detected by ion chromatography, titration, and flow injection analysis.

Results of the water analysis were used to prepare synthetic brine solutions. The corrosion inhibitor (CI-1, CI-2, or CI-3) was dosed into the synthetic brine to prepare a series of standard solutions from 0 to 2000 ppm. A calibration was performed with the standard solutions.

In obtaining samples for residual measurements, 5 mL of the field water sample were passed through a C18 SPE cartridge to remove hydrocarbons. The prepared samples were then used for the SERS analysis.

When samples were analyzed using the SERS method, Solution A was added to keep the solution at a specific pH and prevent precipitation. In the SERS method, the sample preparation for measurement involves first mixing 0.5 mL brine with Cl and 0.5 mL solution A followed by addition of small volume of metal nanoparticle solution and vortex mixing the resultant solution. The mixture is then scanned by a Raman spectrophotometer. This preparation methodology is shown in Figure 1. The sample vial was placed in the hand held Raman spectrometer. The obtained SERS spectra were processed for calibration, validation, and prediction models. The derived prediction models were utilized to analyze field samples.

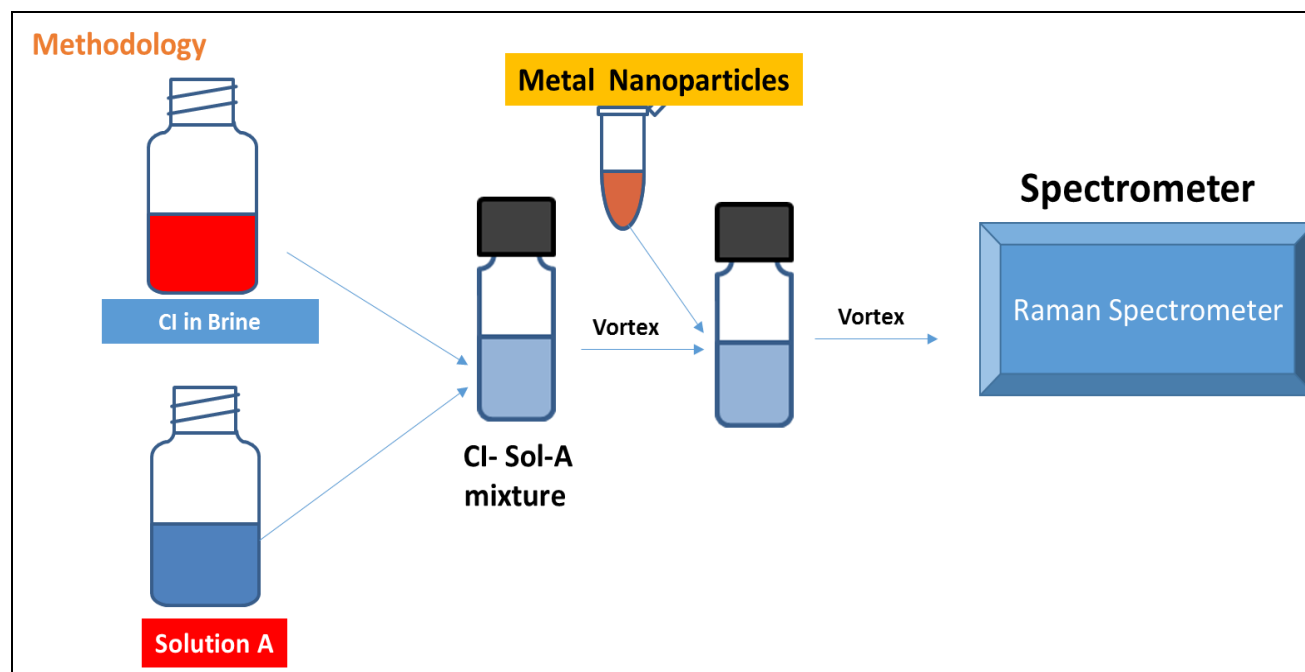


Figure 1. Schematic representation of methodology utilized to analyze water samples.

Field samples were obtained for brines of varying salinity and using their CWA, compositions of synthetic brines were prepared as shown in Table 1.

Table 1. Composition of synthetic brines

Salt	Brine 1 (g/L)	Brine 2 (g/L)	Brine 3 (g/L)
NaCl	154.74	70.70	29.11
KCl	2.98	1.59	0.16
MgCl ₂ ·6H ₂ O	28.57	8.16	0.43
CaCl ₂ ·2H ₂ O	84.51	22.83	0.98
SrCl ₂ ·6H ₂ O	5.16	1.52	0.11
NaOAc	0.69	0.69	0.53