A New Assay Method for Scale Inhibitor Detection at Low Concentrations

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Abstract

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Accurate detection of scale inhibitors has always been crucial to scale control in industry. However, analyzing scale inhibitors at low concentrations, especially with polymeric scale inhibitors, remains an ongoing challenge. This paper presents an assay method designed to detect all types of scale inhibitors, especially at low concentrations, and an expert program developed to guide the method. The program guides the preparation of a field brine barite solution at a fixed barite supersaturation. Scale inhibitor concentration is then measured via the method of standard additions, assuming a linear relationship between the scale inhibitor concentration and the logarithm of barite induction time. Seven different scale inhibitors, including phosphonates, carboxylates and sulfonates, were detected in two typical synthetic brines at low concentrations. In addition, this assay method has also been applied to scale inhibitor detection in actual field brines. In general, this easily-implemented method can directly detect the residual level of any scale inhibitors in field brine about 0.1 mg/L active. Emphasis in this paper is on low concentrations. Measurement of low concentration scale inhibitors not only helps to monitor scaling tendency but also effectively prevents overuse of scale inhibitors and thereby protects the environment and saves money. This is one of the few methods that can detect most scale inhibitors at such low concentrations. Field applications, strengths, and interferences are discussed using laboratory and field examples.
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Chapter 1. Introduction

1.1 Problem statement

Mineral scales form in various water systems, such as oil and gas produced water, cooling water, pulp miller and bleach plant produced water, due to inorganic salt supersaturation (Brown and Chen 1990; Hart and Rudie 2006; Kelland 2010; Kan and Tomson 2012). The most common scales include carbonate, sulfate and sulfide salts of divalent metal ions (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Fe$^{2+}$) and sodium chloride (Kelland 2010). Mineral scale formation can reduce flow rate, water carrying capacity and heat transfer efficiency, causing huge economic loss every year (Vetter 1972) (Brown and Chen 1990). It still remains a big challenge in industry (Kan and Tomson 2012). Injecting scale inhibitors into water systems can effectively inhibit scale formation and hence is widely applied in industry (Kan et al. 2004; Shakkthivel et al. 2004; Kelland 2010).

The accurate detection of residual scale inhibitor concentration is important in scale treatment in order to make sure that appropriate scale inhibitor level is maintained in water. In the oil and gas produced water (abbreviated as produced water), for example, too little amount of scale inhibitor is not enough to prevent scale formation (Tomson et al. 2002). Too much scale inhibitor may precipitate with divalent ions and cause pseudo-scales (Kan et al. 1994; Zhang et al. 2010). For example, aminophosphonate inhibitor react with calcium ions to form calcium phosphonate scale (Kan et al. 1994; Zhang et al. 2010).

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1 This chapter is modified from the paper “A new assay method for scale inhibitor detection at extremely low concentration” submitted to SPE International Oilfield Scale Conference and Exhibition, Aberdeen, UK. 14-15 May, 2014 (Liu et al. 2014).
However, it is often difficult to determine low scale inhibitor concentration using current detection methods, especially with polymeric scale inhibitors (Graham et al. 2010), which is particularly true in produced water that has many interferences. For example, inductively coupled plasma (ICP) is widely applied in scale inhibitor analysis by measuring phosphorus (P) concentration (Graham et al. 2010). But many polymeric scale inhibitors do not contain P, such as sulfonated polycarboxylic acid polymer (SPCA), polyvinylsulfonate polymer (PVS) and carboxy methyl inulin (CMI), so they cannot be detected by ICP. Currently, Hyamine method or high performance liquid chromatography (HPLC) method are used for polymeric scale inhibitors detection (Graham et al. 2010). But they often require time consuming pretreatment, cost highly per sample and are prone to interferences and do not have sufficiently low detection limit (Thompson et al. 2012) (see background and literature review section for details). Therefore, a sensitive, universal, and inexpensive method for scale inhibitor analysis is in strong demand in industry.

1.2 Purpose of the study

The purpose of this study is to develop a new assay method for scale inhibitor measurement and an expert software for guidance. This assay method is based upon a semi-empirical linear relationship between scale inhibitor concentration and the logarithm of the induction time of barite (BaSO$_4$) scale formation (He et al. 1996). This relationship is suggested by classical nucleation theory and confirmed by experimental observations (He et al. 1994; He et al. 1996; Mullin 2001). Using the method of standard additions, scale inhibitor concentration can be measured.

Chapter 2, Background and Literature Review, will introduce in detail the scaling problem, nucleation and crystal growth theory, common scales, scale inhibitors and their detections, and the assay method development history. Chapter 3 gives a full description of the assay method, including the principle of the method, method and materials, and results and discussion. An
improved assay method is presented in Chapter 4 with a revised more convenient procedure and new results and discussion. Chapter 5 concludes both the original and improved assay method, and chapter 6 introduces possible future research.
Chapter 2. Background and Literature Review

2.1 Introduction of scaling

2.1.1 Source and control of scaling problem

Scale is formed by the deposition of inorganic salts from aqueous solutions under super-saturation condition (Kelland 2010). Supersaturated salts can deposit on available surfaces to cause plugging (Figure 1), leading to operation upsets and huge economic loss (Hart and Rudie 2006; Kelland 2010). In the oil industry, scale problems sometimes can be so severe that oil production is reduced from 30,000 Barrels Per Day (4,770 m$^3$/d) to 0 within only 24 hours, which actually happened in a North Sea oil well (Brown 1998; Crabtree et al. 1999).

![Figure 1. Scale in oil pipe (left) (EMEC 2014) and water pipe (right) (Doelman 2014)](image)

In the oil industry, the most common scales are carbonate scales, sulfate scales of divalent metal ions, like Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ and Fe$^{2+}$, sulfide salts of divalent metal ions and sodium chloride (Kelland 2010). Most inorganic ions come from injected water and rock reservoirs. Mineral supersaturation can occur in such situations as incompatible produced water mixing in the down hole area of oil wells, injection of seawater that contains high concentration of $SO_4^{2-}$ into oil wells that have high concentration Ca$^{2+}$ and/or Ba$^{2+}$, and the decrease of temperature and pressure during the
transportation of produced water from down hole to surface (Kan and Tomson 2012). These situations are common in oil production and transportation processes.

Scaling has been a typical and serious problem in many water systems for decades (Kan and Tomson 2012) (Brown and Chen 1990; Hart and Rudie 2006), and many research has been done on scale prediction and control. For scale prediction, researchers in the author’s research group developed an Excel based software named ScaleSoftPitzer (SSP). It can calculate scaling tendencies of at least eleven minerals at a wide range of temperature, pressure and total dissolved solids (TDS) and the minimum effective inhibitor concentration needed to prevent scaling. They developed another Excel based software for the design and prediction of inhibitor return concentrations as well (Kan et al. 2005). As to scale control, one widely applied way is to use scale inhibitors such as ethylenediaminetetraacetic acid (EDTA) chelating agent or phosphonate polymers that can effectively inhibit scale deposition by preventing or retarding scale nucleation and/or crystal growth. Scale inhibitor concentration detection has always been problematic, especially for low concentration detection and polymeric inhibitor detection. This study develops a new assay method for scale inhibitor concentration detection that solves many of these measurement problems.

2.1.2 Solubility, saturation index (SI) and activity coefficient

Scale solubility is the basis of scale prediction and control. Solubility definition and relative theory are introduced as follows.

2.1.2.1 Solubility

Solubility is a property of a substance to dissolve in a solvent to form a homogeneous solution. For an inorganic mineral dissolving in water, its solubility is a function of temperature, pressure
and solution pH. Given a constant temperature, the solubilities of most minerals increase with pressure. As temperature increases, the solubilities of some minerals increase, exemplified by barium sulfate and sodium chloride, but solubilities of other minerals such as calcium carbonate and ferrous carbonate decrease. Solution pH is also an important factor for the solubility of some minerals. For example, calcium carbonate and iron carbonate have higher solubility at low pH values. Furthermore, the presence of hydration inhibitors in the produced water, such as methanol and monoethylene glycol, can significantly decrease the solubility of some minerals, such as barite and halite.

### 2.1.2.2 Saturation index (SI)

SI is a prevalent indicator for scale formation potential. For example, the mineral $M_x N_y \cdot zH_2O$ shows the calculation of SI.

$$M_x N_y \cdot zH_2O \leftrightarrow xM^{y+} + yN^{x-} + zH_2O$$  \hspace{1cm} (1)

$$SI = \log_{10} \frac{ \left\{ M^{y+} \right\}^x \left\{ N^{x-} \right\}^y (a_w)^z }{ K_{sp} (T, P) } = \log_{10} \frac{ \left[ M^{y+} \right]^{y} \left[ N^{x-} \right]^{y} (a_w)^z }{ K_{sp} (T, P) }$$  \hspace{1cm} (2)

$K_{sp}$: solubility product constant, the activity product of the ions when the mineral is equilibrium with aqueous phase. $K_{sp}$ is a function of only temperature and pressure.

$$K_{sp} = \left\{ M^{y+} \right\}^x \left\{ N^{x-} \right\}^y (a_w)^z \text{ (in equilibrium)}$$

$\left\{ M^{y+} \right\}$ (mol/L): the activity of $M^{y+}$

$\left\{ N^{x-} \right\}$ (mol/L): the activity of $N^{x-}$

$a_w$ (mol/L): the activity of water

$[M^{y+}]$ (mol/L): the concentration of $M^{y+}$

$[N^{x-}]$ (mol/L): the concentration of $N^{x-}$
The kinetics of mineral precipitation and dissolution are closely related to the mineral SI, as illustrated in Figure 2 (Kan and Tomson 2012) with barite as an example. If barite SI = 0, the barite solid and solution are in equilibrium. If SI < 0, barite dissolve. If SI > 0, there will be several possibilities. In the case of 0 < SI < circa 1.3 (25 °C), this supersaturation condition is not sufficient for barite solution to precipitate automatically unless barite seed crystals are present. In the SI range of around 1.3 – 3.0 (25 °C), barite precipitation will be quite fast if inhibitors are absent, but it can be prevented or retarded if they are present. The time lag largely depends on barite SI, temperature, pressure, inhibitor and inhibitor amount, and can vary from minutes to days or even longer. Inhibitors cannot easily control barite precipitation when the SI is higher than about 3.0 (25 °C), called critical SI value. These three regimes are also similar for other scales, but the transition SI of three regimes change with temperature, pH, selected inhibitors and target scales.
Figure 2. The relationship between barite SI and barite precipitate or dissolve kinetics (Kan and Tomson 2012)

2.1.2.3 Activity Coefficient

SI calculation involves activity coefficient calculation using one of many available models or equations for activity coefficient calculation, such as Pitzer model, specific ion interaction (SIT) model and Davies equation. Figure 3 shows the applicability of different models as a function of ionic strength (IS) (Donald 1997). The Pitzer model, which has the widest range of applicability, was chosen to calculate ion activity coefficients in this study.
Figure 3. The applicability of different activity coefficient models as a function of ionic strength ($I$, in the figure) for a divalent cation (Note: the dashed tangent to the curve at its origin is a plot of the Debye-Huckel limiting law for the ion) (Donald 1997)

The Pitzer model for describing an individual ion activity coefficient is as follows (Donald 1997).

$$\ln \gamma_i = z_i^2 f^\gamma + \sum_i D_{ij}(IS)m_j + \sum_{ik} E_{ijk}m_jm_k + \cdots$$

(3)
\[ f^\gamma = -0.392 \left[ \frac{IS^{1/2}}{1 + 1.2 \times IS^{1/2}} + \frac{2}{1.2} \ln \left( 1 + 1.2 \times IS^{1/2} \right) \right], \] a modified Debye-Huckel (DH) term.

The first term accounts for long range ion interaction and is extended from DH limiting law. The second term, the binary term, is the sum of short range interactions between two solution species with the opposite or same sign. The third term, as ternary term, represents the interactions among two like-charged and a third unlike-charged species, and is assumed to be independent from IS. The DH and binary terms are the main parts of an ion activity coefficient calculation. The ternary term is usually not necessary for the calculation of an ion activity coefficient value if the solution IS is under around 3.5 mol/kg. As the IS increases, the ternary term will become large and should be taken into account (Donald 1997; Dai 2013). Pitzer model equations are often extremely long, involving many parameters and substitutions (Pitzer 1987; Weare 1987), and is usually computed using a computer. Those parameters are functions of temperature, pressure, IS and/or solution composition (see Plummer et al. (Plummer et al. 1988) for a list of published useful parameters for the Pitzer model).

Accurate calculation of ion activity coefficient and SI are important for scale prediction and control. They are keys to accurate SI calculation of barite in this study.

2.1.3 Scale nucleation and crystal growth

The solubility of a mineral in water is limited. If the dissolved mineral is beyond its corresponding solubility, mineral will precipitate until the solid-aqueous system restores its balance. The precipitation can be divided into two processes, nucleation and crystal growth.
2.1.3.1 Nucleation

In classical nucleation theory, there are two kinds of nucleation, primary and secondary nucleation (Figure 4). Primary nucleation means the nucleation happens in a system without crystalline matter, and it has two subtypes, homogeneous and heterogeneous nucleation. Homogeneous nucleation occurs spontaneously in a water system without any foreign condensation nuclei, while heterogeneous nucleation needs foreign particles. Secondary nucleation is induced by present or intentionally added crystals of solute (Mullin 2001). There are two types, contact nucleation and seeding. Contact nucleation is sweeping away nuclei that would otherwise form a crystal to become new crystals, which is attributable to fluid shear (McCabe et al. 1993). Seeding induced nucleation is collision of formed crystals with seed crystals or other formed crystals (McCabe et al. 1993). In order to induce secondary nucleation, seed crystals are not necessarily the same crystals that are forming. Isomorphous substances can also induce nucleation in some cases (Mullin 2001). For instance, silver iodide (AgI) has a crystal lattice similar to that of ice, which makes AgI a perfect artificial rain maker (Mullin 2001).

![Figure 4. Nucleation tree (Mullin 2001)](image)

The nucleation process necessarily involves free energy change. In homogeneous nucleation, the overall free energy, $\Delta G$, for the formation of a small solid particle of solute from the solution
equals the sum of the surface excess free energy, $\Delta G_s$, and the volume excess free energy, $\Delta G_v$, as shown in equation 4 (eq. 4) (assuming the particle is a sphere with a radius of $r$) (Mullin 2001).

$$\Delta G = \Delta G_s + \Delta G_v = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v$$  \hspace{1cm} (4)

$\Delta G_s$: the surface excess free energy that means the excess free energy between the surface of the particle and the bulk of the particle. It is positive and proportional to $r^2$.

$\Delta G_v$: the volume excess free energy that is the excess free energy between an infinite large particle (with infinite diameter) and the solute in solution. It is negative and its absolute value is proportional to $r^3$.

$r$: radius of the particle

$\gamma$: the interfacial tension, also called surface free energy

$\Delta G_v$: the free energy change of the volume transformation per unit volume

The relationship of $\Delta G$ and particle radius $r$ is shown in Figure 5. Only when the particle size is larger than the critical size $r_c$, can a particle be stable and continue growing. $r_c$ is calculated by the differential of eq. 4, \( \frac{d \Delta G}{dr} = 0 \), and the final calculation equation is eq. 5. Critical size corresponding overall excess free energy, $\Delta G_{crit}$, can be calculated by eq. 4 and 5, as displayed in eq. 6 (Mullin 2001).

$$r_c = \frac{-2\gamma}{\Delta G_v}$$  \hspace{1cm} (5)

$$\Delta G_{crit} = \frac{16\pi \gamma^3}{3(\Delta G_v)^2} = \frac{4\pi \gamma r_c^3}{3}$$  \hspace{1cm} (6)
However, homogeneous nucleation is not easy to achieve in industry or lab, and most common nucleation is heterogeneous. It has been reported that more than $10^6$ foreign particles with size less than 1 µm exist in 1 ml solution that a lab prepared, and the most active heteronuclei are particles with size of 0.1 to 1 µm (Mullin 2001). With the presence of proper foreign particles, the overall excess free energy $\Delta G^\prime_{\text{crit}}$ is likely to reduce, $\Delta G^\prime_{\text{crit}} = \phi \Delta G_{\text{crit}}$ ($\phi \leq 1$) (Mullin 2001). $\Delta G_{\text{crit}}$ is the overall excess free energy under homogeneous condition. $\phi$ value depends on the contact angel ($\theta$) between the foreign particle surface and the crystalline (nuclei) deposit (eq. 7) (Volmer 1939; Mullin 2001), and $\theta$ corresponds to the wetting angle of solid and liquid (Figure 6 and eq. 8) (Mullin 2001).
\[ \phi = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \]  

(7)

**Figure 6. Interfacial tensions between liquid solution, crystalline deposition and solid surface** (Mullin 2001)

\[ \gamma_{sl} = \gamma_{cs} + \gamma_{cl} \cos \theta \]  

(8)

\( \gamma_{sl} \): the interfacial tension between the foreign solid surface and the liquid solution  
\( \gamma_{cs} \): the interfacial tension between the crystalline deposit and the foreign solid surface  
\( \gamma_{cl} \): the interfacial tension between the crystalline deposit and the liquid solution  
\( \theta \): the contact angel between the foreign particle surface and the crystalline deposit

In the case of \( \theta = 0^\circ \) that corresponds to complete wetting between crystalline deposit and the foreign solid, then \( \Delta G'_{\text{crit}} = 0 \). This situation occurs when the foreign particles happen to be the same crystals that are currently crystallized, which is theoretically secondary nucleation. If \( \theta = 180^\circ \), \( \Delta G'_{\text{crit}} = \Delta G_{\text{crit}} \), which corresponds to complete non-wetting, same as homogeneous nucleation. Figure 7 shows how \( \phi \) changes with \( \theta \) (Mullin 2001). Based on this analysis, the \( \Delta G'_{\text{crit}} \) of heteronucleation and secondary nucleation are much smaller than homogeneous nucleation, which makes heterogeneous nucleation and secondary nucleation easier to happen.
The overall excess free energy determines if the nucleation can happen, and the nucleation kinetic is measured by nucleation rate. The Arrhenius reaction velocity form (eq. 9) is used in the calculation of nucleation rate, J. With eq. 9, the final expression of J calculation is in eq. 10. It is suggested that temperature T, degree of supersaturation S and interfacial tension γ are the main factors that control J (Mullin 2001).

\[
J = A \exp\left(\frac{-\Delta G}{kT}\right)
\]  
(9)

A: the pre-exponential constant, determined by experiment
k: Boltzmann constant. \( k = 1.3805 \times 10^{-23} \text{ J/K} \)

\[
J = A \exp\left(\frac{-16\pi \gamma^3 v^2}{3kT^3 (\ln S)^2}\right)
\]  
(10)

v: the molecular volume
S: degree of supersaturation. $S = c/c^*$ ($c$ is solution concentration; $c^*$ is the solution concentration at equilibrium saturation) (Mullin 2001)

According to eq. 10, it will take approximately $10^{62}$ years to nucleate spontaneously (homogenous) for supercooled water vapor with degree of supersaturation $= 2.0$ (Mullin 2001), which is not consistent with daily observations. Nucleation must involve heterogeneous nucleation that has lower energy barrier ($\Delta G_{\text{crit}}^' \leq \Delta G_{\text{crit}}$) and corresponds to higher nucleation rate. Secondary nucleation is also involved in some nucleation processes.

2.1.3.2 Crystal growth

Stable nuclei formed in a supersaturated system will continue to grow into crystals of visible size. This process is called crystal growth. There are many proposed theories to explain the crystal growth process. In consideration of the limited size of this thesis, only diffusion-reaction theory, which is the foundation of several others, is introduced here.

In diffusion-reaction theory, crystal growth contains two steps, diffusion of the solute from the bulk of the fluid phase to the surface of crystal solid (eq. 11) and reaction of the solute merge into the crystal lattice (eq. 12) (Berthoud 1912; Mullin 2001).

