APPLICATION NOTE

Simplified High Range Chloride Measurement In Hydraulic Fracturing Applications Using the Hach IntelliCAL™ Chloride ISE

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Simplified High Range Chloride Measurement In Hydraulic Fracturing Applications Using the Hach IntelliCAL™ Chloride ISE

The Hach IntelliCAL™ Chloride Ion Sensitive Electrode (ISE) allows operators to easily obtain real-time Chloride values. The Chloride ISE overcomes the challenges inherent in current Chloride titrimetric methods resulting in fast and accurate results that can be perfomed at the well site. Having access to this critical information allows operators to react quickly to changes to avoid potential issues that could delay well development and/or production.

Overview

Chloride is a key water quality parameter in hydraulic fracturing applications that is needed to optimize performance and avoid potential problems. Chloride is commonly found in the additives used in fracturing fluids as well as in the shale formations themselves often leading to samples with extremely high concentrations. These high Chloride concentrations are difficult to measure with the traditional methods, which use titration. In addition, these existing methods have draw backs that make them time consuming and difficult to perform on site. Hach has overcome these issues through the development its breakthrough *IntelliCAL™ Chloride Ion Sensitive Electrode (ISE). With performance proven in the field, the ISE allows the operator to quickly and easily obtain Chloride concentrations at the well site where they are needed most.*

Chloride in Hydraulic Fracturing Applications

Chloride in hydraulic fracturing samples comes from many different sources and can reach extremely high concentrations relative to traditional wastewater samples. Chloride is a common component found in the additives that are mixed with the large volumes of water and sand that form the fracturing fluid. In addition, chloride can occur naturally in the shale formations or even from the source water itself, if a brackish resource is used. Due to these factors Chloride can sometimes be present at concentrations that exceed 150,000 mg/L as Cl^- in both flowback and produced waters.

A firm understanding of the Chloride concentration in hydraulic fracturing waters is needed to maximize production and avoid costly issues. Chloride is a key parameter needed to accurately mix the additives in fracturing fluid, optimize blending of source water with flowback or produced water, and avoid interferences that could otherwise limit the effectiveness of the fracture. It is also an important parameter in understanding how to effectively treat flowback or produced water and is often one of the first ions to indicate breakthrough when filtration is used.

Challenges with Existing Methods

Chloride has traditionally been measured using titrimetric methods; however, the high Chloride concentrations along with the variability of the sample, both within and between each shale play, makes the measurement difficult for these applications. Without knowing a starting concentration range, Chloride titrations can require multiple iterations before arriving at a final concentration, which often is very time consuming and can require a significant amount of titrant. This limitation is magnified at extremely high concentrations. In addition, the standard Chloride titrations only go up 10,000 mg/L as Cl^-, so dilutions are typically required to reach the range of interest for this application.

Chloride titrations can also be challenging in other respects. Titrations are often based on visual verification by the user, which can be somewhat subjective leading to variation in results from user to user and sample to sample. Also, the Chloride titrant contains RCRA (Resource

Conservation and Recovery Act) metals, so care needs to be taken to ensure that the resulting solution is dispposed of properly and that contact with skin and clothing is avoided.

Breakthrough in Chloride Measurement

Hach has recently launched the IntelliCAL™ Chloride Ion Sensitive Electrode (ISE), which greatly simplies the Chloride measurement in the high concentration, complex sample matrices commonly found in hydraulic fracturing (and other oil & gas) applications. Using this new Chloride ISE, an operator can easily obtain fast, stable, and accurate results for this parameter at the well site in real time. This ISE can be used on Hach's portable HQd multimeter making it highly transportable, thereby drastically reducing the amount of equipment and time needed to make this critical measurement. Furthermore, it is a solid-state sensor eliminating the need for membrane replacements and allowing for dry storage of the ISE.

Results from the Herkimer and Eagle Ford Shales

This sensor has been used by Global Petroleaum Research Institute (GPRI) at Texas A&M University-College Station to monitor Chloride in its produced water treatment system in the Herkimer and Eagle Ford Shale Plays. GPRI uses a membrane based technology to reduce the TDS concentration of produced water. GPRI wanted a fast and reliable way to monitor Chloride levels, so it could evaluate membrane performance. Using the Chloride ISE, GPRI has been able to easily identify breakthrough events giving it the information needed to step in and stop the process before damage to the membrane occurs. Speaking to the performance of the sensor, Keith McLeroy, Analytical Advisor at GPRI, stated, "Upon receiving…the High Range Chloride ISE probe, GPRI has successfully conducted two large scale field studies in the Herkimer (New York) and Eagle Ford (Texas) Gas Shales. The waters from these formations were very high in salts, oils, color and solids…and the Chloride ISE probe was well capable of analyzing as high as 300,000 mg/L in oily waters."

Performance Verification in Flowback and Produced Waters

In addition to these and other field tests, Hach has also tested the performance of the IntelliCAL™ Chloride ISE on flowback and produced waters from