For diffusion,

$$R_G = \frac{1}{A} \cdot \frac{dm}{dt} = k_d (c - c_i) \quad (11)$$

$R_G$: crystal growth rate per surface area
A: surface area of the crystal
$k_d$: mass transfer coefficient of diffusion
c: solute concentration in the solution (supersaturated)
c_i: solute concentration in the solution at the crystal-solution interface
For reaction:

\[
R_G = \frac{1}{A} \frac{dm}{dt} = k_r (c_i - c^*)^r
\]

(12)

\(k_r\): rate constant of the surface reaction
\(c^*\): the solution concentration at equilibrium saturation
\(r\): reaction order, often \(r \geq 1\)

By combining eq. 11 and 12, the overall reaction rate is expressed as eq. 13.

\[
R_G = \frac{1}{A} \frac{dm}{dt} = K_G (c - c^*)^g
\]

(13)

\(K_G\): overall crystal growth coefficient
\(g\): overall crystal growth order, often \(1 \leq g \leq 2\)

With eq. 11 and 12, crystal growth rate \(R_G\) value can be calculated if the reaction order \(r\) is certain (eq. 14).

\[
R_G = k_r \left( \frac{R_G}{k_d} \right)^r, \text{ where } \Delta c = c - c^*
\]

(14)

2.1.3.3 Induction time

Induction time \((t_{\text{ind}})\) is the time needed to form stable and detectable nuclei in a supersaturated solution (Mullin 2001). Induction time is composed of several parts. First, a supersaturated system needs relaxation time \((t_r)\) to achieve a quasi-steady state distribution of molecular clusters; second, a quasi-steady state system spends nucleation time \((t_n)\) to form stable nuclei; third, stable nuclei needs growth time \((t_g)\) to achieve detectable size. Thereby, \(t_{\text{ind}} = t_r + t_n + t_g\) (Mullin 2001). After induction time, there is a latent period \((t_{\text{lp}})\) that refers to the time when massive nucleation occurs,
which is reflected in notable data change of the measuring instrument (Figure 8). During the period shorter than or equal to induction time, change in the concentration of solute is not noticeable since there is little amount of crystal formed. Whilst, in the latent period, a significant decrease of solute concentration starts.

![Diagram of solute concentration change with time](image)

**Figure 8. Solute concentration in liquid phase change with time (Mullin 2001)**

Induction time can be influenced by such factors as saturation index, agitation speed, presence of impurities and others. The effect of impurities on induction time vary substantially depending on the properties of the impurities. For example, the addition of scale inhibitors in the produced water can remarkably prolong scale induction time, so as to prevent scale precipitation in the oil wells and pipelines. It is observed in this study that only 0.3 mg/L phosphine polycarboxylic acid (PPCA), a widely used polymeric scale inhibitor, can prolong the induction time of barite with SI = 2.1 approximate 20 min.
Moreover, foreign ions may also affect induction time (He 1995), because foreign ions sometimes can play the role as a structure breaker during crystallization. Take barite scale for example. As shown in Figure 9, high concentration Ca$^{2+}$ (> 1000 mg/L), Sr$^{2+}$ (> circa 200 mg/L) and Pb$^{2+}$ (> 155 mg/L) significantly prolong barite induction time. The higher the Ca$^{2+}$ and Pb$^{2+}$ concentrations, the longer the barite induction time. While, the effect of Zn$^{2+}$ on barite induction time seems random, and Mg$^{2+}$ appears to have no significant effect on barite induction time. Furthermore, foreign ions may strengthen or weaken the inhibition effect of some inhibitors. For instance, high concentration Ca$^{2+}$ can enhance the inhibition effect of diethylene triamine penta(methylene phosphonic acid) (DTPMP) on barite, while Mg$^{2+}$ appears to weaken DTPMP, but neither Ca$^{2+}$ nor Mg$^{2+}$ have significant impact on barite inhibition behavior of polymer inhibitors, polyvinyl sulfonate potassium polymer (PVS) and PPCA (Boak et al. 1999). Induction time is significant in this study, and more information related to it will be presented later.

**Figure 9. The effect of divalent cations on barite induction time** (He 1995)
2.1.4 Common Scales

Prevalent scales in water systems include divalent metal salts of carbonate, sulfate and sulfide ions, and sodium chloride. They can be roughly divided into two classes, pH-sensitive and pH-independent (Kan and Tomson 2012). Sulfate scales and sodium chloride belong to pH independent scales because their solubility is not sensitive to pH change. Carbonate and sulfide scales are pH sensitive scales and can dissolve more in the acidic solution. Knowledge of scale properties can improve scale inhibition and control.

2.1.4.1 Carbonate scales

The major carbonate scale is calcium carbonate (CaCO$_3$), the most widespread scale found (Kan and Tomson 2012) and a common substance in rock. It often exists in three phase, calcite (the most popular phase), aragonite and vaterite (Figure 10). Calcite has a low solubility product, only 4.8×10$^{-9}$ at 25 °C (Patnaik 2003). As temperature increases, calcite solubility decreases, which is atypical compared to other salts. Calcite solubility increases with pressure increases, which is true for all other divalent salts (Kan and Tomson 2012). In the oil industry, the main reason for calcite scale formation is pressure drop during produced water being transported from underground to the surface. Pressure drop not only decreases calcite solubility, but also removes carbon dioxide (CO$_2$) from solution and increases solution pH (Kan and Tomson 2012). As shown in the reaction equation (eq. 15), given a certain amount of HCO$_3^-$, CO$_2$ pressure reduction will increase CO$_3^{2-}$ concentration and promote CaCO$_3$ precipitation. pH increase will also result in more CO$_3^{2-}$ and more CaCO$_3$ precipitation.

\[
2\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + H_2O + \text{CO}_2(g) \tag{15}
\]
Calcite crystals formed in the produced water are mainly composed of calcium carbonate, but often iron (Fe\(^{2+}\)) and/or magnesium (Mg\(^{2+}\)) substitute into the calcite lattice, so the formula for calcite can be written as Ca\(_{0.8\text{ to }1.0}\)(Fe, Mg)\(_{0.2\text{ to }0.0}\)CO\(_3\).

Figure 10. Crystals of calcite (up left) (Gardiner 2003), aragonite (up right) (Wikipedia 2014) and vaterite (down middle) (Kato 2014)

2.1.4.2 Sulfate scales

Sulfate scales are mostly sulfate salts of group II ions except magnesium (Mg\(^{2+}\)). Barium sulfate and calcium sulfate are most common. Sulfate scales in oil wells often happen in seawater flooded reservoirs since seawater contains high concentration SO\(_4^{2-}\) (about 2800 mg/L).

Barite (Figure 11), the mineral name of barium sulfate (BaSO\(_4\)), is a most insoluble and stable scale, with a solubility product of only 1.08 \(\times\) 10\(^{-10}\) at 25 \(^{\circ}\)C. The solubility of barite decreases as
temperature and pressure decrease, which is inevitable during produced water transportation from down hole to the surface (Kan and Tomson 2012). Barite scale in the oil wells typically occurs in the following two situations. First, a high barium produced water from one zone mixes with a high sulfate produced water from another (Kan and Tomson 2012). The mixing of brines from different zones at down hole is common in oil wells. Second, high sulfate water such as seawater is injected into a high barium zone during water flooding operation (Kan and Tomson 2012). In those two situations, barite SI is often too high to be controlled by scale inhibitors. Once barite is formed, it is extremely hard to re-dissolve. When barite is formed rapidly, besides the main composition BaSO\(_4\), SrSO\(_4\) may merge into barite lattice and its formula becomes Ba\(_{0.88}\)Sr\(_{0.12}\)SO\(_4\) (Kan and Tomson 2012; Zhang 2013). The substitution of Sr\(^{2+}\) into barite lattice affects the precipitation kinetics and induction time of “barite” (He 1995), probably due to different solubilities of BaSO\(_4\) and SrSO\(_4\). Also, barite can co-precipitate with radium (Ra\(^{2+}\)) ions to form “technically enhanced naturally occurring radioactive material” (TE-NORM) (BaRa\(_{\text{trace}}\)SO\(_4\)).

Figure 11. Barite (BaSO\(_4\)) crystal (Gallery 2013)

Another typical sulfate scale is calcium sulfate (CaSO\(_4\)). Compared with other sulfate scales, CaSO\(_4\) is easy to dissolve due to its relatively high solubility product, 4.93 × 10\(^{-5}\) (in anhydrous form at 25 °C) (Lide 2004). But CaSO\(_4\) precipitation is common because of high Ca\(^{2+}\) concentration
in the produced water. Calcium sulfate has two major phases, anhydrite (CaSO₄) and gypsum (CaSO₄·2H₂O) (Figure 12), and one transition phase, hemihydrate (CaSO₄·1/2H₂O) (Rolnick 1954; Lu et al. 2012). These three phases can transfer from one to another depending on the supersaturation state, temperature, pressure, and water activity (Lu et al. 2012; Dai 2013). As shown in Figure 13, calcium sulfate favors gypsum phase at low temperature and anhydrite phase at high temperature, but the transition temperature varies depending on other conditions. At any certain temperature, the higher the salt concentration in solution, the fewer the water-of-hydration molecules in calcium sulfate crystal formula (Kan and Tomson 2012). Calcium sulfate scale normally occurs in such cases like high sulfate injection water mixing with high calcium formation water during water flooding, pressure drop during produced water transportation from down hole to the surface, and temperature increase in membrane filtration, stream flood and so forth (Kan and Tomson 2012).

Figure 12. Anhydrite (CaSO₄) (left) (Wikimedia 2010) and gypsum (CaSO₄·2H₂O) (right) (Wikipedia 2014) crystals
Figure 13. The calcium sulfate-water system equilibrium diagram at temperatures from 0-220 °C (Rolnick 1954)

2.1.4.3 Sulfide scales

The main sulfide scales in the produced water include iron sulfide (FeS), iron disulfide (FeS₂), zinc sulfide (ZnS) and lead sulfide (PbS), calcium sulfide (CaS) (Kelland 2010; Kan and Tomson 2012). Sulfide ions (S²⁻) mainly come from the reduction of sulfate ions (SO₄²⁻) by sulfate reducing bacteria (SRBs) or thermal reduction of SO₄²⁻, as shown in the following reaction,
\[ SO_4^{2-} + 4H_2 \rightarrow S^{2-} + 4H_2O \] (Kelland 2010). Ferrous ions (Fe\(^{2+}\)) are mostly from corrosion of steel pipes. Zinc (Zn\(^{2+}\)) and lead (Pb\(^{2+}\)) ions originate from the dissolution of sphalerite (ZnS) and galena (PbS) minerals into formation water, injection water that reacts with those minerals, and zinc bromide completion fluid (Collins and Jordan 2001). Sulfide scales are sparingly soluble in water and they precipitate rapidly. For example, the precipitation rate constant of FeS with SI = 0.96 at 25 °C is as high as 1152.9 L·mol\(^{-1}\)·min\(^{-1}\) in a second order reaction model (Wang et al. 2014). It is nearly impossible to stop FeS formation once it is supersaturated. Also, FeS helps stabilizing unwanted oil water emulsions in the produced water and impedes the remove of crude oil from produced water (Fink 2011). Sulfide scales need to be seriously controlled given their low solubility, even though they are not as prevalent as carbonate and sulfate scales. Unfortunately, sulfide scale control is difficult, in spite of some progress (Ke and Qu 2007; Chen et al. 2010; Fink 2011).

### 2.1.4.4 Sodium Chloride

Two highest concentration ions in the produced water are generally sodium (Na\(^{+}\)) and chloride (Cl\(^{-}\)). Sodium and chloride ions can form large amounts of halite (NaCl) (Figure 14) scale. Halite, the mineral name of sodium chloride (NaCl), has a solubility of as high as 359,000 mg/L at 25°C that is far away larger than those of the above scales. Halite scale generally happens when temperature and/or pressure drops in high TDS solutions where halite is nearly saturated. Halite scale also forms in low water producing gas wells, as the pressure drops and water evaporates. Given the high solubility of halite, once precipitation happens, halite scale mass is quite large and it precipitates quickly (Kelland 2010; Kan and Tomson 2012).
Besides the above mentioned scales, there are some other scales, such as siderite (FeCO₃), celestite (SrSO₄), iron hydroxide (Fe(OH)₃) and silica (SiO₂), that sometimes appear in water systems. In some produced waters, cooling water or other water systems, multiple scales form simultaneously.

### 2.2 Scale inhibitors

“Scale inhibitor” is the general name for the chemicals that can effectively inhibit the deposition of inorganic scales, such as calcite, barite and gypsum. There are two classes of scale inhibitors, thermodynamic and kinetic inhibitors (Fink 2011). Thermodynamic inhibitors are normally complexing and chelating reagents, such as EDTA and nitrilo triacetic acid (NTA) (Fink 2011). Thermodynamic inhibitors can chelate with the cation or anion of being formed scale to decrease scale SI and preventing scale formation. Kinetic inhibitors can prolong scale induction time and retard scale formation. With a large dosage of kinetic inhibitor, scales may be completely inhibited. The concentration of kinetic inhibitors is the determinant of scale inhibition when other conditions are constant.
Different industries have different standards for inhibitor selection. Here are the selection standards of scale inhibitors in the oil industry (Fink 2011).

1. Effective inhibition effect even at low inhibitor concentration;
2. Compatibility with produced water;
3. Balance of adsorption on the rock first and then slow desorption into produced water;
4. Tolerance of high temperature;
5. Low toxicity and high biodegradability; and

Other industries should have similar selection standards, except the third standard that is related to scale inhibitor squeeze treatment. Squeeze treatment is utilized in scale inhibitor application in oil industry to help maintaining enough amount of scale inhibitors in the produced water in a long term (Kelland 2010). Scale inhibitor concentration has to reach a certain value in order to be effective. First, scale inhibitors are injected into oil wells by squeeze treatment, and scale inhibitors adsorb onto rock. Then, as oil and water flow, absorbed inhibitors slowly release into produced water for scale inhibition and finally flow out of oil well with produced water. If the inhibitor fails to absorb onto the rock, it will be flushed out and wasted, leaving the pipelines unprotected. If the inhibitor too strongly adsorbs onto rock with little desorption, inhibitor concentration in the produced water will not be enough to inhibit scale formation. Only if the inhibitor adsorption and desorption is well balanced can produced water have enough scale inhibitor to prevent scale formation for a long time. The balance can be reflected on inhibitor squeeze lifetime that refers to the time period from the beginning of inhibitor squeeze injection to the time when scale inhibitor concentration is too low to prevent scale formation in the produced water. Thereby, squeeze lifetime becomes an important property of scale inhibitors.
Considering that thermodynamic inhibitors are more expensive than kinetic inhibitors and kinetic inhibitors perform well on scale control, kinetic inhibitors are more popular in industry. The scale inhibitors discussed in this section are kinetic inhibitors.

2.2.1 Scale inhibitor mechanism

Scale inhibitors prevent or retard scale formation mainly through nucleation inhibition, crystal growth inhibition, and/or scale dispersion (Yuan et al. 1998; Kelland 2010). The mechanisms of how inhibitors inhibit scale formation have been studied for many years, but still not well known yet. Besides, the inhibition mechanisms change with different scale inhibitors and different scales. There are two popular theories with regard to nucleation and crystal growth inhibition brought up by previous researchers (Tomson et al. 2002; Kelland 2010; Fink 2011).

2.2.1.1 Adsorption

It is widespread that scale inhibitors can adsorb on scale nuclei and block active growth sites. If no active sites are left for crystal ions to adhere, crystal nucleation and/or growth will be impeded (Kelland 2010; Fink 2011). Amjad (Amjad 1988) observed notable decreases of gypsum crystal growth rate and formed gypsum in the presence of polyacrylate inhibitor. Based on his experimental results, Amjad (Amjad 1988) proposed that surface adsorption of inhibitor onto nuclei is the main reason. According to Tomson et al.’s research (Tomson et al. 2002), for complete barite inhibition, the required aminophosphonate inhibitor amount is about 16% surface coverage of the scale surface. Tomson et al. (Tomson et al. 2002) also pointed out that the primary driving force of inhibitor adsorption is hydrophobic repulsion of macro neutral inhibitor molecules from liquid solution, instead of the generally presumed specific inhibitor-surface interaction. Inhibitor molecules are mostly macro molecules and become dissociated in water solution. Then, inhibitors are neutralized by cations (except protons) in the water, which makes inhibitors large neutral or
nearly neutral molecules. Some research even found out that only metal-complexed PPCA can effectively inhibit barite formation, and un-complexed PPCA cannot (Xiao et al. 2001). The adsorption theory is applicable for both polymer and non-polymer inhibitors (Tomson et al. 2002; Graham et al. 2003).

### 2.2.1.2 Morphologic change

Some inhibitors inhibit scale formation by complexing foreign ions that can insert into the scale lattice. Inserted foreign ions distort the scale lattice structure and connected inhibitors help forming complex surface or crystalline nets, which makes crystals hard to grow (Kelland 2010; Fink 2011). This mechanism is called morphologic change. A typical example is aminophosphonate inhibitor complexed with Ca\(^{2+}\) inhibit barite formation by means of Ca\(^{2+}\) insert into barite lattice and change barite morphology (Sorbie and Laing 2004). The inhibition effect of aminophosphonate inhibitor on barite increase significantly with increasing Ca\(^{2+}\) concentration (Graham et al. 2003). Moreover, Kimberley et al. observed that phosphate could change CaCO\(_3\) crystal morphology, decrease crystal numbers and enlarge crystal size, as shown in Figure 15 (Gallagher et al. 2013). It appears that phosphate altered crystal morphology, and strongly altered nuclei cannot grow, but dissolve and dissolved Ca\(^{2+}\) and CO\(_3^{2-}\) attach to unaffected nuclei, which makes less crystal numbers and larger crystal size. Still, crystal growth were affected by phosphate, so the morphology of final crystals became different from what CaCO\(_3\) crystals are expected.
Figure 15. “The effect of phosphate on the morphology and size of calcium carbonate” (Gallagher et al. 2013)
Besides nucleation and crystal growth inhibition, some scale inhibitors have dispersion effect on the formed scales, so that formed small scale particles cannot gather together and precipitate. For instance, one phosphonate inhibitor was observed to exert dispersing effect on iron oxide (Amjad 2014). The mechanism of how scale inhibitors work is more complicated, more investigation is required.

2.2.2 Common scales inhibitors

There is a broad variety of scale inhibitors used in industry because different scales need different inhibitors for the best control. Carbonate and sulfate scale inhibitors, such as SPCA, PPCA and DTPMP, often cannot inhibit halite scale or sulfide scales. It is probably because halite contains only monovalent ions with different property from divalent ion scales (Kelland 2010), and sulfide scales have always been difficult to deal with due to their sparing solubility, acidity and other properties. Hexacyanoferrate salts and nitrilotrialkanamides and quaternary salts are two kinds of typical halite inhibitors. Trishydroxymethylphosphine (THP) has been reported to be able to control iron sulfide, but its high effectiveness needs other compounds to work together (Fink 2011). Furthermore, some inhibitors have specific preference for certain types of scales. For example, PVS is excellent at barite inhibition; CMI performs well with carbonate scale inhibition, but relatively poorly with sulfate scales (Kelland 2010). In general, most scale inhibitors can inhibit several similar types of scales. Since group II (from Mg\(^{2+}\) to Ba\(^{2+}\)) carbonate and sulfate scales are most common and of concern to industry, this section only discuss inhibitors of these minerals.

Based on functional groups, inhibitors are divided into three types, polysulfonates, polycarboxylates and phosphorus (P) containing scale inhibitors. Non-polymers with only sulfonate and/or carboxylate groups are fairly poor inhibitors, so commercial inhibitors with only sulfonate and/or carboxylate groups are usually polymers. P containing scale inhibitors have
several sub-types: polyphosphates, phosphate esters, non-polymeric phosphonates, polyphosphonates and polyphoninates.

2.2.2.1 Polysulfonates

Polysulfonates is an excellent group of scale inhibitors. Representatives are SPCA and PVS (Figure 16). Polysulfonates have the following advantages. First, polysulfonates have high thermal stability, which makes them applicable at high temperature oil wells (Kelland 2010). Second, polysulfonates can tolerate high concentration Ca\(^{2+}\) and Mg\(^{2+}\) due to lower stability constants with these two ions, especially at lower temperatures (Kelland 2010). Third, sulfonic acid is a strong acid with low pKa value, which enable polysulfonates to work well in low pH solutions. These advantages make sure the good performance of polysulfonates in scale inhibition at harsh conditions, such as high temperature, high Ca\(^{2+}\) concentration, and low pH. Furthermore, polymers with vinyl sulfonic acid group have been found to be effective to prevent barite scale (Emmons 1987; Sorbie and Laing 2004; Kelland 2010) which is one of the most troublesome scales in the oil industry.

![Polyvinyl sulfonate sodium polymer (PVS) (Sigma-Aldrich 2014)](image)

However, polysulfonates also have some disadvantages. For instance, polysulfonates adsorption to rock is weaker than other groups of inhibitors, resulting in a short squeeze lifetime and the need
of frequent inhibitor addition (Kelland 2010; Yan et al. 2014). The longer the lifetime of the inhibitor, the longer the inhibitor preventing scale formation (section 2.2.3.). Some efforts have been made to lengthen polysulfontes squeeze lifetime, for example, the incorporation of phosphate ester group into polysulfonates (Kelland 2010).

### 2.2.2.2 Polycarboxylates

Polycarboxylates are traditional scale inhibitors. There are three classical types of polycarboxylic acids, polyacrylic acid, polymethacrylic acid and polymaleic acid (Figure 17) (Kelland 2010). Polycarboxylates is relatively low cost, which is one of the reasons for their wide application.

![Figure 17. The structures of polyacrylic acid (left) (Sigma-Aldrich 2014), polymethacrylic acid (middle) (Sigma-Aldrich 2014), and polymaleic acid (right) (Olson and Hammel 2012)](image)

Polycarboxylates usually combine with other groups to form better scale inhibition performance. Polycarboxylates added with a percentage of amide or hydroxyl groups show much better performance on scale inhibition and calcium tolerance (i.e. inhibitor does not form precipitation with high concentration Ca$^{2+}$), compared with polycarboxylates alone (Guzmann et al. 2007). Also, the addition of quaternary amine, phosphonate or phosphinate groups into polycarboxylates can increase inhibitor adsorption affinity to rock so as to prolong squeeze lifetime (Chen et al. 2008; Montgomerie et al. 2008). For example, PPCA (Figure 18) has longer squeeze lifetime and higher calcium compatibility and better barite scale inhibition than polycarboxylic acid (Smith et al. 1976;
Furthermore, combination of polyacrylic acid with cationic monomers, for example, methacryloxy ethyltrimethyl ammonium chloride, shows biocidal and anticorrosion functions in addition to scale inhibition (Trabitzsch et al. 1981; Kelland 2010).

Figure 18. Structure of phosphino polycarboxylic acid (PPCA) (Darden and Triebel 1987)

One big drawback of polycarboxylates, especially polyacrylic acid, is low biodegradability that endangers surrounding environment. Low biodegradability limits polycarboxylates deployment in regions with strict environmental regulation. However, after years of efforts, some biodegradable polycarboxylate inhibitors have been invented, such as polyaspartate salts, polytartaric acid and CMI (Figure 19). Polyaspartate is a highly biodegradable inhibitor with good performance on both scale and corrosion inhibition (Fan et al. 1999; Collins et al. 2001; Fan et al. 2002). It has been used as scale inhibitor in North Sea basin where ≥ 20% biodegradability is required (Kelland 2010). Polytartaric acid and CMI have been commercialized as oilfield scale inhibitors too.
Figure 19. The structures of polyaspartate sodium (up left) (Wikipedia 2014), polytartaric acid (up right) (Kelland 2010) and carboxymethylxylulutin (CMI) (down middle) (Wikipedia 2014)

2.2.2.3 Polyphosphates and phosphate esters

Polyphosphates (Figure 20) are famous for carbonate scale inhibition with high thermal stability. They are often used in boiler water for scale control (Kelland 2010). Phosphate esters (Figure 21) are good inhibitors for CaCO₃, CaSO₄ and BaSO₄ scales in neutral and alkaline solutions. Sometimes, phosphate esters also inhibit corrosion (Hollingshad 1976). They have limited thermal stability (Kelland 2010), which limits their application. However, they are environmental friendly and have good affinity to rock in the oil wells. The addition of phosphate ester group, for example, monomer ethylene glycol methacrylate phosphate, into vinyl carboxylic or vinyl sulfonic monomer inhibitors can significantly enhance the inhibitor adsorption / desorption ability to rock, so as to extend the inhibitor squeeze lifetime (Crossman and Holt 2006; Kelland 2010).
2.2.2.4 Non-polymeric phosphonates

Phosphonates often join with other groups to form new effective scale inhibitors (Kelland 2010). There are two main types of non-polymeric phosphonate inhibitors.

First type is aminophosphonates that contain 1 ~ 3 amine groups and several phosphonate groups. Aminophosphonates have been used for carbonate and sulfate scale control for many years (Kelland 2010). Aminophosphonate inhibitor representatives, shown in Figure 22, include nitrilo trimethylphosphonic acid (NTMP), 1,2-diamino ethane tetrakis(methylene phosphonic acid) (EDTMP) and DTPMP. They are effective and popular inhibitors in the oil industry. Unfortunately, most commercial aminophosphonates have two shortcomings, low biodegradability and low calcium compatibility (Kelland 2010). High concentration phosphonates in water system will result in eutrophication, which limits their use in sensitive regions. But some aminophosphonate
inhibitors with enhanced calcium compatibility have been synthesized, such as dihexamethylene triamine pentakis(methylene phosphonic acid) (Figure 23) (Kelland 2010). Some aminiphosphonate inhibitors were reported to be less thermally stable than polymer inhibitors (Dyer et al. 2004; Fink 2011), so their deployment in high temperature reservoir is limited to some extent.

Figure 22. Structures of nitrilo trimethylphosphonic acid (NTMP) (left) (Sigma-Aldrich 2014), 1,2-diamino-ethanetetrakis (methylene-phosphonic acid) (EDTMP) (middle) (Yancui 2011), and diethylene triamine penta(methylene phosphonic acid) (DTPMP) (right) (Dongtao 2011)

Figure 23. Dihexamethylene triamine pentakis(methylene phosphonic acid) (Lookchem 2008)

Second type of non-polymeric phosphonate inhibitors are made of one phosphonate group and several carboxylate groups, such as 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) that is a good CaCO₃ inhibitor, and 1-hydroxyethane-1,1-diphosphonic acid (HEDP) (Figure 24).
Figure 24. Structures of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) (left) (Inc. 2014) and 1-hydroxyethane-1,1-diphosphonic acid (HEDP) (Wikipedia 2013)

2.2.2.5 Polyphosphonates

Polyphosphonate inhibitors are divided into two major types based on different backbone, polyamine and polyvinyl backbones (Kelland 2010). N-phosphono methylated amino-2-hydroxy propylene polymer is a typical polyphosphonate inhibitor with polyamine backbone. It shows good performance on barite scale inhibition with a long squeeze lifetime (Singleton et al. 2000). Polyphosphonates with polyvinyl backbone can combine with some other monomers, such as carboxylate and/or sulfonate to become better scale inhibitors (Kelland 2010).

2.2.2.6 Polyphosphinates

Inhibitors made of only polyphosphinates are not common. Instead, polyphosphinate usually form copolymers with other group that could be carboxylate, sulfonate or phosphonate groups. For example, phosphino polymers with phosphonate group as end cap displays good barite inhibition, high thermal stability and long squeeze lifetime (Davis et al. 2003).

2.2.3 Current scale inhibitor detection methods

As stated in Chapter 1, residual scale inhibitor determination is crucial to scale treatment, but current methods have difficulty in low concentration detection, especially polymeric inhibitors.
Table 1 briefly compares several detection methods and detailed descriptions of these methods are as follow.

**Table 1. Comparison of different scale inhibitor detection methods (Graham et al. 2010; Fuller et al. 2011; Poynton et al. 2012; Thompson et al. 2012)**

<table>
<thead>
<tr>
<th>Methods</th>
<th>Detectable Inhibitors</th>
<th>Detection Limit</th>
<th>Interference</th>
<th>Pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP</td>
<td>P containing inhibitors</td>
<td>20 µg/L P</td>
<td>background P; high salty produced water</td>
<td>required (sometimes)</td>
</tr>
<tr>
<td>Hyamine</td>
<td>partial polymers</td>
<td>2 mg/L active</td>
<td>chloride ions; other polyelectrolytes; particles</td>
<td>required</td>
</tr>
<tr>
<td>HPLC</td>
<td>most</td>
<td>0.5 mg/L active (in the lab)</td>
<td>high salty produced water</td>
<td>required (sometimes)</td>
</tr>
<tr>
<td>Fluorescence tag</td>
<td>fluorescence tagged polymer inhibitors</td>
<td>2 mg/L</td>
<td>background interference</td>
<td>required</td>
</tr>
<tr>
<td>This study</td>
<td>most</td>
<td>0.1 mg/L active</td>
<td>small</td>
<td>no</td>
</tr>
</tbody>
</table>

### 2.2.3.1 Inductively coupled plasma (ICP)

ICP has been applied for P-containing inhibitor detection for many years due to its high accuracy in P detection. ICP detects total P concentration in water solution and then convert P concentration into inhibitor concentration on the basis of P percentage in inhibitor. However, there are quite a few problems with ICP detection. First, background P interference. Sometimes oil wells release inorganic P into produced water, which makes ICP overestimates scale inhibitor concentration (Thompson et al. 2012). There are also some other background P sources.

Second, high salty matrix interference. Some water solution, for example produced water, are high TDS solution. At low concentration scale inhibitor detection in which dilution times is small, high
concentration salts in water solution will affect ICP detection and increase P detection limit (Graham et al. 2010). Scale inhibitor separation by C 18 cartridge or other solid phase exchange (SPE) may be able to alleviate these two interferences. But C 18 cartridge may also release trace amount of P, which will cause big errors in low concentration P detection (Graham et al. 2010).

Third, even without background P and high concentration salts interference, some P-containing inhibitor detection by ICP is still problematic because of the low P content (Graham et al. 2010). For instance, P content in PPCA is less than 0.5%, which means the detection limit of P, about 20 µg/L, corresponds to more than 4 mg/L PPCA that is relatively high. As to P-tagged scale inhibitors, low P percentage and uneven P distribution often happen, resulting in large errors in inhibitor concentration detection. Of course, as to inhibitors with known chemical structures and constant P content, such as DTPMP and NTMP, ICP has no such problem in their detection.

Last but not least, commercial scale inhibitors are typically not 100% active scale inhibitors, so there are some “impurities” exist in scale inhibitors. When scale inhibitors go through oil wells, they absorb on rock first and then gradually dissolve into produced water. Considering the polydisperse nature of polymers and their selective adsorption on and desorption from the rock, coming out polymers are not necessarily same as the injected polymers with same percentage of active scale inhibitor (Graham et al. 2010). It they become different, big errors will occur by converting an element concentration to inhibitor concentration. This interference is not just with ICP; some other detection methods also face it. The assay method developed in this study can successfully avoid this problem.

Besides the above stated problems or interferences, ICP cannot detect P-free inhibitors, but many popular polymeric inhibitors do not contain P, such as SPCA, PVS and CMI. Polymeric scale
inhibitors are becoming more popular in the oil industry because they are more stable at high temperature and often less harmful to the environment, compared to non-polymeric ones (Choi et al. 2002; Boak and Sorbie 2010; Yan et al. 2012). Currently, these polymeric inhibitors are often analyzed by Hyamine method or HPLC methods (Graham et al. 2010).

2.2.3.2 Hyamine method

Hyamine method was designed for polymeric scale inhibitor detection. The principle is that the complex of polymeric scale inhibitor and hyamine (i.e. quaternary amine) increase solution turbidity and the increased turbidity is linear to inhibitor concentration. Based on a previously constructed calibration curve of inhibitor concentration and turbidity, inhibitor concentration can be determined. Ultraviolet–visible spectrometer (UV/Vis) is often used for turbidity measurement. Hyamine method is generally accurate and robust, but it still has some drawbacks.

First, hyamine method is often interfered with high concentrations of chloride ions because chloride ions can react with hyamine to form precipitation (Graham et al. 2010). In case of high concentration scale inhibitor detection, diluting detected water solution will alleviate chloride interference. But at low concentration detection (ppm level) which is required in the long term of squeeze treatment, this interference cannot be overcome, which largely increases the detection limit of the hyamine method. Second, other polyelectrolytes in water solution may complex with hyamine and their complex can interfere with the turbidity response of inhibitor-hyamine complex (Graham et al. 2010). Third, dissolved organics and particles in the water solution increase solution turbidity, which makes the hyamine method overestimate scale inhibitor concentration (Graham et al. 2010).
To overcome partial interferences, it was proposed to separate scale inhibitors from water solution. PPCA, polyacrylate and polymaleic based inhibitors are able to be separated from water solution by C 18 cartridge with high recovery rates, but the separation process is time consuming (Graham et al. 2010). Besides, some other polymer inhibitors such as PVS and sulfonate polyacrylate copolymers cannot be separated by C 18 cartridge (Graham et al. 2010). Although some other separation methods were investigated, they are not developed and more time consuming, which impedes their wide application. Furthermore, pretreatment by C 18 cartridge, SPE or membrane will largely increase the analytical cost per sample. In general, in spite of the accuracy and robust, hyamine method is only applicable for certain types of polymer inhibitors with time consuming pretreatment and also it easily suffers from interferences from solution.

2.2.3.3 High performance liquid chromatography (HPLC)

HPLC is a promising analysis method for both polymer and non-polymeric scale inhibitors. It determines scale inhibitors by detecting specific compounds and can distinguish different scale inhibitors (Thompson et al. 2012). The latest generation of HPLC has good accuracy, sensitivity and specificity, but it has not been tested in real produced water yet (Thompson et al. 2012). Also, there still exist some drawbacks of HPLC in scale inhibitor detection. For example, HPLC suffers from high salty matrix interference, especially at low concentration detection. Inhibitor pretreatment, such as inhibitor separation from produced water by C 18 cartridge or SPE, may be necessary before HPLC detection, which significantly lengthens analysis time. Moreover, HPLC costs per sample are high and it needs a highly trained operator (Thompson et al. 2012). These factors certainly hold up HPLC application.
2.2.3.4 Fluorescence tag method

Florescence analytical technique has been used for organic and inorganic compound detection for many years, especially in life science field. Inspired by life science, fluorescence tag method was developed for scale inhibitor detection recently (Fuller et al. 2011; Poynton et al. 2012). Fluorophore was chemically added onto the backbone of polymer scale inhibitors. By determining fluorophore concentration with a fluorometer, scale inhibitor concentration can be calculated (Poynton et al. 2012). Fluorophore analysis is sensitive and accurate with low detection limit. However, fluorophore percentage in scale inhibitors is usually low, about 0.01 – 1% (Fuller et al. 2011), which considerably increases scale inhibitor detection limit. Moreover, before fluorophore concentration detection by fluorometer, pretreatment by SPE is usually required in order to avoid background interferences from water solution (Poynton et al. 2012). SPE pretreatment again involves other issues, such as high cost, time consuming and low recovery rate (some scale inhibitors).

2.3 Assay Method

2.3.1 The development of an assay method

As stated in the introduction (section 2.1.3.3.), induction time is affected by many factors, including SI, temperature and scale inhibitor concentration. It was assumed by Mullin et al. (Mullin 2001) that induction time is inversely proportional to the rate of nucleation, \( t_{\text{ind}} \propto J^{-1} \). With some revision by He et al. (He et al. 1994; 1995), the logarithm of the induction time is proposed to be inversely proportional to the square of SI (eq. 16).

\[
\log t_{\text{ind}} = -\frac{\beta y^3 V_m^2 N_A f}{(2.3RT)^3 (SI)^2} - C
\]

\( \beta \): geometric shape factor
$V_m$: molar volume of the crystal
$N_A$: Avogadro number
$f$: a correction factor for heterogeneous nucleation (assumed to be 0.01)
$C$: a constant

This equation is supported by experimental data (He et al. 1994; 1995). He et al. also suggested that scale inhibitors can lengthen scale induction time through increasing crystal interfacial tension. The nature and concentration of scale inhibitor determines the increase in interfacial tension (He et al. 1994). In He’s further research, a linear relationship between scale inhibitor concentration and the logarithm of barite induction time was observed (He et al. 1996) (eq. 17).

$$\log t_{inh} = b \times C_{inh} + \log t_0$$

(17)

$t_0$ (sec): the induction time in the absence of scale inhibitor
$t_{inh}$ (sec): the induction time in the presence of scale inhibitor, $C_{inh}$ (mg/L)
$C_{inh}$ (mg/L): the scale inhibitor concentration (mg/L)
$b$ (L/mg): the slope whose value depends on the nature of scale inhibitor and solution composition

Such linear relationships between scale induction time and scale inhibitor concentration have been observed numerous times (He et al. 1999; Fan et al. 2010). The assay method developed in this study for scale inhibitor concentration is based on this semi-empirical liner equation (eq. 17). At fixed barite SI, solution composition, temperature and agitation speed, scale inhibitor concentration is measured via the method of standard additions. Specific details about the assay method will be presented in chapter 3.

Besides the linear equation, He et al. (He et al. 1996) developed an equation for prediction of barite induction time in the presence and absence of scale inhibitors based on nucleation kinetics. Later research refined He’s equations. There are prediction equation of barite induction time $\log t_0$ (eq.
(18) and HexaMethyleneDiamineTetra (MethylenePhosphonic Acid) (HDTMP) inhibitor slope (eq. 19) (Fan et al. 2010). Induction time in the presence of inhibitors can also be calculated by combing eq. 17, 18 and 19.

\[
\log t_{0, \text{barite}} = 1.83 - \frac{12.1}{SI} - \frac{885.8}{T} + \frac{5460.3}{SI \cdot T} 
\]

(18)

\[
\log b_{\text{barite}}^{HDTMP} = -0.006 - 1.43 \cdot SI + 968.6 / T + 0.102 \cdot pH + 0.137 \cdot \log R 
\]

(19)

R: Ba/SO₄ molar ratio

Induction time prediction equations helps determining experimental conditions, such as SI and T of the assay method in this study. But for scale inhibitor quantity determination, considering interferences from solution, induction time should be measured by experiment instead of calculated by equations. Each induction time was measured by experiments in this study.

### 2.3.2 What is an assay

An assay is an analytical procedure whereby the concentration of a substance (analyte) is determined by measuring an intensive property of the analyte and expressing it with relevant measurement units (Mifflin 2000). Assay is popular in biological, biochemical and chemical analysis. For examples, 23S rRNA gene mutations can be determined by a PCR-oligonucleotide ligation assay (Stone et al. 1997); a determination method of citrate in biological fluids is developed based on citrate inhibition on calcium fluoride crystal growth (Grases et al. 1991). This assay method makes use of the fact that scale inhibitors extend scale induction time and the logarithm of induction time has been found to be linear with scale inhibitor concentration.
Chapter 3. Assay Method

3.1 Methods and Materials

3.1.1 Overview of the proposed assay method

Induction time is the time (s) needed to form stable and detectable nuclei in a supersaturated solution (Mullin 2001). A method of known additions (Eaton et al. 1995) is used to calculate the concentration of scale inhibitor based upon the observed linear relationship between scale inhibitor concentration and the logarithm of barite induction time (He et al. 1994; 1995; He et al. 1996; Mullin 2001), as shown in eq. 17:

\[
\log t_{inh} = b \times C_{inh} + \log t_0
\] (17)

\(t_0\) (sec): the induction time in the absence of scale inhibitor
\(t_{inh}\) (sec): the induction time in the presence of scale inhibitor, \(C_{inh}\) (mg/L)
\(C_{inh}\) (mg/L): the scale inhibitor concentration (mg/L)
\(b\) (L/mg): the slope whose value depends on the nature of scale inhibitor and solution composition

Induction times are calculated based on solution turbidity curves that are recorded by a recording turbidity meter in this study (see section 3.1.2.3 for details). Induction time is when solution turbidity becomes 0.1 NTU higher than the average value of background turbidity. Figure 25 shows four solution turbidity curves and their induction times.

Barite was chosen as the target scale in the assay method for several reasons. First, barite is one of the most common scales in the oil field (Kelland 2010). Barite inhibitors and other inhibitors

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2 This chapter is modified from the paper “A new assay method for scale inhibitor detection at extremely low concentration” submitted to SPE International Oilfield Scale Conference and Exhibition, Aberdeen, UK. 14-15 May, 2014 (Liu et al. 2014).
that work for calcite or gypsum scales control can generally inhibit barite as well (Kelland 2010), which makes the assay method applicable for a variety of inhibitors. Second, barite has extremely low solubility and high stability (Blount 1977). Barite precipitation can occur rapidly when barite SI is large. Once barite is formed, it is hard to redissolve. Last, barite solubility is insensitive to solution pH. In comparison with barite, calcite is a pH sensitive scale. Carbonate concentration changes with solution pH, which makes it hard to calculate and control calcite SI precisely, since pH determination and control are not easy in the field brine (Kan and Tomson 2012). Also, Ca\(^{2+}\) concentration is high in some field brines, which makes high Ca\(^{2+}\)/CO\(_3^{2-}\) ratio when SI of CaCO\(_3\) is fixed. Calcium sulfate scale has the same high Ca\(^{2+}\) problem. Besides, calcium sulfate has three phases, anhydrite, hemihydrate and gypsum, and the three have different solubilities. Minor temperature or water activity change may lead to different phase and different induction time.

It is shown that the best detection sensitivity of this assay method at room temperature occurs when \(\log t_0\) is equal to 2 to 2.5 log units, and each known addition of scale inhibitor causes an increase in the induction time by about 0.15 to 0.30 log units. From experience, these criteria can be met if the barite saturation index, SI \(\approx\) 2.1 at 25 °C, and each scale inhibitor addition is about 0.1 mg/L. The original field brine, or produced water, should be diluted by trial and error so that the concentration of scale inhibitor in the diluted brine is about 0.1 mg/L, although this concentration can vary considerably. This diluted brine is called “sample”, abbreviated “S”, and its corresponding induction time is \(t_S\). S with scale inhibitor addition of 0.1 mg/L is supplemental sample 1 (SS1), with a corresponding induction time, \(t_{S+1}\). S with 0.2 mg/L scale inhibitor addition is supplemental sample 2 (SS2), with a corresponding induction time, \(t_{S+2}\). The value of \(t_0\) is measured with a solution that is similar to S, but without scale inhibitor. The solution is named “blank” (B) and its preparation will be introduced later.
The original field brine has $C_f$ mg/L scale inhibitor. Scale inhibitor concentration is estimated as $C_f^{estimated}$ mg/L and diluted to 0.1 mg/L by trial and error. The dilution factor (DF) = $C_f^{estimated} / 0.1$. The diluted brine, S, contains $C_s$ mg/L scale inhibitor, $C_s = C_f / DF$. Ba$^{2+}$ and SO$_4^{2-}$ are added during dilution so that S has barite SI = 2.1 and the ratio of Ba$^{2+}$ to SO$_4^{2-}$ as close to 1.00 as possible – see procedure below. The amount of added Ba$^{2+}$ and SO$_4^{2-}$ depends on the field brine composition and TDS and the calculations are shown in the next section. Prepared B, S, SS1 and SS2 solutions are monitored by a recording turbidity meter for induction time measurement.

![Figure 25. The turbidity curves and induction times of four solutions, B, S, SS1 and SS2](image)

With four selected induction times and two added inhibitor concentrations, the inhibitor concentration in the original field brine can be calculated. With the three data points (0.0, log $t_s$), (0.1 mg/L, log $t_{SS1}$), and (0.2 mg/L, log $t_{SS2}$), the following equation is formed and the slope
$b \ (L/mg)$ and intercept $a$ are calculated using the least squares trendline function in Excel, as illustrated in Figure 26.

$$\log t_{inh} = b \times (C_{inh} - C_s) + a$$

(20)

The intercept $a$ is the logarithm of the induction time of S that contains $C_s \ (mg/L)$ scale inhibitor (i.e. $C_{inh} = C_s$). Using $\log t_0$ and its corresponding $C_{inh} = 0$, the value of $C_s \ (mg/L)$ can be calculated:

$$C_s = \frac{a - \log t_0}{b}$$

(21)

In this case (Figure 26), $C_s = \frac{2.6174 - \log 196}{2.7263} = 0.119 \ mg/L$.

By multiplying the dilution factor the concentration of scale inhibitor in the original field brine can be calculated:

$$C_f = C_s \times DF$$

(22)

In this example, $C_f = 0.119 \times 10 = 1.19 \ mg/L$.

The standard deviation (SD) of $C_f \ (mg/L)$ is calculated by (Bader 1980):

$$SD = C_f \left( \left( \frac{db}{b} \right)^2 \ + \ \left( \frac{da}{a} \right)^2 \right)^{0.5}$$

(23)

The $b$ and $a$ are fitted slope and intercept and $db$ and $da$ are their standard deviations respectively. The calculation of standard deviations of slope and intercept can be found in Sawyer’s book (Sawyer et al. 2003).
In this example, $SD = 1.19 \times \left( \frac{0.2085}{2.7263} \right)^2 + \left( \frac{0.0269}{2.6174} \right)^2 = 0.09$, so $C_f = 1.19 \pm 0.09$ mg/L.

**Figure 26. Scale inhibitor calculation based on the linear relationship between scale inhibitor concentration and the logarithm of induction time**

The above discussion presents the major principles of the assay method. Based on the principle of the assay method, it can be concluded that what this assay method detects is the equivalent inhibitor concentration (EIC), which provides a better evaluation of the scaling tendency of field brine and can be expressed as $C_f$ mg/L EIC as reference scale inhibitor. For instance, if a field brine contains several scale inhibitors, all scale inhibitors can be detected by the assay method in one test with PVS as the reference scale inhibitor. The result is $C_f$ mg/L EIC as PVS. Moreover, some scale inhibitors in the field brine may lose scale inhibition functions and they will be excluded in scale
inhibitor analysis by the assay method. Therefore, the assay method will detect effective equivalent scale inhibitor concentration, or EIC.

3.1.2 Procedure of the assay method and related materials

Below is a brief summary of this assay procedure and related materials. Even though the actual calculation is tedious, it can be handled easily by using the Microsoft Excel based expert program available to the Brine Chemistry Consortium. The expert program provides detailed guidance and procedures (Figure 27) (see appendix for more information about the expert program).

![Figure 27. Scale inhibitor assay method expert program](image)

3.1.2.1 Simulated brine and required reagents preparations

First, it is necessary to prepare a simulated brine with the same composition of the field brine but without scale inhibitors. The concentrations of cations and anions in the field brine should be
measured by ICP titration as shown in Table 2. All cations are prepared with chloride salts and all
anions are prepared with sodium salts. Prior to the addition of sodium bicarbonate, add a volume
of 1 mol/L hydrochloride (HCl), so that the concentration of HCl corresponds to the acid amount
added to field brine for water solution preservation. This simulated brine will be used for $t_0$ (s)
measurement. Worksheet “Simulated Brine” in the expert program has detailed procedure for
simulated brine preparation.

Table 2. Compositions of three synthetic brines, tap water and three field brine

<table>
<thead>
<tr>
<th>Components</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>TW</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ (mg/L)</td>
<td>19872.0</td>
<td>11020.0</td>
<td>35357.0</td>
<td>34.0</td>
<td>48010.8</td>
<td>67809.7</td>
<td>6190.0</td>
</tr>
<tr>
<td>K$^+$ (mg/L)</td>
<td>500.0</td>
<td>408.4</td>
<td>469.0</td>
<td>3.7</td>
<td>136.9</td>
<td>477.1</td>
<td>118.0</td>
</tr>
<tr>
<td>Mg$^{2+}$ (mg/L)</td>
<td>54.0</td>
<td>1322.0</td>
<td>0.0</td>
<td>3.9</td>
<td>698.8</td>
<td>2012.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Ca$^{2+}$ (mg/L)</td>
<td>6500.0</td>
<td>421.9</td>
<td>0.0</td>
<td>30.0</td>
<td>4737.2</td>
<td>10695.9</td>
<td>146.0</td>
</tr>
<tr>
<td>Sr$^{2+}$ (mg/L)</td>
<td>700.0</td>
<td>6.9</td>
<td>0.0</td>
<td>0.0</td>
<td>1610.9</td>
<td>791.1</td>
<td>32.9</td>
</tr>
<tr>
<td>Ba$^{2+}$ (mg/L)</td>
<td>550.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
<td>23.7</td>
<td>4.6</td>
<td>17.9</td>
</tr>
<tr>
<td>Fe$^{2+}$ (mg/L)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>43.6</td>
<td>15.5</td>
<td>12.2</td>
</tr>
<tr>
<td>Zn$^{2+}$ (mg/L)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.1</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$ (mg/L)</td>
<td>43438.3</td>
<td>19838.0</td>
<td>55653.7</td>
<td>23.0</td>
<td>60206.3</td>
<td>93789.3</td>
<td>8637.5</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (mg/L)</td>
<td>0.0</td>
<td>2775.0</td>
<td>0.0</td>
<td>66</td>
<td>4.0</td>
<td>104.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SiO$_2$ (mg/L)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>0.0</td>
<td>8.4</td>
<td>101.4</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>281.0</td>
<td>145.0</td>
<td>0.0</td>
<td>86.0</td>
<td>427.0</td>
<td>183.0</td>
<td>729.4</td>
</tr>
<tr>
<td>Alkalinity (mg/L as HCO$_3^-$)</td>
<td>281.0</td>
<td>145.0</td>
<td>0.0</td>
<td>86.0</td>
<td>427.0</td>
<td>183.0</td>
<td>729.4</td>
</tr>
<tr>
<td>Scale Inhibitor</td>
<td>varied</td>
<td>varied</td>
<td>varied</td>
<td>varied</td>
<td>unknown</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>71895.4</td>
<td>35937.2</td>
<td>91479.6</td>
<td>250.7</td>
<td>115500.0</td>
<td>175602.1</td>
<td>15323.4</td>
</tr>
</tbody>
</table>

Note: S1, S2 and S3 are synthetic brine abbreviations. They are not related to “sample” (S).
In order to adjust barite SI to 2.1 and make Ba/SO$_4$ ratio to 1.0, five other reagents are prepared; their compositions are shown in Table 3. All inhibitor concentrations are as mg/L active inhibitor in this paper. Worksheet “Reagents” in the expert program has detailed reagent information and preparation procedures.

**Table 3. The names, compositions and preparations of five reagents required for the assay method**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Detailed name</th>
<th>Composition and preparation</th>
</tr>
</thead>
</table>
| R1      | High ionic strength pH buffered solution | 35357 mg/L Na$^+$, 469 mg/L K$^+$, 3353 mg/L Pipes, 55654 mg/L Cl$^-$.
  Prepared with NaCl, KCl, Pipes (1.5 Na) solids and DI water. |
| R2      | Ba$^{2+}$ stock solution ($C_{R2}^{Ba^{2+}}$ (mg/L)) | 10,000 mg/L Ba$^{2+}$.
  Prepared with BaCl$_2$ solid as solute and R1 reagent as solvent. |
| R3      | SO$_4^{2-}$ stock solution ($C_{R3}^{SO_4^{2-}}$ (mg/L)) | 10,000 mg/L SO$_4^{2-}$.
  Prepared with Na$_2$SO$_4$ solid as solute and R1 reagent as solvent. |
| R4      | PIPES buffer solution ($C_{R4}^{mol}$ (mol/L)) | 0.5 mol/L PIPES (1.5 moles Na$^+$/mole PIPES).
  Prepared with PIPES (1.5 Na), sodium 1,4-piperazinediethanesulfonate, powder with DI water. |
| R5      | Reference scale inhibitor solution ($C_{R5}^{mg}$ (mg/L)) | 20 mg/L active scale inhibitor
  Prepared with reference scale inhibitor as solute and R1 reagent as solvent. The reference scale inhibitor should be the same or at least similar to the detected scale inhibitor. |

**3.1.2.2 Dilution of field brine and simulated brine**

The dilution of field brine and simulated brine are conducted separately but follow almost identical procedures. The dilution process is comprised of preparing the cationic and anionic solutions. The cationic solution will contain the added Ba$^{2+}$ ions and the anionic solution will contain the added SO$_4^{2-}$ ions, to make the final solution that has a barite SI = 2.1 at molar Ba/SO$_4$ as close to 1.0 as possible. The test solution S in Figure 25 is prepared by mixing equal volumes of the cationic and
the anionic solutions. The preparation of the cationic and anionic solutions differs and is dependent on the Ba$^{2+}$ and SO$_4^{2-}$ concentrations in field brine.

If Ba$^{2+}$ concentration (in mol/L) in the field brine is equal to or higher than SO$_4^{2-}$, the procedure is as follows. Filter the field brine with 0.45 µm cellulose acetate filters to remove impurities. The field brine has $C_f$ mg/L scale inhibitor. Scale inhibitor concentration is estimated as $C_f^{estimated}$ mg/L and diluted to 0.1 mg/L. If the estimated scale inhibitor concentration is greater than 100 mg/L, the solution should be diluted twice to be 0.1 mg/L. The cationic solution is made from: field brine, R4, R2, and R1 reagents. The total volume, $V_{cat}$, is arbitrary, but generally $V_{cat} = 0.050 \text{ L}$ is sufficient. The procedure for calculating $V_{cat}$, and the cationic solution composition is outline in eq. 24 to 27:

$$V_f = \frac{2 \times C_{inh}^{added} V_{cat}}{C_f^{estimated}}$$  \hspace{1cm} (24)$$

$V_f$ (L): Volume of field brine to be used.

$C_f^{estimated}$ (mg/L): Estimated scale inhibitor concentration in the field brine.

The factor “2”: accounts for the equal volume mixing of cationic and anionic solutions.

$C_{inh}^{added}$ (mg/L): Incremental concentration of reference scale inhibitor to be added into S and $C_{inh}^{added} = 0.1 \text{ mg/L}$ in this present procedure.

$V_{cat}$ (L): The volume of cationic solution.

$$V_{R4} = \frac{C_{acid} V_f}{C_{R4}}$$  \hspace{1cm} (25)$$

$V_{R4}$ (L): Volume of reagent R4 to be added.

$C_{R4}$ (mol/L): Concentration of PIPES buffer in reagent R4; $C_{R4} = 0.5 \text{ mol/L}$ in this procedure.

$C_{acid}$ (mol/L): Concentration of strong acid in the acid preserved brine.
\[ V_{R2} = \frac{1}{C_{Ba^{2+}}^{\text{Stock}}} \times \left( 2 \times 10^3 \times MW_{Ba^{2+}} \times \left( \frac{10^{SI_{\text{Barite}}} \cdot K_{sp(Barite)}}{\gamma_{Ba^{2+}} \cdot \gamma_{SO_4^{2-}}^*} \right)^{0.5} \right) DV_{\text{cat}} - C_{Ba^{2+}}^{\text{Brine}} \gamma_f \]  

and if \( V_{R2} < 0 \), then \( V_{R2} = 0 \)

\[ D = (kg \text{ water } / \text{ liter of solution}) = 1 - 3.60 \times 10^3 \times TDS (mg / L) \]

for a solution that is predominated by reagent R1 (Kan et al. 2005).

\[ V_{R2} \ (L): \] Volume of reagent R2 to be added.

\[ C_{Ba^{2+}}^{\text{Stock}} \ (mg/L): \] Concentration of \( Ba^{2+} \) in reagent R2; \( C_{Ba^{2+}}^{\text{Stock}} = 10,000 \ mg/L \) in this example.

\[ MW_{Ba^{2+}} \ (g/mol): \] Molecular weight of \( Ba^{2+} \); \( MW_{Ba} = 137.33 \ g/mol. \)

\[ SI_{\text{Barite}}: \] Saturation index of barite; SI = 2.1 in this example.

\[ K_{sp(Barite)}: \] Solubility product constant of barite.

\[ \gamma_{Ba^{2+}}: \] Activity coefficient of \( Ba^{2+} \) and it can be calculated with modified Pitzer theory (Kan and Tomson 2012).

\[ \gamma_{SO_4^{2-}}: \] Activity coefficient of \( SO_4^{2-} \) and it can be calculated with modified Pitzer theory (Kan and Tomson 2012).

\[ D \ (kg \ H_2O / L): \] Unit convertor.

\[ C_{Ba^{2+}}^{\text{Brine}} \ (mg/L): \] Concentration of \( Ba^{2+} \) in the field brine.

\[ V_{R1(\text{cat})} = V_{\text{cat}} - V_f - V_{R4} - V_{R2} \]  

\[ V_{R1(\text{cat})} \ (L): \] Volume of reagent R1 to be added in cationic solution.

Again, if \( Ba^{2+} \) concentration in the original brine is equal to or higher than \( SO_4^{2-} \), the anionic solution is prepared with only reagents R3 and R1, eq. 28 and 29. In this calculation, it is assumed that \( V_{\text{cat}} = V_{\text{ani}}. \)

\[ V_{R3} = \frac{1}{C_{SO_4^{2-}}^{\text{Stock}}} \times \left( 4 \times 10^6 \times MW_{Ba^{2+}} \times MW_{SO_4^{2-}} \times \left( \frac{10^{SI_{\text{Barite}}} \cdot K_{sp(Barite)}}{\gamma_{Ba^{2+}} \cdot \gamma_{SO_4^{2-}}^*} \right)^{0.5} \right) \left( C_{Ba^{2+}}^{\text{Brine}} \gamma_f + C_{Ba^{2+}}^{\text{Stock}} \gamma_f V_{R2} \right) \]  

and if \( V_{R3} < 0 \), then \( V_{R3} = 0 \)

\[ V_{R3} \ (L): \] Volume of reagent R3 to be added.
\( C_{SO_4^{2-}}^{\text{Stock}} \) \( (mg/L) \): Concentration of \( SO_4^{2-} \) in reagent R3; \( C_{SO_4^{2-}}^{\text{Stock}} = 10,000 \, mg/L \) in this example.

\( MW_{SO_4^{2-}} \) \( (g/mol) \): Molecular weight of \( SO_4^{2-} \); \( MW_{SO_4^{2-}} = 96.06 \, g/mol \).

\( V_{\text{ani}} \) \( (L) \): Volume of anionic solution.

\( C_{SO_4^{2-}}^{\text{Brine}} \) \( (mg/L) \): Concentration of \( SO_4^{2-} \) in the field brine.

\[ V_{R1(ani)} = V_{\text{ani}} - V_{R3} \] (29)

\[ V_{R1(ani)} \] \( (L) \): Volume of reagent R1 to be added into anionic solution.

In the case of \( Ba^{2+} \) concentration (in \( mol/L \)) in the field brine is smaller than \( SO_4^{2-} \) concentration, the procedure is slightly changed. Filtration and scale inhibitor concentration estimation are the same as before. Anionic solution is made of field brine, R4, R3 and R1 and their volumes are respectively calculated by eq. 30, 25, 31 and 32 for a 50 ml anionic solution preparation.

\[ V_f = \frac{2 \times C_{\text{inh}}^{\text{added}} V_{\text{ani}}}{C_{\text{from}}^{\text{estimated}}} \] (30)

\[ V_{R3} = \frac{1}{C_{SO_4^{2-}}^{\text{Stock}}} \times \left( 2 \times 10^3 \times MW_{SO_4^{2-}} \left( \frac{10^{S_{\text{Barite}}} K_{\text{Barite}}}{\gamma_{Ba^{2+}} \gamma_{SO_4^{2-}}} \right)^{0.5}DV_{\text{ani}} - C_{SO_4^{2-}}^{\text{Brine}} V_f \right) \] (31)

and if \( V_{R3} < 0 \), then \( V_{R3} = 0 \)

\[ V_{R2(ani)} = V_{\text{ani}} - V_f - V_{R4} - V_{R3} \] (32)

Cationic solution contains only R2 and R1 reagents, and their volumes are calculated with eq. 33 and 34 for a 50 ml cationic solution.

\[ V_{R2} = \frac{1}{C_{Ba^{2+}}^{\text{Stock}}} \times \left( 4 \times 10^6 \times MW_{Ba^{2+}} \times MW_{SO_4^{2-}} \left( \frac{10^{S_{\text{Barite}}} K_{\text{Barite}}}{\gamma_{Ba^{2+}} \gamma_{SO_4^{2-}}} \right) V_{\text{ani}} \right) \frac{1}{C_{SO_4^{2-}}^{\text{Stock}} + C_{SO_4^{2-}}^{\text{Stock}} V_{R3}} D^2 V_{\text{cat}} - C_{Ba^{2+}}^{\text{Brine}} V_f \] (33)

and if \( V_{R2} < 0 \), then \( V_{R2} = 0 \)

\[ V_{R2(ani)} = V_{\text{cat}} - V_{R2} \] (34)
Record the dilution factor as DF,

$$DF = \frac{C_{f \text{ estimated}}}{C_{\text{inh added}}}$$

(35)

The prepared cationic and anionic solutions with field brine are referred as CF and AF, respectively. Similarly, another set of cationic and anionic solutions is prepared with simulated brine instead of field brine by following the same steps and exact solution volumes, and they are referred as CS and AS, respectively. These solutions are filtered with 0.45 µm cellulose acetate filters before use.

S (see Figure 25, 26) is prepared by mixing equal volumes of CF and AF. S contains $C_s$ mg/L scale inhibitor, and $C_s = C_f / DF$. Similarly, B (see Figure 25, 26) is prepared by mixing equal volumes of CS and AS. SS1 and SS2 are prepared by adding the reference scale inhibitor R5 into AF before mixing with CF at equal volume. The volumes of R5 in SS1 and SS2 are determined by eq. 36 and 37, respectively.

$$V_{R5(SS1)} = \frac{C_{\text{inh added}} \left( V_{\text{cat added}} + V_{\text{ani added}} \right)}{C_{R5}}$$

(36)

$V_{R5(SS1)}$: Volume of reagent R5 to be added into SS1.

$V_{\text{cat added}}$: Volume of cationic solution to be used; $V_{\text{cat added}} = 7 \text{ ml}$ is sufficient in this example.

$V_{\text{ani added}}$: Volume of anionic solution to be used; $V_{\text{ani added}} = 7 \text{ ml}$ is sufficient in this example.

$C_{R5}$: Concentration of reference scale inhibitor in reagent R5.

$$V_{R5(SS2)} = \frac{2 \times C_{\text{inh added}} \left( V_{\text{cat added}} + V_{\text{ani added}} \right)}{C_{R5}}$$

(37)

$V_{R5(SS2)}$: Volume of reagent R5 to be added into SS2.
3.1.2.3 Induction time detection and selection

B is prepared by pipetting 7 ml AS into a clean turbidity vial that contains a stir bar, and then pipetting 7 ml CS into the same vial. The time was recorded immediately following the mixing. Vigorously shake the vial for about 20 sec for complete mixing and insert the vial into the turbidity meter and record turbidity every 2 seconds. A stir plate is placed just below the turbidity meter for solution mixing (Figure 28). The recording is stopped once the turbidity reaches a few NTU, see Figure 25. The preparations of S, SS1 and SS2 are the same as B, except that AS and CS are replaced with AF and CF respectively and R5 addition. R5 is added into AF before adding CF.

![Image of turbidity meter and stir plate](image)

**Figure 28. The setup of turbidity meter and stir plate**

With recorded turbidity curves, there are a few steps to determine induction time that is the time when solution turbidity start to increase. The method of induction time determination is developed based on trial and error on experimental data of this study, and it works for most turbidity data.

First, the turbidity curve is smoothed with a modified running median smooth method (Velleman 1980). Choose the median among every 19 data, as in eq. 38.
\[ y_k = \text{median}[x_{k-9}, x_{k-8}, \ldots, x_{k-1}, x_k, x_{k+1}, \ldots, x_{k+9}], 10 \leq k \leq (n-9). \] (38)

The \( n \) in the equation is the number of total turbidity data points. The medians are calculated as in eq. 39.

\[ z_k = \frac{1}{8} y_{k-2} + \frac{1}{4} y_{k-1} + \frac{1}{4} y_k + \frac{1}{4} y_{k+1} + \frac{1}{8} y_{k+2}, 12 \leq k \leq (n-11) \] (39)

The \( z_k \) (NTU) is the final smoothed turbidity value (Figure 29). Second, select the turbidity data points \( (z_k) \) that are in the range of minimum \( z_k \) to minimum + 0.06 NTU and calculate the average value \( (z_{ave}) \). From experience, the range of minimum \( z_k \) to minimum + 0.06 NTU can represent the background turbidity. Last, induction time equals to the time when turbidity is higher than \( z_{ave} \) by 0.1 NTU. Following the above three steps, the induction times of B \( (t_0) \), S \( (t_S) \), SS1 \( (t_{SS1}) \) and SS2 \( (t_{SS2}) \) are determined sequentially. Figure 30 shows smoothed turbidity curves and induction times of four turbidity curves shown in Figure 25.
Figure 29. Original turbidity curve and smoothed turbidity curve of S (S is shown in Figure 25)

Figure 30. Smoothed turbidity curves and induction times of four solutions, B, S, SS1 and SS2
3.1.2.4 Scale inhibitor concentration calculation

The calculation details have been described in the above overview of the assay method. This is a brief summary. First, fitting three points (0.0, log \(t_S\)), (0.1 mg/L, log \(t_{SS1}\)), and (0.2 mg/L, log \(t_{SS2}\)) with a linear equation. With fitted constants, slope \(b\) and intercept \(a\), the scale inhibitor concentration \(C_f\) in the field brine is calculated by eq. 20, 21 and 22. Standard deviation is calculated by eq. 23.

3.1.3 Other materials

3.1.3.1 Three synthetic brines and three field brines

Three synthetic brines, S1, S2 and S3, tap water (TW), and three field brines, F1, F2 and F3, were used to test the assay method in this research. Their compositions are shown in Table 2. Synthetic brine preparation procedure is the same as that of a simulated brine. As for scale inhibitor containing synthetic brine, scale inhibitor was added during brine preparation process. S1 and S2 are representatives of typical field brines. S1 is a simulated onshore field brine containing high \(\text{Ba}^{2+}\) and \(\text{Ca}^{2+}\). S2 is synthetic seawater with high \(\text{SO}_4^{2-}\) and represents offshore field brine. S3 was made of high concentration sodium chloride and potassium chloride. Tap water is from Rice University. F1, 2 and 3 are actual oil field brines.

3.1.3.2 Seven scale inhibitors

Seven scale inhibitors were used in this paper. They are sulfonated polycarboxylic acid polymer (SPCA), polyvinylsulfonate polymer (PVS), phosphorous incorporated maleic acid polymer (PMAC), phosphine polycarboxylic acid (PPCA), carboxy methyl inulin (CMI), diethylenetriamine penta(methylene phosphonic acid) (DTPMP) and nitrilo trimethylphosphonic acid (NTMP). These are frequently used scale inhibitors in the oil and gas industry (Kelland 2010).
DTPMP and NTMP are non-polymer scale inhibitors with phosphonate groups, and the other five are polymeric scale inhibitors with phosphonate, sulfonate and/or carboxylate groups.

3.2 Results and Discussion of the assay method

Three synthetic brines and three field brines were used to test the assay method. Seven different scale inhibitors were tested with synthetic brines, S1 and S2. Three tests were run with field brines. First, a known concentration of scale inhibitor was added to the field brine and then its concentration was analyzed with the assay method by ignoring the original scale inhibitor in the field brine. This is to check if the assay method works well in actual oil field brine. Second, the assay method was used to measure the original scale inhibitor concentrations of field brines. Thirdly, a known amount of reference inhibitor was added to the field brine to double the native inhibitor concentration and the assay method was run to determine if the assay was able to measure twice the inhibitor concentration, as confirmation. The assay method was examined at both low (e.g. 0.3 - 1 mg/L) and high concentration (e.g. 50 mg/L) detections.

3.2.1 Low concentration detection

3.2.1.1 Low concentration detection in synthetic brine

As mentioned in the introduction, low concentration measurement of scale inhibitors in field brine remains a big challenge which we hope to be solved by our assay method. The assay method was tested by seven different scale inhibitor detections at 0.3 and 1.0 mg/L in S1 and 0.5 and 1.0 mg/L in S2. The assay results are presented in Table 4.

As displayed in Table 4, detected concentrations are close to the real concentrations with low standard deviations. Some experiments were repeated, exemplified by 0.3 mg/L DTPMP in S1 and 1 mg/L SPCA in S2, and they all showed good reproducibility. No significant difference was
observed in detection errors and standard deviations among 0.3, 0.5 and 1.0 mg/L detections, although they come from different brine and their Ba/SO$_4$ ratios in the mixed solution vary from 0.04 to 1.21. This observation suggests that the assay method is tolerant to distinct brine and varied Ba/SO$_4$ ratio. Besides, the detection results of polymer and non-polymer scale inhibitors have no significant difference, which demonstrates that the assay method works equally well for both polymer and non-polymer scale inhibitor concentration detection.

**Table 4. The detection results of seven scale inhibitors in two synthetic brines, S1 and S2 at low concentrations**

<table>
<thead>
<tr>
<th>Brine</th>
<th>S1</th>
<th>S2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prepared concentration (mg/L)</td>
<td>0.3</td>
</tr>
<tr>
<td>SPCA</td>
<td>0.35±0.05</td>
<td>1.00±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.29±0.17</td>
</tr>
<tr>
<td>PVS</td>
<td>0.22±0.07</td>
<td>1.26±0.37</td>
</tr>
<tr>
<td>PMAC</td>
<td>0.40±0.03</td>
<td>1.16±0.25</td>
</tr>
<tr>
<td>PPCA</td>
<td>0.41±0.04</td>
<td>1.19±0.15</td>
</tr>
<tr>
<td>CMI</td>
<td>0.40±0.07</td>
<td>0.69±0.01</td>
</tr>
<tr>
<td>DTPMP</td>
<td>0.28±0.03</td>
<td>0.95±0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30±0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTMP</td>
<td>0.22±0.07</td>
<td>1.03±0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>0.32±0.04</td>
<td>1.07±0.16</td>
</tr>
</tbody>
</table>

From experimental results on Table 4, the three P-free scale inhibitors, SPCA, PVS and CMI, were successfully detected by the assay method at low concentrations (0.3 - 1.0 mg/L) in S1 and S2 brines. Their results are quite reasonable and reproducible with low standard deviations.

CMI, a new “green” scale inhibitor, contains only C, hydrogen (H) and oxygen (O) elements, which makes it difficult for ordinary analysis methods to detect. To be detectable, P (Graham et
al. 2010) or fluorescence (Fuller et al. 2011) was often tagged on these C, H and O composed scale inhibitors, for example, PMAC. However, considering that the different fractions of poly-disperse scale inhibitors retains in the reservoir rock, accurate detection of P or fluorescence does not necessarily indicates accurate measurement of effective scale inhibitor concentration (Graham et al. 2010). Besides, P content in P tagged scale inhibitor is often less than 0.5%, which makes it more difficult to detect low concentration scale inhibitors (Graham et al. 2010). The assay method, nevertheless, can avoid those problems and detect the effective scale inhibitor concentration directly, as illustrated in Table 4 for PMAC.

3.2.1.2 Low concentration detection in tap water (TW)

In addition to low concentration scale inhibitor detection in synthetic brines, 0.3 and 1 mg/L PPCA in TW were also determined by assay method. TW is the normally used water in a cooling water system and PPCA is a typical acrylic acid polymer scale inhibitor that are popular in cooling water systems (Zeng and Yan; Brown and Chen 1990). The detection results are shown in Table 5. The detected 1.06 and 0.95 mg/L PPCA are very close to the actual PPCA concentration, 1.0 mg/L. But there are relatively large errors in 0.3 mg/L PPCA detection, which may due to storage and adsorption to containers. More tests will be done to find out the actual reasons. While, in comparison with synthetic brine, the standard deviations of all detections in TW are very low, which is probably because TW composition is much simpler and result in less interferences during inhibitor detection.
Table 5. The detection results of scale inhibitor PPCA in TW at low concentrations

<table>
<thead>
<tr>
<th>Salt solution</th>
<th>TW (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared concentration (mg/L)</td>
<td>0.3</td>
</tr>
<tr>
<td>PPCA</td>
<td>0.21±0.00</td>
</tr>
<tr>
<td></td>
<td>0.19±0.00</td>
</tr>
</tbody>
</table>

3.2.2 Field brine detection

3.2.2.1 Known added scale inhibitor detection in three field brine

Three oil field brines, F1, F2, and F3, were used to test the assay method. 1.0, 5.0 and 2.5 mg/L PVS was added into F1, F2, and F3 and the assay method detected the added scale inhibitor concentrations. In order to ignore the original scale inhibitors in the field brine, field brine itself was used as simulated brine to prepare CS and AS solutions. The detection results are displayed in Table 6. Detected PVS concentrations are close to the added concentrations, especially 2.5 and 5.0 mg/L detection in F2 and F3 respectively. Observed standard deviations are not high. Overall, this result indicates that the assay method works for actual field brine’s scale inhibitor detection as well.

Table 6. The detection results of extra added scale inhibitor in three field brine

<table>
<thead>
<tr>
<th>Salt solution</th>
<th>F1 (mg/L)</th>
<th>F2 (mg/L)</th>
<th>F3 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared concentration (mg/L)</td>
<td>1.0</td>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>PVS</td>
<td>0.75±0.09</td>
<td>4.33±0.70</td>
<td>2.69±0.15</td>
</tr>
</tbody>
</table>

3.2.2.2 Scale inhibitor concentration detections in three field brine

The assay method was used to detect actual scale inhibitor concentrations in three field brines, separately. Neither scale inhibitor types nor concentrations in these three field brines were known,
so PVS and NTMP were selected as reference scale inhibitors for R5 reagents preparation and assay detection. The reason for selecting PVS and NTMP is that they have known chemical structures and are available as reagent grade material from chemical suppliers. Table 7 showed the scale inhibitor concentrations assayed as NTMP or PVS in these three field brines. All three brines contain trace concentrations of scale inhibitors.

**Table 7. Three field brine scale inhibitor concentration detection and confirmation results**

<table>
<thead>
<tr>
<th>Brine</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale inhibitor</td>
<td>PVS</td>
<td>PVS</td>
<td>PVS</td>
<td>NTMP</td>
</tr>
<tr>
<td>C_i (mg/L)</td>
<td>0.37±0.03</td>
<td>0.81±0.12</td>
<td>1.94±0.38</td>
<td>3.68±0.56</td>
</tr>
<tr>
<td>C_a (mg/L)</td>
<td>0.5</td>
<td>1</td>
<td>2.5</td>
<td>4</td>
</tr>
<tr>
<td>C_t (mg/L)</td>
<td>0.87</td>
<td>1.81</td>
<td>4.44</td>
<td>7.68</td>
</tr>
<tr>
<td>C_dt (mg/L)</td>
<td>0.92±0</td>
<td>1.83±0.22</td>
<td>6.34±0.85</td>
<td>8.12±1.01</td>
</tr>
</tbody>
</table>

\( ^{a}_{ \text{C}_i \text{, initial detected scale inhibitor concentration; C}_a \text{, added scale inhibitor concentration; C}_t \text{, the sum of initially detected and added scale inhibitor concentrations; C}_dt \text{, detected total scale inhibitor concentration.} \)

**3.2.2.3 Scale inhibitor detection confirmations**

To confirm the assay results, an equal quantity of scale inhibitor was added into field brine to double the field brine scale inhibitor concentration and then the assay method was used to analyze the total concentrations of scale inhibitors. If the detected total scale inhibitor concentration (C_dt) equals to the sum (C_t) of initial detected scale inhibitor concentration (C_i) and the added scale inhibitor concentration (C_a) (i.e. \( C_{dt} = C_t = C_i + C_a \)), then it might be assumed that the detected EICs were accurate. If \( C_{dt} \neq C_t \) with a significant difference, the detected EICs were probably not accurate. The result are shown in Table 7. For field brine F1, F2 and F3, most C_dt matched with C_i (except F3 detection with PVS as reference inhibitor), which indicates that assay method successfully detected scale inhibitor concentrations in real produced water. For F3, a relative difference of 43.2% between C_dt and C_i was observed when PVS was used as reference inhibitor.
This relative difference is too large compared with those of other brines that are typically less than 9.1%. The possible reason for the big difference may be that PVS and the original scale inhibitor may have synergistic effects on inhibiting barite formation, since detected total concentration is significantly larger than theoretical total concentration (Persinski et al. 1987). But this possible explanation needs to be further investigated. For now, we recommend using the same or at least similar scale inhibitor as reference scale inhibitor for scale inhibitor concentration determination by the assay method.

Although F1 and F3 contains small amount of oil emulsions in the brine before filtration, their scale inhibitor assays were not affected. Commonly existing organic compounds in field brine may interfere with barite precipitation. Such interfering effects on the assay method and more field brine should be tested in the future research.

3.2.3 High concentration detection

3.2.3.1 High concentration detection in synthetic brine, field brine and TW

Besides low concentrations, the assay method was also tested at high concentrations. 50 mg/L PVS was added into S3, F2 and TW and each brine was detected three times by the assay method. The detected results are presented in Table 8. The average value of three detections is close to the prepared concentration in all three solutions.
Table 8. Detection results of 50 mg/L PVS in S3, F2 and TW

<table>
<thead>
<tr>
<th>Prepared concentration (mg/L)</th>
<th>S3</th>
<th>F2</th>
<th>TW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PVS</td>
<td>61.29±10.88</td>
<td>40.73±7.55</td>
<td>42.84±2.62</td>
</tr>
<tr>
<td></td>
<td>44.05±6.22</td>
<td>38.83±0.08</td>
<td>41.35±0.19</td>
</tr>
<tr>
<td></td>
<td>51.44±11.02</td>
<td>53.28±13.02</td>
<td>56.04±0.26</td>
</tr>
<tr>
<td>Average</td>
<td>53.93±6.54</td>
<td>41.6±6.50</td>
<td>46.76±1.02</td>
</tr>
</tbody>
</table>

3.2.3.2 High concentration detection with a modified assay method

DI water was used to replace the high ionic strength solution R1 in cationic and anionic solution preparations. This is referred to as a “modified assay method”. Consequently, for 50 mg/L inhibitor detection, the TDS of S or B becomes circa 120 mg/L, while the original mixed solution’s TDS is over 80,000 mg/L. 50 mg/L PVS, CMI and PPCA in S1 and 50 mg/L PPCA in TW were detected with the modified assay method. S1 was used in this experiment.

Table 9 displays the results of high scale inhibitor concentration detection with the modified assay method. The detection accuracy improves. Each single detection result is close to the real concentration, with relative errors of less than 10% in most cases and low standard deviations. There is no significant difference among the detected results of PVS, CMI and PPCA.

Comparing the detection results of the original and modified assay method, the modified one has higher accuracy and reproducibility and lower standard deviation. One possible reason could be less ion interactions in the low TDS solution (Benton et al. 1993). Replacing R1 with DI water could possibly improve the accuracy and reproducibility of the assay method. More testing will be conducted to confirm the generality of this observation. However, DI water dilution will decrease the TDS of S solution so that Ba$^{2+}$ and SO$_4^{2-}$ activity coefficients change significantly with TDS.
(Figure 31) (Kan et al. 2005). The Equation, 

\[ \log_{10} \text{activity coefficient} = A_0 + A_1 \cdot TDS^{0.5} + A_2 \cdot TDS^{1.0} + A_3 \cdot TDS^{1.5} + A_4 \cdot TDS^{2.0} \]

is a simplified equation for calculation of activity coefficients of \( \text{Ba}^{2+}, \text{SO}_4^{2-} \) and their product. At low TDS area, it is difficult to calculate barite SI accurately. Also, ionic strength (IS) is closely related to TDS, so minor IS may affect induction time. In the modified assay method, IS of S and B vary significantly depending on the composition of the detected brine and inhibitor concentration. Thereby, the replacement of R1 by DI water in the assay method requires more consideration.

Table 9. Detection results of 50 mg/L PVS, CMI and PPCA in S1 and TW by the modified assay method

<table>
<thead>
<tr>
<th>Brine</th>
<th>S1</th>
<th>TW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared concentration (mg/L)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>PPCA</td>
<td>50.69±6.79</td>
<td>44.57±4.15</td>
</tr>
<tr>
<td></td>
<td>56.66±2.30</td>
<td>46.06±4.29</td>
</tr>
<tr>
<td>PVS</td>
<td>49.48±0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.73±7.45</td>
<td></td>
</tr>
<tr>
<td>CMI</td>
<td>47.36±5.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>47.21±4.15</td>
<td></td>
</tr>
</tbody>
</table>
Figure 31. Activity coefficients of Ba$^{2+}$, SO$_4^{2-}$ and their product change with TDS and their trend lines

3.2.4 Application of the assay method in squeeze treatment

The assay method has been applied in scale inhibitor detection in squeeze treatment (Yan et al. 2014). As mentioned in the section of literature review and background, it is hard for ICP to detect inhibitor in the long term of squeeze treatment because of low concentration, even for phosphorus contained inhibitors. Yan et al. used the assay method to detect PPCA under 5 mg/L (Figure 32) and phosphonated carboxylate polymer under 1 mg/L (Figure 33) in the returning brine of squeeze treatment (Yan et al. 2014). Yan et al. also compared the PPCA concentrations detected by ICP and the assay method for several solutions in which PPCA are above 5 mg/L, and the differences were less than 30% (Yan et al. 2014). The assay method can therefore be used. Accurate low inhibitor concentration detection by the assay method not only help checking if the remaining inhibitor in the returning solution is enough for scale inhibition, but also help squeeze treatment model development.
Figure 32. “PPCA return concentration for inhibitor with and without zinc in packed column experiment in log-linear scale” (Yan et al. 2014)

Figure 33. “Phosphonated carboxylate polymer return concentration for inhibitor with and without zinc at high (left) and low (right) concentration range” (Yan et al. 2014)

3.2.5 Comparison of laser and turbidity meter

A laser-based apparatus was recently developed to detect the onset of precipitation as a possible replacement for the turbidity meter (Yan et al. 2014).
Figure 34 shows the laser apparatus, including a red laser, a set of convex and concave lens and a photo-detector (Yan et al. 2014). As stated in Yan et al.’s paper (Yan et al. 2014), “The photo-detector has a wide wavelength range with peak sensitivity at 960 nm. A set of convex and concave lens controls the beam diameter so that it can intercept more particles and increase the sensitivity. Temperature and mixing are precisely controlled by an external water bath and magnetic stir plate respectively. The photo-current output is constant when the laser is shining through a clear solution prior to scale formation. Once scale occurs, the beam is scattered by scale particles, which cause a decrease in photo-current.” Yan et al. used this laser method to study barite nucleation kinetics (Yan et al. 2014).

Figure 34. “Diagram (left) and picture (right) of laser apparatus” (Yan et al. 2014)

As shown in Figure 35, using this apparatus, the log $t_{ind}/t_0$ of barite vs. SPCA concentration has a good linear relationship (Yan 2013). They also compared induction time detection among red laser, green laser and turbidity meter (Figure 36). Red laser and turbidity meter detected induction times are close and the generated slope values are similar, which indicates that red laser and turbidity meter have similar sensitivity in the measurement of solution turbidity (Yan et al. 2014). Green laser measured induction times are shorter and the generated slope is smaller than that using the
turbidity meter, which may suggest that green laser is able to detect earlier nuclei and be more sensitive in scale formation detection (Yan et al. 2014). The laser method has two advantages over turbidity meter. First, temperature, pressure and oxygen level can be customized and controlled (Yan et al. 2014). Temperature is an important factor of induction time in the assay method. Second, a set of laser apparatus costs much less than a turbidity meter. Considering these advantages, the replacement of turbidity meter with laser method would be a significant improvement to the assay method developed herein.

![Image](image.png)

Figure 35. The linear relationship between inhibitor concentration and the logarithm of barite induction time that detected by laser method (Yan 2013)
Chapter 4. Improved Assay Method

Based on the above results, the assay method has been proven to be able to detect scale inhibitor concentrations in the oil field brine and tap water. But there is one drawback in the assay method, the preparation of simulated brine. Not only simulated brine preparation is troublesome, but also it is hard to assemble a same composed brine, which may cause detection error due to field brine complicated composition. Considering that, the author revised the assay method by omitting simulated brine preparation, and the revised assay method is called, “Improved Assay Method”.

4.1 Improved assay method description

4.1.1 Principle of the improved assay method

The simulated brine is theoretically the same as the field brine without scale inhibitors. Simulated brine prepared B (scale inhibitor free) has induction time $t_0$ that is essential in inhibitor concentration $C_s$ calculation in eq. 21. Without point $(0, \log t_0)$, one way to calculate $C_s$ is to have

Figure 36. “Comparison among red laser, green laser and turbidity meter” (Yan et al. 2014).
point \((2C_s, \log t_{TS})\). The point \((2C_s, \log t_{TS})\) comes from a solution called “twofold-sample” (TS) that contains \(2C_s\) mg/L inhibitor and has induction time of \(t_{TS}\). TS is prepared by diluting field brine with half of DF times and preparation details will be shown in the procedure section. The three data points \((0.0, \log t_S)\), \((0.1\) mg/L, \(\log t_{SS1})\), and \((0.2\) mg/L, \(\log t_{SS2})\) can form eq. 20 with fitted slope \(b\) \((L/mg)\) and intercept \(a\).

\[
\log t_{inh} = b \times (C_{inh} - C_s) + a 
\]

With the point \((2C_s, \log t_{TS})\), inhibitor calculation equation becomes,

\[
C_s = \frac{\log t_{TS} - a}{b} 
\]

Due to the above change in the assay method, the limit of quantification increases from 0.3 mg/L to 0.5 mg/L, but still in the same of magnitude.

4.1.2 Procedure of the improved assay method and related materials

The updated expert program can provide detailed guidance and procedure for the improved assay method.

4.1.2.1 Required reagents preparation

The preparation of five required reagents are the same, as shown in Table 3.

4.1.2.2 Dilution of field brine

The dilution process is composed of preparing the cationic and anionic solutions. The preparation of the cationic and anionic solutions differs and is dependent on the \(Ba^{2+}\) and \(SO_4^{2-}\) concentrations in the field brine. Field brine is diluted two different times and used to prepare two pairs of cationic and anionic solutions to assemble S and TS. One pair of cationic and anionic solutions for S preparation are respectively named CF and AF, same as before. The other pair for TS preparation
are named CT and AT, respectively. S and TS have same barite SI of 2.1 and same molar Ba/SO$_4$ ratio as close to 1.0 as possible.

If Ba$^{2+}$ concentration (in mol/L) in the field brine is equal to or higher than SO$_4^{2-}$, the procedure is as follows. Filter the field brine with 0.45 µm cellulose acetate filters to remove impurities. The field brine has $C_f$ mg/L scale inhibitor. Scale inhibitor concentration is estimated as $C_f^{estimated}$ mg/L and diluted to 0.1 mg/L (for S) or 0.2 mg/L (for TS). If the estimated scale inhibitor concentration is greater than 100 mg/L, the solution should be diluted by two to reduce error in dilution. Both CF and CT are made from four solutions, field brine, R1, R2 and R4, but with different composition ratios. For CF or CT, the total volume, $V_{CF}$ or $V_{CD}$, is arbitrary, but generally 0.05 L is sufficient.

First, for CT preparation, the procedure for calculating $V_{cat(CT)}$ of CT and CT composition is outline in eq. 41 to 44:

$$V_f(CT) = \frac{4 \times C_{inh}^{added} V_{CT}}{C_f^{estimated}}$$

(41)

$V_f(CT)$ (L): Volume of field brine to be used in CT preparation.

The factor “4”: accounts for two times of $C_{inh}^{added}$ and the equal volume mixing of cationic and anionic solutions.

$V_{CT}$ (L): The volume of cationic solution CT.

$$V_{R4(CT)} = \frac{C_{acid} V_f(CT)}{C_{R4}}$$

(42)

$V_{R4(CT)}$ (L): Volume of reagent R4 to be added in CT.
\[ V_{R2(CT)} = \frac{1}{C_{Stock}^{Ba^{2+}}} \times \left( 2 \times 10^3 \times MW_{Ba^{2+}} \times \frac{10^{SI_{Brine}} K_{sp(Barite)}}{\gamma_{Ba^{2+}} \gamma_{SO_4^{2-}}} \right)^{0.5} DV_{CT} - C_{Brine}^{Ba^{2+}} V_{f(CT)} \] 

and if \( V_{R2(CT)} < 0 \), then \( V_{R2(CT)} = 0 \)

\[ D = (kg \text{ water} / \text{liter of solution}) = 1 - 3.60 \times 10^7 \times TDS (mg/L) \]  
(Kan et al. 2005)

\( V_{R2(CT)} \) (L): Volume of reagent R2 to be added in CT.

\[ V_{R1(CT)} = V_{CT} - V_{f(CT)} - V_{R4(CT)} - V_{R2(CT)} \]  
(44)

\( V_{R1(CT)} \) (L): Volume of reagent R1 to be added in CT.

Again, if \( Ba^{2+} \) concentration in the original brine is equal to or higher than \( SO_4^{2-} \), AT is prepared with only reagents R3 and R1, eq. 45 and 46.

\[ V_{R3(AT)} = \frac{1}{C_{Stock}^{SO_4^{2-}}} \times \left( 4 \times 10^6 \times MW_{Ba^{2+}} \times MW_{SO_4^{2-}} \times \frac{10^{SI_{Brine}} K_{sp(Barite)}}{\gamma_{Ba^{2+}} \gamma_{SO_4^{2-}}} \right) DV_{AT} - C_{Brine}^{SO_4^{2-}} V_{f(CT)} \] 

and if \( V_{R3(AT)} < 0 \), then \( V_{R3(AT)} = 0 \)

\( V_{R3(AT)} \) (L): Volume of reagent R3 to be added in AT.

\( V_{AT} \) (L): Volume of anionic solution AT.

\[ V_{R1(AT)} = V_{AT} - V_{R3(AT)} \]  
(46)

\( V_{R1(AT)} \) (L): Volume of reagent R1 to be added into AT.

Second, CF is prepared by the below procedure and calculation eq. 47 to 50.

\[ V_{f(CF)} = \frac{2 \times C_{\text{added}}^{inh} V_{CF}}{C_{estimated}^{f}} \]  
(47)

\( V_{f(CF)} \) (L): Volume of field brine to be used in CF preparation.

The factor “2”: accounts for the equal volume mixing of cationic and anionic solutions.

\( V_{CF} \) (L): The volume of cationic solution CF.
\[ V_{R4(CF)} = \frac{C_{\text{acid}} V_{f(CF)}}{C_{R4}} \]  

\[ V_{R4(CF)} (L) \]: Volume of reagent R4 to be added in CF.

\[ V_{R2(CF)} = \frac{1}{C_{\text{Stock}}} \times \left( 2 \times 10^3 \times MW_{Ba^{2+}} \left( \frac{10^{S_{\text{brine}} K_{sp(Ba)} R}}{\gamma_{Ba^{2+}}/\gamma_{SO_4^{2-}}} \right)^{0.5} \right) \]
\[ DV_{CF} - C_{\text{Brine}} V_{f(CF)} \]  

\[ R = \left[ \frac{Ba^{2+}}{SO_4^{2-}} \right] = \left( C_{\text{Stock}} \frac{V_{f(CF)}}{V_{R2(CF)}} \right) \frac{V_{CF} MW_{SO_4}}{V_{CT} MW_{Ba}} \]

and if \( V_{R2(CF)} < 0 \), then \( V_{R2(CF)} = 0 \)

49 is to make sure S and TS have same Ba/\( SO_4 \) ratio.

\[ V_{R2(CF)} (L) \]: Volume of reagent R2 to be added in CF.

\[ V_{R1(CF)} = V_{CF} - V_{f(CF)} - V_{R4(CF)} - V_{R2(CF)} \]  

\[ V_{R1(CF)} (L) \]: Volume of reagent R1 to be added in CF.

AF preparation is shown in eq. 51 and 52.

\[ V_{R3(AF)} = \frac{1}{C_{\text{SO}_4^{2-}}} \times \left( 4 \times 10^6 \times MW_{Ba^{2+}} \times MW_{SO_4} \left( \frac{10^{S_{\text{brine}} K_{sp(Ba)} V_{CF}}}{\gamma_{Ba^{2+}}/\gamma_{SO_4^{2-}}} \left( C_{\text{Brine}} V_{f(CF)} + C_{\text{Stock}} V_{R3(AF)} \right) \right) \right) \]
\[ D^2V_{AF} - C_{\text{Brine}} V_{f(CF)} \]  

\[ \text{and if } V_{R3(AF)} < 0, \text{ then } V_{R3(AF)} = 0 \]

\[ V_{R3(AF)} (L) \]: Volume of reagent R3 to be added in AF.

\[ V_{AF} (L) \]: Volume of anionic solution AF.

\[ V_{R1(AF)} = V_{AF} - V_{R3(AF)} \]  

\[ V_{R1(AF)} (L) \]: Volume of reagent R1 to be added into AF.

In the case of Ba\(^{2+}\) concentration (in mol/L) in the field brine is smaller than SO\(_4^{2-}\) concentration, the procedure is slightly changed. Filtration and scale inhibitor concentration estimation are the
same as before. AF and AT are made from field brine, R1, R3 and R4, with different composition ratios.

First, for AT, the volumes of field brine, R4, R3 and R1 are respectively calculated by eq. 53, 54, 55 and 56.

\[ V_{f(AT)} = \frac{4 \times C_{\text{inh}}^{\text{added}} V_{AT}}{C_f^{\text{estimated}}} \]  \hspace{1cm} (53)

\[ V_{f(AT)} (L): \text{Volume of field brine to be used in AT.} \]

\[ V_{R4(AT)} = \frac{C_{\text{acid}} V_{f(AT)}}{C_{R4}} \]  \hspace{1cm} (54)

\[ V_{R4(AT)} (L): \text{Volume of reagent R4 to be added in AT.} \]

\[ V_{R3(AT)} = \frac{1}{C_{\text{Stock}}^{\text{SO}_2^2}} \times \left( 2 \times 10^3 \times MW_{SO_2^2} \left( \frac{10^{4S_{\text{ave}}} K_{\text{sp}(Barite)}}{\gamma_{Ba^2+} \gamma_{SO_2^2^-}} \right)^{0.5} \left( DV_{AT} - c^{\text{Brine}}_{SO_2^2^-} V_{f(AT)} \right) \right) \]  \hspace{1cm} (55)

\[ \text{and if } V_{R3(AT)} < 0, \text{then } V_{R3(AT)} = 0 \]

\[ V_{R1(AT)} = V_{AD} - V_{f(AT)} - V_{R4(AT)} - V_{R3(AT)} \]  \hspace{1cm} (56)

CT is composed of only R2 and R1 reagents, and their volumes are calculated by eq. 57 and 58, respectively.

\[ V_{R2(CT)} = \frac{1}{C_{\text{Stock}}^{\text{Ba}_2^2+}} \times \left( 4 \times 10^6 \times MW_{Ba^2+} \times MW_{SO_2^2^-} \frac{10^{4S_{\text{ave}}} K_{\text{sp}(Barite)} V_{AT}}{\gamma_{Ba^2+} \gamma_{SO_2^2^-} (C_{\text{Stock}}^{\text{Brine}} V_{f(AT)} + C_{\text{Stock}}^{\text{SO}_2^2} V_{R3(AT)})} \right) D^2 V_{CT} - c^{\text{Brine}}_{Ba^2+} V_{f(AT)} \]  \hspace{1cm} (57)

\[ \text{and if } V_{R2(CT)} < 0, \text{then } V_{R2(CT)} = 0 \]

\[ V_{R1(CT)} = V_{CT} - V_{R2(CT)} \]  \hspace{1cm} (58)

Second, AF is prepared by following below procedure and calculation eq. 59 to 62.
\[ V_{f(AF)} = \frac{2 \times C_{\text{inh}}^{\text{added}} V_{AF}}{C_f} \] (59)

\( V_{f(AF)} (L) \): Volume of field brine to be used in AF.

\[ V_{R4(AF)} = \frac{C_{\text{acid}} V_{f(AF)}}{C_{R4}} \] (60)

\( V_{R4(AF)} (L) \): Volume of reagent R4 to be added in AF.

\[ V_{R3(AF)} = \frac{1}{C_{SO_4_{2-}}^{\text{Stock}}} \times \left( 2 \times 10^3 \times MW_{SO_4^{2-}} \left( \frac{10^{S_{\text{brine}} K_{sp}(\text{Barite})}}{R Bal^2 \gamma_{SO_4^{2-}}^{\gamma}} \right)^{0.5} D_{AF} - C_{SO_4_{2-}}^{\text{Brine}} V_{f(AF)} \right) \] (61)

and if \( V_{R3(AF)} < 0, \) then \( V_{R3(AF)} = 0 \)

\[ R = \left[ \frac{Ba^{2+}}{SO_4^{2-}} \right] = \left( \frac{C_{Ba}^{\text{Brine}} V_{f(AF)} + C_{SO_4_{2-}}^{\text{Stock}} V_{R2(CT)}}{C_{SO_4_{2-}}^{\text{Brine}} V_{f(AF)} + C_{SO_4_{2-}}^{\text{Stock}} V_{R3(CT)}} \right) V_{AT} MW_{SO_4_{2-}} \] in eq. 61.

\[ V_{R1(AF)} = V_{AF} - V_{f(AF)} - V_{R4(AF)} - V_{R3(AF)} \] (62)

CF preparation is also composed of R2 and R1, and their volumes are calculated by eq. 63 and 64 respectively.

\[ V_{R2(CF)} = \frac{1}{C_{Ba^{2+}}^{\text{Stock}}} \times \left( 4 \times 10^6 \times MW_{Ba^{2+}} \times MW_{SO_4^{2-}} \left( \frac{10^{S_{\text{brine}} K_{sp}(\text{Barite})} V_{AF}}{R Bal^2 \gamma_{SO_4^{2-}}^{\gamma}} \right)^{0.5} D_{CF} - C_{Ba^{2+}}^{\text{Brine}} V_{f(AF)} \right) \] (63)

and if \( V_{R2(CF)} < 0, \) then \( V_{R2(CF)} = 0 \)

\[ V_{R1(CF)} = V_{CF} - V_{R2(CF)} \] (64)

Record dilution factor of S as DFs,

\[ DF_S = \frac{C_f^{\text{estimated}}}{C_{\text{inh}}^{\text{added}}} \] (65)

Record dilution factor of TS as DF_{TS}. 

\[ DF_{TS} = \frac{C_{\text{estimated}}}{2} = \frac{DF_S}{2} \]  

\[(66)\]

AF, AT, CF and CT solutions were filtered with 0.45 µm cellulose acetate filters before use.

S, SS1 and SS2 preparation procedure are exactly same as before. TS is prepared by mixing equal volumes of CT and AT, containing \( C_{TS} \) mg/L inhibitor. \( C_{TS} = \frac{C_f}{DF_{TS}} = 2\frac{C_f}{DF_S} = 2C_s \).

### 4.1.2.3 Induction time detection and selection

The procedure of induction time detection and selection are the same as the original assay method (Section 3.1.2.3.)

### 4.1.2.4 Scale inhibitor concentration calculation

The calculation details have been described in the principle of the improved assay method. This is a brief summary. First, fitting three points (0.0, \( \log t_s \)), (0.1 mg/L, \( \log t_{SS1} \)), and (0.2 mg/L, \( \log t_{SS2} \)) with a linear equation. With fitted constants, slope \( b \) and intercept \( a \), and point (\( 2C_s, \log t_{TS} \)) the scale inhibitor concentration \( C_f \) in the field brine is calculated by eq. 20 and 40. Standard deviation is calculated by eq. 23.

### 4.1.3 Other materials

#### 4.1.3.1 Changed S1 brine

To meet experiment requirements, synthetic brine S1 was slightly changed and changed S1 are named S1+Ca, S1+Sr, S1+Zn, and S1+Pb. Table 10 showed their compositions. These changed brines are made by dissolving appropriate amount of chloride salts of divalent cations (i.e. \( \text{CaCl}_2 \), \( \text{SrCl}_2 \), \( \text{ZnCl}_2 \) and \( \text{PbCl}_2 \)) solids with S1. S1+Ca contains extremely high \( \text{Ca}^{2+} \), 20,000 mg/L; S1+Sr has particular high \( \text{Sr}^{2+} \), 6,200 mg/L; S1+Zn and S1+Pb contain 35 mg/L \( \text{Zn}^{2+} \) and 18 mg/L \( \text{Pb}^{2+} \) respectively.
Table 10. Compositions of changed S1, S1+Ca and S1+Sr, S1+Zn and S1+Pb

<table>
<thead>
<tr>
<th>Components</th>
<th>S1+Ca</th>
<th>S1+Sr</th>
<th>S1+Zn</th>
<th>S1+Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺ (mg/L)</td>
<td>19872.0</td>
<td>19872.0</td>
<td>19872.0</td>
<td>19872.0</td>
</tr>
<tr>
<td>K⁺ (mg/L)</td>
<td>500.0</td>
<td>500.0</td>
<td>500.0</td>
<td>500.0</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>54.0</td>
<td>54.0</td>
<td>54.0</td>
<td>54.0</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>20,000.0</td>
<td>6500.0</td>
<td>6500.0</td>
<td>6500.0</td>
</tr>
<tr>
<td>Sr²⁺ (mg/L)</td>
<td>700.0</td>
<td>6,200.0</td>
<td>700.0</td>
<td>700.0</td>
</tr>
<tr>
<td>Ba²⁺ (mg/L)</td>
<td>550.0</td>
<td>550.0</td>
<td>550.0</td>
<td>550.0</td>
</tr>
<tr>
<td>Zn²⁺ (mg/L)</td>
<td>0.0</td>
<td>0.0</td>
<td>35.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pb²⁺ (mg/L)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Cl⁻ (mg/L)</td>
<td>67319.3</td>
<td>47888.8</td>
<td>43476.3</td>
<td>43444.5</td>
</tr>
<tr>
<td>HCO₃⁻ Alkalinity</td>
<td>281.0</td>
<td>281.0</td>
<td>281.0</td>
<td>281.0</td>
</tr>
<tr>
<td>(mg/L as HCO₃⁻)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scale Inhibitor</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>(mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>109276.3</td>
<td>81845.8</td>
<td>71968.3</td>
<td>71919.5</td>
</tr>
</tbody>
</table>

4.1.3.2 Artificial field brine

Artificial field brine is to mimic real field brine contaminated with crude oil and/or demulsifier that come from oil water separation process. S1 was selected to prepare artificial field brine and the preparation details is as follows.

70 ml S1 containing 0.5 mg/L PPCA was mixed with 20 ml three different crude oil, C1, C2 and C3, separately. After mixing overnight, 5 ml demulsifier was added into each mixed solution to separate brine from crude oil. With the help of centrifuge and demulsifier, mixed solution became two separate layers. Removed the upper layer oil and filtered the lower layer brine with cellulose acetate filters because brine were still contaminated with trace amounts of oil. Cellulose acetate is a hydrophilic material, so most oil can be removed by it. Finally, three artificial field brine were prepared and named SC1, SC2 and SC3 respectively.
4.2 Results and Discussion

4.2.1 Linear relationship confirmation

Although S and TS have same barite SI and same Ba/\text{SO}_4 ratio, their compositions are slightly different because field brine are diluted at different times with R1, especially in low concentration inhibitor detection when dilution factor is small.

\[
\text{Difference of cation} = \frac{[\text{cation}]}{DF_{TS}} - \frac{[\text{cation}]}{DF_S} = \frac{[\text{cation}]}{DF_S}, \quad (DF_{TS} = DF_S / 2) \quad (67)
\]

\text{Difference of cation: cation concentration difference in S and TS.}

\text{[cation]: cation concentration in the field brine.}

Previous research showed that some divalent cations that frequently appear in the field brine, such as Ca\textsuperscript{2+} and Sr\textsuperscript{2+}, may affect barite induction time, especially when they are at high concentrations (He 1995). It hence becomes necessary to identify whether or the degree to which different solution composition, especially different concentrations of divalent cations, affect barite induction time and the improved assay method detection. Supposing a field brine was diluted with R1 with three different dilution times by following the improved assay method procedure, the three different composed diluted solutions have the same barite SI = 2.1 and same Ba/\text{SO}_4 ratio, with 0.1, 0.2 and 0.3 mg/L inhibitor respectively. If the inhibitor concentrations of three dilution brines are perfectly linear to their corresponding barite induction time logarithms, different solution composition do not significantly affect barite induction time and the accuracy of the improved assay method. S1 contains high concentration Ca\textsuperscript{2+} and Sr\textsuperscript{2+}, as high as 6500 mg/L and 700 mg/L respectively, and it was selected as the test brine.

1 mg/L PPCA in S1 was diluted to 0.1, 0.2 and 0.3 mg/L by following the improved assay method procedure. The 0.1 and 0.2 mg/L PPCA diluted solutions is actually S and TS. The 0.3 mg/L PPCA
diluted solution was prepared by estimating inhibitor concentration as 0.33 mg/L and follow the procedure to prepare S. The compositions of three diluted solutions are shown on Table 11. The concentration differences of divalent cations between 0.1 and 0.3 mg/L diluted solution are 1300 mg/L for Ca$^{2+}$, 140 mg/L for Sr$^{2+}$ and 10.8 mg/L for Mg$^{2+}$. Experiment shows that inhibitor concentration is still linear to the logarithm of induction time (Figure 37), despite their solution compositions and divalent cation concentrations are different. This observation indicates that even if divalent cations affect induction time, the improved assay method can endure divalent cations differences between S and TS to a certain degree, for example 1300 mg/L Ca$^{2+}$ and 140 mg/L Sr$^{2+}$ differences, and keep the linear relationship and inhibitor detection accuracy.

**Table 11. Compositions of three diluted solutions from synthetic brine S1**

<table>
<thead>
<tr>
<th>Components</th>
<th>0.1 mg/L diluted solution</th>
<th>0.2 mg/L diluted solution</th>
<th>0.3 mg/L diluted solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ (mg/L)</td>
<td>33808.5</td>
<td>32260.1</td>
<td>30711.6</td>
</tr>
<tr>
<td>K$^+$ (mg/L)</td>
<td>472.1</td>
<td>475.2</td>
<td>478.3</td>
</tr>
<tr>
<td>Mg$^{2+}$ (mg/L)</td>
<td>5.4</td>
<td>10.8</td>
<td>16.2</td>
</tr>
<tr>
<td>Ca$^{2+}$ (mg/L)</td>
<td>650.0</td>
<td>1300.0</td>
<td>1950.0</td>
</tr>
<tr>
<td>Sr$^{2+}$ (mg/L)</td>
<td>70.0</td>
<td>140.0</td>
<td>210.0</td>
</tr>
<tr>
<td>Ba$^{2+}$ (mg/L)</td>
<td>166.2</td>
<td>166.4</td>
<td>166.7</td>
</tr>
<tr>
<td>Cl$^-$ (mg/L)</td>
<td>54388.4</td>
<td>53123.0</td>
<td>51857.6</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (mg/L)</td>
<td>116.1</td>
<td>116.1</td>
<td>116.1</td>
</tr>
<tr>
<td>Scale Inhibitor (mg/L)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>89478.4</td>
<td>87476.1</td>
<td>85473.9</td>
</tr>
</tbody>
</table>
4.2.2 Low concentration detection in synthetic brine

1 and 0.5 mg/L PPCA in S1 were measured by the improved assay method to test its accuracy of the new method. Table 12 shows the detection result. The improved assay method accurately detected PPCA concentration with good reproducibility. According to this experiment result, the improved assay method works equally well or even better than the original assay method, in spite of the potential interferences from divalent cations, which is consistent with the linear relationship confirmation experiment.

Moreover, according to USGS data about field brine (Survey 2002), Ca\(^{2+}\) concentration in S1 is much higher than the average (4896 mg/L) and mean (1921 mg/L) values of Ca\(^{2+}\), so does Sr\(^{2+}\). Also, the detected inhibitor concentration, 0.5 mg/L, is the limit of quantification, which correspond to the lowest dilution factor, only 5 times dilution for S and 2.5 times for TS. In such a case, divalent cation concentration differences between S and TS are the highest. But based on

Figure 37. The linear relationship of the logarithm of induction time and inhibitor concentration in S1
the detection results, the improved assay method accurately detected inhibitor concentration and was not interfered by other divalent cations.

In most actual situations, field brine contained divalent cations are not as much as S1 and inhibitor concentration is usually much higher than 0.5 mg/L, so divalent cations concentration differences between S and TS will be lower and their interference on the improved assay method will be less. Thereby, the improved assay method for inhibitor concentration detection should be reliable in most cases.

Table 12. Detection results of 0.5 and 1 mg/L PPCA in S1

<table>
<thead>
<tr>
<th>Brine</th>
<th>S1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared concentration (mg/L)</td>
<td>0.5</td>
</tr>
<tr>
<td>PPCA</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
</tr>
</tbody>
</table>

4.2.3 Low concentration detection in synthetic brine with extremely high divalent cations

To determine how much error the improved assay method would make if it is applied in inhibitor detection in such brine that contains extremely low concentration inhibitor (e.g. 0.5 mg/L) and extremely high concentration of divalent cations (e.g. 20,000 mg/L Ca\(^{2+}\) or 6,200 mg/L Sr\(^{2+}\)), the following experiments were conducted. 0.5 mg/L PPCA in S1+Ca that containing 20,000 mg/L Ca\(^{2+}\) and S1+Sr that containing 6,200 mg/L Sr\(^{2+}\) were separately detected by the improved assay method. The compositions of S1+Ca and S1+Sr are shown in Table 10.

The detection results are displayed in Table 13. Detected PPCA concentration is slightly higher than the prepared concentration. The obvious reason is that TS contains more Ca\(^{2+}\) or Sr\(^{2+}\) than S due to different dilution times, and high concentration Ca\(^{2+}\) or Sr\(^{2+}\) can prolong barite induction
time (He 1995). But the detection results (0.6 and 0.7 mg/L) are still acceptable in industry. As a matter of fact, seldom produced waters contain such high concentration Ca\(^{2+}\) (20,000 mg/L) or Sr\(^{2+}\) (6,200 mg/L) (Guerra et al. 2011), because such high concentration Ca\(^{2+}\) or Sr\(^{2+}\) is easy to precipitate with CO\(_3^{2-}\) or SO\(_4^{2-}\), most common divalent anions in produced water. Furthermore, if such extreme brine contains more than 0.5 mg/L inhibitor, divalent cation differences between S and TS will be less and the detect result will be more accurate. Therefore, from currently obtained research results, the improved assay method is definitely a reliable method for inhibitor detection at low concentrations.

Meanwhile, it should be pointed out that some divalent cations, such as Ca\(^{2+}\), Sr\(^{2+}\) and Mg\(^{2+}\) may not only affect barite induction time under no inhibitor condition (He 1995), but also interact with some types of inhibitors (Boak et al. 1999; Xiao et al. 2001; Barouda et al. 2007). They may strengthen or weaken inhibitor inhibition effect on barite, which reflect on barite induction time. Take high concentration Ca\(^{2+}\) for example. For some inhibitors (most polymeric inhibitors), such as PPCA and PVS, their inhibition effect on barite are not affected by Ca\(^{2+}\) (Boak et al. 1999); while for some other inhibitors (most phosphonate inhibitors), for example, DTPMP, their inhibition effect on barite improves significantly in the presence of Ca\(^{2+}\) (Boak et al. 1999). But it is not known whether or the degree to which different concentration Ca\(^{2+}\) in solution affect DTPMP inhibition effect, which will directly affect the improved assay method detection. Phosphonate inhibitors detection with the improved assay method should be conducted in the future research.

Table 13. The detection results of 0.5 mg/L PPCA in S1+Ca and S1+Sr

<table>
<thead>
<tr>
<th>Brine</th>
<th>S1+Ca</th>
<th>S1+Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared conc. (mg/L)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>PPCA</td>
<td>0.68</td>
<td>0.61</td>
</tr>
</tbody>
</table>
4.2.4 Low concentration detection in synthetic brine with trace divalent cations

Zn\(^{2+}\) and Pb\(^{2+}\) are trace divalent cations in the filed brine. Previous research (He 1995) showed that low concentration Pb\(^{2+}\) (0.001 – 100 mg/L) has no significant effect on barite induction time in the absence of inhibitor, while low concentration Zn\(^{2+}\) (0.001 – 65 mg/L) has random irregular effect on barite induction time under no inhibitor condition. While, some other research reported that Zn\(^{2+}\) can increase barite precipitation rate in the presence of inhibitor (Barouda et al. 2007). Based on scant research results, it is hard to determine whether trace divalent cations interfere with barite induction time in the presence and absence of inhibitor and affect the detection result of the improved assay method. The following experiments were therefore conducted.

The improved assay method detected 0.5 mg/L PPCA in S1+Zn and S1+Pb whose compositions are displayed in Table 10. 35 mg/L Zn\(^{2+}\) and 18 mg/L Pb\(^{2+}\) are reasonably high values in field brine (Guerra et al. 2011). But the detect results are unreasonable (Table 14). The results of S1, S1+Zn, S1+Pb detection suggest that trace amounts of Zn\(^{2+}\) or Pb\(^{2+}\) indeed interfere the improved assay method probably through changing barite induction time or inhibitor performance.

Considering Zn\(^{2+}\) and Pb\(^{2+}\) have higher chelating ability with EDTA than any other cations in S1, Zn\(^{2+}\) and Pb\(^{2+}\) corresponded equivalent amounts of EDTA was added into S1+Zn and S1+Pb separately to chelate Zn\(^{2+}\) and Pb\(^{2+}\). 0.5 mg/L PPCA in two EDTA treated brines were detected by the improved assay method. Table 14 shows the inhibitor detection results, and detected PPCA concentrations are close to the actual ones. Therefore, EDTA could largely relieve the interference of Zn\(^{2+}\) and Pb\(^{2+}\) on inhibitor detection by the improved assay method, and make the method works better.
Table 14. The detection results of 0.5 mg/L PPCA in S1+Zn, S1+Pb, S1+Zn+EDTA and S1+Pb+EDTA

<table>
<thead>
<tr>
<th>Brine</th>
<th>S1+Zn</th>
<th>S1+Pb</th>
<th>S1+Zn+EDTA</th>
<th>S1+Pb+EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>prepared conc. (mg/L)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>PPCA</td>
<td>1.40</td>
<td>1.66</td>
<td>0.45</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.64</td>
<td>0.43</td>
</tr>
</tbody>
</table>

4.2.5 Low concentration detection in artificial field brine

Field brine are usually separated from oil water mixture by demulsifier, and the final separated field brines are usually contaminated by crude oil and/or demulsifier to some degree. Crude oil, especially dissolvable organics, and demulsifier may affect barite induction time and interfere the improved assay method detection, so three different artificial field brine, SC1, SC2 and SC3, were prepared to have the tests. Each brine contained 0.5 mg/L PPCA and was detected by the improved assay method.

The detected PPCA concentrations, shown in Table 15, are close to the prepared ones, which is consistent with field brine detection with the original assay method (section 3.2.2.). These two experimental results suggest that the improved and original assay method can tolerate dissolve organics and demulsifier interferences to a certain degree, and still detect inhibitor concentration accurately.

Table 15. Detection results of 0.5 mg/L PPCA in three artificial field brines

<table>
<thead>
<tr>
<th>Artificial field brine</th>
<th>SC1</th>
<th>SC2</th>
<th>SC3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared conc. (mg/L)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>PPCA</td>
<td>0.48</td>
<td>0.61</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>0.46</td>
<td>0.62</td>
<td>0.40</td>
</tr>
</tbody>
</table>
Only PPCA and synthetic brine S1 were used in the improved assay method tests. But according to the results of seven different inhibitors detections in S1, S2 and S3 (section 3.2.1.1.), there is no significant difference in detection accuracy between different inhibitors and different synthetic brines. Therefore, PPCA detection results in S1 could probably indicate that the improved assay method works equally well in other inhibitors detection in other brines or TW.
Chapter 5. Conclusion

In summary, using this assay method, based on the linear relationship between scale inhibitor concentration and the logarithm of induction time, scale inhibitor concentrations in various water solutions can be measured. Both the original and improved assay method have been successfully tested with synthetic brine and field brine. In comparison with other inhibitor detection methods, this assay method has several advantages.

First, the assay method may be applicable for most scale inhibitors, including polymeric and non-polymeric scale inhibitors.

Second, the assay method has detection limit, about 0.1 mg/L effective scale inhibitor, which is an important breakthrough for scale inhibitor analysis in the oil field brine.

Third, the assay method detects equivalent inhibitor concentration (EIC) that directly reveals the scaling tendency of the brine.

Fourth, the assay method can detect scale inhibitors in various water solutions, produced water, tap water or cooling water.

Fifth, the assay method does not require complicated pretreatment before scale inhibitor analysis.

Last, the assay method is low cost per analytical sample. An inexpensive turbidity meter is the only machine used in the assay method, and a set of laser apparatus is even cheaper. Besides, no highly trained operator is required, in that the every procedure is guided by the expert program.
Finally, the scale inhibitor determination assay method is sensitive, universal and inexpensive. An expert program as guidance has been developed. The author is still working on further improvement of this assay method.
Chapter 6. Future Research

This assay method has withstood tests in both synthetic and field brines, but future opportunities for refinements remain.

As mentioned in section 3.2.3.2., IS affects barite induction time to some extent, based on the author’s experimental observations. S and TS have different IS in the improved assay method. If the IS difference is too much, there might be an error in inhibitor detection result. In all experiments of chapter 4, S1 TDS (71895.4 mg/L) is close to R1 TDS (91479.6 mg/L), so the IS difference between S and TS is not significant and the inhibitor detection were not affected. But this method is designed to detect inhibitor in various solutions, including oil and gas field brine, cooling water and other produced waters. The TDS of these solutions can vary from 0 to 400,000 mg/L or even higher, as does IS. In the case that the detected solution has extremely high (e.g. 400,000 mg/L) or low TDS (e.g. 50 mg/L) with low concentration inhibitor inside (e.g. 0.5 mg/L), dilution factor will be small and the TDS difference between S and TS will be large. Different TDS usually leads to different IS that probably result in inhibitor detect failure. A proposed solution for this potential problem is to adjust the IS of R1 to make sure S and TS have the same IS in the final, which makes the improved assay method becomes more accurate and reliable. The detailed calculation will be conducted by the software and the general procedure will not change much. This solution will be tested in the future research.

Besides the above proposal, there are other refinements. First, the test of other types of inhibitors and other water solutions proves the wide applicability of the improved assay method. Second, investigation of the effects of other interferences from field brine, such as methanol, monoethylene glycol, ferrous iron (Fe^{2+}) and silica (SiO_2), on the assay method would improve the applicability
of this method. Third, more field tests can examine the accuracy and reliability of the assay method. These tests may lead to revision in the method, if necessary, to meet detection requirements in the field. Finally, making the assay method more automatic and reducing manual use will increase convenience when the method is applied in industry.
Nomenclature

Scale inhibitor abbreviations:
CMI: carboxy methyl inulin
DTPMP: diethylenetriamine penta(methylene phosphonic acid)
NTMP: nitrilo trimethylene phosphonic acid
PMAC: phosphorous incorporated maleic acid polymer
PPCA: phosphine polycarboxylic acid
PVS: polyvinylsulfonate polymer
SPCA: sulfonated polycarboxylic acid polymer

Other abbreviations:
AF: sample (S) corresponded anionic solution prepared by field brine
AT: twofold-sample (TS) corresponded anionic solution prepared by field brine
AS: blank (B) corresponded anionic solution prepared by simulated brine
a: intercept
B: blank
b: slope
C_f: scale inhibitor concentration in field brine
C_f^{estimated}: estimated scale inhibitor concentration in field brine
C_s: scale inhibitor concentration in sample (S)
CF: sample (S) corresponded cationic solution prepared by field brine
CT: twofold-sample (TS) corresponded cationic solution prepared by field brine
CS: blank (B) corresponded cationic solution prepared by simulated brine
DF: dilution factor
EIC: equivalent inhibitor concentration

F1, F2, F3: three field brines

IS: ionic strength

P: phosphorus

S: sample

SC1, SC2, SC3: three artificial field brines

SI: saturation index

SS1: supplemental sample 1 which is sample with extra added 0.1 mg/L inhibitor

SS2: supplemental sample 2 which is sample with extra added 0.2 mg/L inhibitor

S1, S2, S3: three synthetic brines

S1+Ca: synthetic brine S1 with 20,000 mg/L Ca$^{2+}$

S1+Pb: synthetic brine S1 with 18 mg/L Pb$^{2+}$

S1+Pb+EDTA: synthetic brine S1 with 18 mg/L Pb$^{2+}$ and corresponding amount of EDTA

S1+Sr: synthetic brine S1 with 6,200 mg/L Sr$^{2+}$

S1+Zn: synthetic brine S1 with 35 mg/L Zn$^{2+}$

S1+Zn+EDTA: synthetic brine S1 with 18 mg/L Zn$^{2+}$ and corresponding amount of EDTA

t$_0$: the induction time of blank (B)

t$_S$: the induction time of sample (S)

t$_{SS1}$: the induction time of supplemental sample 1 (SS1)

t$_{SS2}$: the induction time of supplemental sample 2 (SS2)

t$_{TS}$: the induction time of two-fold sample (TS)

TDS: total dissolved solids

TS: twofold-sample
TW: tap water
Reference


Dai, Z. 2013. Improvement of thermodynamic modeling of calcium carbonate and calcium sulfates at high temperature and high pressure in mixed electrolytes. *Civil and Environmental Engineering* Rice University, Rice University. Master of Science.


Ke, M. and Qu, Q. 2007. Method for inhibiting or controlling inorganic scale formations, Google Patents.


Yan, C. 2013. The linear relationship between inhibitor concentration and the logarithm of barite induction time that detected by laser method. A. n. l. d. m. t. s. k. o. s. p. r. a. inhibition. Brine Chemistry Consortium, Rice University, Brine Chemistry Consortium


Zeng, D. and Yan, H. Study on an Eco-Friendly Corrosion and Scale Inhibitor in Simulated cooling water.


Appendix

Below are pictures of the assay method expert program.

Title page
Instruction and tips sheet can help using this assay method. (Note: this sheet has not been finished yet)

### Procedures:

1. Prepare a synthetic brine that has the same composition with the detected field brine but without scale inhibitor. Procedure for its preparation is shown in worksheet "Synthetic Brine".
2. Prepare 11 needed reagents in "Reagents" worksheet.
3. In "Water Composition" worksheet, input the composition of the detected field brine in Cells C10-C25, estimated inhibitor concentration (0.5 - 100 mg/l) in Cells C30 and inhibitor active content in C31. If acid was added into the brine for preservation, input the values of brine and acid in Cells K7 and K8.
4. Click the button "Click here to Run Calculation" in "Water Composition" worksheet. Follow procedures in "Procedure" worksheet to prepare cationic and anionic solutions and measure induction times of four mixed solutions with turbidity meter.
5. In "Time selection" worksheet, click button "Click here to clear previous data before start" to clear previous data if there are some. Copy four turbidity data to appropriate cells. Click button "Click here to get induction time" and induction time of four solutions will be automatically calculated.
6. Input four induction times in Cells F7, I13, I21 and I29 in worksheet "Procedure" and Cell H37 will immediately show the inhibitor concentration in the field brine. The error of detected result is ±30% at low concentration (0.3 to 5 mg/l) detection.
7. If the ratio of detected / estimated inhibitor concentration is in the range of 0.5 - 2.0, then detected result is reliable. Otherwise, re-estimate inhibitor concentration based on the first detection result and re-detect inhibitor concentration.

### Remedies and tips:

1. The detection limit:
   - For polymer inhibitors: 0.3 - 100 mg/l active inhibitor, if \([\text{Ba}] < 2500 \text{ mg/l and } [\text{SO}_4] < 1600 \text{ mg/l}\) in the detected field brine. The low detection limit increases as \[\text{Ba}\] or \[\text{SO}_4\]\ concentration increases. Program will give warning if beyond detection limit.
   - For non-polymer inhibitors: 0.5 - 100 mg/l active inhibitor, if \([\text{Ba}] < 2300 \text{ mg/l and } [\text{SO}_4] < 1300 \text{ mg/l}\) in the detected field brine. The low detection limit increases as \[\text{Ba}\] or \[\text{SO}_4\]\ concentration increases. Program will give warning if beyond detection limit.
2. If initial inhibitor concentration is estimated to be larger than 100 mg/l, please dilute to below 100 mg/l before detection.
3. Choose the same or at least similar scale inhibitor with the detected inhibitor for K6 and K7 reagents preparation. If the detected inhibitor is unknown, P45 (MW=5000) is the default inhibitor for polymer inhibitors and NMP for non-polymer inhibitors in K6 and K7 prepare.
4. During induction time measurement, if "sample"'s induction time is more than 300s longer than "blank"'s induction time, estimated inhibitor concentration would be much smaller than the real concentration. You may dilute "sample" with "blank" to dilute inhibitor and shorten induction time. Record the dilution factor, which helps you re-estimate inhibitor concentration.
5. What this assay method detected is the effective inhibition capacity of brine and express it as mg/l XX inhibitor. The XX inhibitor is the one in K6 and K7 reagents. Moreover, there might be other chemicals besides applied scale inhibitor have scale inhibition effect in the brine, and they will also be detected and expressed as inhibitor.
Water composition sheet is for field brine composition information input.

| Component       | Unit  | A   | B   | C   | D   | E   | F   | G   | H   | I   | J   | K   |
|-----------------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Na⁺             | (mg/l)| 19872.00 | 35357.0 | 33808.5 |
| K⁺              | (mg/l)| 500.00  | 699.0 | 472.1 |
| Mg²⁺            | (mg/l)| 54.00   | 0.0   | 5.4  |
| Ca²⁺            | (mg/l)| 6500.00 | 0.0   | 650.0 |
| Sr²⁺            | (mg/l)| 700.00  | 0.0   | 70.0 |
| Ba²⁺            | (mg/l)| 550.00  | 0.0   | 166.2 |
| Fe³⁺            | (mg/l)| 0.00    | 0.0   | 0.0  |
| Zn²⁺            | (mg/l)| 0.00    | 0.0   | 0.0  |
| Pb⁺             | (mg/l)| 0.00    | 0.0   | 0.0  |
| Cl⁻             | (mg/l)| 43000.00 | 55653.7 | 54388.4 |
| SO₄²⁻           | (mg/l)| 0.00    | 0.0   | 116.1 |
| F⁻              | (mg/l)| 0.00    | 0.0   | 0.0  |
| Br⁻             | (mg/l)| 0.00    | 0.0   | 0.0  |
| SiO₂             | (mg/l)| 0.00    | 0.0   | 0.0  |
| HCO₃⁻ (Alkalinity (mg/l as HCO₃⁻)) | 201.00 | 0.0 |
| CO₂⁻ (Alkalinity (mg/l as CO₂⁻)) | 0.00 | 0.0 |
| Carboxylic acids | (mg/l) | 1.04 | 1.1 |
| Ammonia         | (mg/l)| NH₃    | 0.00  | 0.0  |
| Borate          | (mg/l)| 0.00    | 0.0   | 0.0  |
| TDS (Measured)  | (mg/l)| 71458.04 | 91480.7 | 89478.4 |
| Initial Guess: Inh Conc. | (mg/L) | 1.0 |
| Active Inh Conc. | (%) | 50 | 0%  |
| Barite SI       |       |       |       | 1.9  |
| Celestite SI    |       |       |       | 1.1  |
| Halite SI       |       |       |       | 1.9  |
| Polymer inhibitor |     |       |       | Choose inhibitor type |
| Non-Polymer inhibitor | |       |       | 0%  |
Procedure sheet provides detailed experimental procedure of the assay method and inhibitor concentration calculation.

<table>
<thead>
<tr>
<th>Procedure:</th>
<th>Volume (ml)</th>
<th>Weight (g)</th>
<th>Conc Unit (mg/L M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Prepare the brine solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Filter the sample with a 0.22 micron filter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Pipet a filtered brine to a 50 ml volumetric flask (Suggested sample volume calculated from water composition)</td>
<td>10.000</td>
<td>10.448</td>
<td></td>
</tr>
<tr>
<td>3. Add reagent R1</td>
<td>37.888</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Add PIPES buffer (See Cell D16 for reagent), mixed well</td>
<td>0.000</td>
<td>0.000</td>
<td>R11</td>
</tr>
<tr>
<td>5. Add Ba stock solution (See Cells D16 for reagent)</td>
<td>1.112</td>
<td>1.176</td>
<td>R2</td>
</tr>
<tr>
<td>6. Add SO₄ stock solution (See Cell D17 for reagent)</td>
<td>0.000</td>
<td>0.000</td>
<td>0</td>
</tr>
<tr>
<td>7. Fill up to 50 ml with reagent R1 and label solution as Cetion</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Target Ba or SO₄ concentration in brine solution</td>
<td>Ba</td>
<td>332</td>
<td></td>
</tr>
<tr>
<td>B. Prepare a counter ion (Ba or SO₄) solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Add Ba stock solution (See Cells D22 for reagent)</td>
<td>0.000</td>
<td>0.000</td>
<td>0</td>
</tr>
<tr>
<td>2. Add SO₄ stock solution (See Cell D23 for reagent)</td>
<td>1.161</td>
<td>1.228</td>
<td>R3</td>
</tr>
<tr>
<td>3. Fill up to 50 ml with reagent R1 and label solution as Anion</td>
<td>48.839</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Target Ba or SO₄ concentration in counter ion solution</td>
<td>SO₄</td>
<td>232</td>
<td></td>
</tr>
<tr>
<td>5. Calculate the method dilution factor (V/V)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Calculated standard Addition Inhibitor Concentration</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Calculated mixed brine barite saturation index (S1)</td>
<td>2.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Turbidity tests by standard addition method

1. Barite nucleation time of inhibitor free synthetic brine
   - a. Pipet 7 ml anionic solution prepared by synthetic brine to a turbidity cell
   - b. Pipet 7 ml cationic solution prepared by the synthetic brine to the same turbidity cell and start timing
   - c. Vigorously mixed the solution for 20 seconds. Insert the turbidity cell to the turbidity meter immediately after mixing
   - d. Observe turbidity reading change with time and save turbidity data when NTU is over 7.0. Calculate inhibitor concentration in brine

2. Barite nucleation time of brine sample
   - a. Pipet 7 ml anionic solution to a turbidity cell
   - b. Pipet 7 ml cationic solution to the same turbidity cell and start timing
   - c. Vigorously mixed the solution for 20 seconds. Insert the turbidity cell to the turbidity meter immediately after mixing
   - d. Observe turbidity reading change with time and save turbidity data when NTU is over 7.0. Calculate inhibitor concentration in brine

3. Barite nucleation time of brine after the 1st standard addition
   - a. Pipet 7 ml anionic solution to a new turbidity vial
   - b. Add Reagent R7 to the turbidity cell
   - c. Pipet 7 ml cationic solution to the same turbidity cell and start timing
   - d. Vigorously mixed the solution for 20 seconds. Insert the turbidity cell to the turbidity meter immediately after mixing
   - e. Observe turbidity reading change with time and save turbidity data when NTU is over 7.0. Calculate inhibitor concentration in brine

4. Barite nucleation time after the 2nd standard addition
   - a. Pipet 7 ml anionic solution to a new turbidity vial
   - b. Add Reagent R7 to the turbidity cell
   - c. Pipet 7 ml cationic solution to the same turbidity cell and start timing
   - d. Vigorously mixed the solution for 20 seconds. Insert the turbidity cell to the turbidity meter immediately after mixing
   - e. Observe turbidity reading change with time and save turbidity data when NTU is over 7.0. Calculate inhibitor concentration in brine

### Calculation of concentration from Standard Addition method

<table>
<thead>
<tr>
<th>Input four induction times in cells 17, 113, 121 and 129</th>
<th>Inh Conc. (mg/L)</th>
<th>log time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic brine sample</td>
<td>2.297</td>
<td></td>
</tr>
<tr>
<td>Field brine sample</td>
<td>2.606</td>
<td></td>
</tr>
<tr>
<td>First standard addition</td>
<td>2.910</td>
<td></td>
</tr>
<tr>
<td>Second standard addition</td>
<td>3.141</td>
<td></td>
</tr>
<tr>
<td>Intercept and slope</td>
<td>2.701</td>
<td></td>
</tr>
<tr>
<td>Brine's Inhibitor Concentration (mg/L)</td>
<td>1.19</td>
<td></td>
</tr>
</tbody>
</table>

**PCA**

---

**Table Notes:**
- Blank Time: 196
- Sample Time: 404.0
- Sample+1 Time: 812.0
- Sample+2 Time: 1384.0
Time selecting sheet is induction time determination with recorded turbidity curves.
Simulated brine sheet provides preparation procedure of simulated brine.

<table>
<thead>
<tr>
<th>A</th>
<th>Brine composition (mg/L)</th>
<th>Conc. (M)</th>
<th>Chemicals</th>
<th>WT(g)</th>
<th>final composition (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>19872.00</td>
<td>NaCl</td>
<td>5.0245</td>
<td>19872.00</td>
</tr>
<tr>
<td>2</td>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>500.00</td>
<td>KCl</td>
<td>0.0953</td>
<td>500.00</td>
</tr>
<tr>
<td>3</td>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>54.00</td>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt; * 6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.0452</td>
<td>54.00</td>
</tr>
<tr>
<td>4</td>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>6500.00</td>
<td>CaCl&lt;sub&gt;2&lt;/sub&gt; * 2H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>2.3841</td>
<td>6500.00</td>
</tr>
<tr>
<td>5</td>
<td>Sr&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>700.00</td>
<td>SrCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2130</td>
<td>700.00</td>
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<tr>
<td>6</td>
<td>Ba&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>550.00</td>
<td>BaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.0978</td>
<td>550.00</td>
</tr>
<tr>
<td>7</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.00</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt; * 4H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>8</td>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
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<td>ZnCl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>0.00</td>
</tr>
<tr>
<td>9</td>
<td>Pb&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.00</td>
<td>PbCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>43438.31</td>
<td></td>
<td>5.0245</td>
<td>43438.31</td>
</tr>
<tr>
<td>11</td>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>0.00</td>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>0.00</td>
</tr>
<tr>
<td>12</td>
<td>F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.00</td>
<td>NaF</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>13</td>
<td>Br&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.00</td>
<td>NaBr</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>14</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.00</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>15</td>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>281.00</td>
<td>NaHCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.0387</td>
<td>281.00</td>
</tr>
</tbody>
</table>

Reagent sheet has detailed information of all reagents required in the assay method. (Note: there are more reagents on sheet than described in this study and reagent numbers are different either. The reason is some reagents have two different concentrations)
<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagents: All solutions should be prepared in volumetric flasks. You may change the volumes of solutions in green cells. Store 10 ml solutions in HACH titration cartridge as indicated (if HACH titrator is used).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1 Ionic strength buffer (1.780 ml): Prepared in a volumetric flask with DI water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>MW</td>
<td>wt (g)</td>
<td>Ions</td>
<td>M</td>
<td>MW (g)</td>
<td>Ion conc. (mg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>58.44</td>
<td>178.00</td>
<td>Na⁺</td>
<td>1.5379</td>
<td>22.99</td>
<td>33357</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>74.55</td>
<td>1.784</td>
<td>K⁺</td>
<td>0.0120</td>
<td>39.098</td>
<td>469</td>
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<td></td>
</tr>
<tr>
<td>PIPES, 1.5 Na</td>
<td>335.34</td>
<td>6.706</td>
<td>PIPES</td>
<td>0.0100</td>
<td>333.34</td>
<td>333.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cl⁻</td>
<td>1.5699</td>
<td>35.45</td>
<td>55654</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume of Soln (L)</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>R2 High Ba solution: Prepare 10000 mg/L Ba solution using solution R1.</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>FW</td>
<td>MW (Ba)</td>
<td>Conc. (M)</td>
<td>wt (g)</td>
<td>Solution R1 (ml)</td>
<td>Ba mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCl₂</td>
<td>244.28</td>
<td>137.33</td>
<td>0.073</td>
<td>1.7788</td>
<td>100.00</td>
<td>10000.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Store solution in HACH titration cartridge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R3 High SO₄ solution: Prepare 10000 mg/L SO₄ solution using solution R1.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>FW</td>
<td>MW (SO₄)</td>
<td>M</td>
<td>wt (g)</td>
<td>Solution R1 (ml)</td>
<td>SO₄ mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>142.04</td>
<td>96.09</td>
<td>0.104</td>
<td>1.4785</td>
<td>100.00</td>
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<tr>
<td>Store solution in HACH titration cartridge</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>R4 Low Ba solution: Dilute solution R2 to 1000 mg/L Ba with Solution R1.</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soln R2 (High Ba soln, ml)</td>
<td>Solution R1 (ml)</td>
<td>Total Vol (ml)</td>
<td>Ba mg/l</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>100</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Store solution in HACH titration cartridge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R5 Low SO₄ solution: Dilute solution R3 to 1000 mg/L SO₄ with Solution R1.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soln R3 (High SO₄ Soln) (ml)</td>
<td>Solution R1 (ml)</td>
<td>Total Vol (ml)</td>
<td>SO₄ mg/l</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>100</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Store solution in HACH titration cartridge</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R6 Inhibitor sol 1: Input inhibitor name and active content. Prepare ~5000 mg/L active inhibitor solution with DI water. Consult suggested inhibitor weight in cell D28 and input the actual inhibitor weight in cell E28.</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Inhibitor Name</td>
<td>Active content (mg/L)</td>
<td>Suggested wt (g)</td>
<td>Actual wt (g)</td>
<td>Reagent R1 (ml)</td>
<td>Suggested Active Inh Conc. (mg/L)</td>
<td>Inh Conc. (mg/L as product)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPCA</td>
<td>50</td>
<td>0.5000</td>
<td>0.5021</td>
<td>50</td>
<td>5000</td>
<td>10.042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R7 Inhibitor stock solution 2: Dilute Solution R6 to about 10 mg/L active inhibitor with solution R1.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inhibitor Name</td>
<td>Soln R6 (Scale Inh soln 1) (ml)</td>
<td>Solution R1 (ml)</td>
<td>Total Vol (ml)</td>
<td>Suggested Active Inh Conc. (mg/L)</td>
<td>Inh Conc. (mg/L as product)</td>
<td></td>
<td></td>
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<tr>
<td>PPCA</td>
<td>0.2</td>
<td>49.8</td>
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<td>10</td>
<td>40.168</td>
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<td></td>
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</tr>
<tr>
<td>Store solution in HACH titration cartridge</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R9 1 M HCl</td>
<td>HCl (M)</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Store solution in HACH titration cartridge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>R10 0.5 M PIPES, 1.5 Na: Prepared 0.500 M buffer solution with DI water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buffer</td>
<td>FW</td>
<td>wt (g)</td>
<td>Total Vol (ml)</td>
<td>PIPES (M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIPES, 1.5 Na</td>
<td>335.34</td>
<td>16.767</td>
<td>100</td>
<td>0.500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piperazine-N,N'-bis(2-ethanesulfonic acid), 1.5 Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R11 0.1 M PIPES, 1.5 Na: Prepared 0.100 M with DI water. You may dilute R10 to desired concentration</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Buffer</td>
<td>FW</td>
<td>wt (g)</td>
<td>Final Vol (ml)</td>
<td>PIPES (M)</td>
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<tr>
<td>PIPES, 1.5 Na</td>
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<td>3.3534</td>
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<td>0.100</td>
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<tr>
<td>Piperazine-N,N'-bis(2-ethanesulfonic acid), 1.5 Na</td>
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</table>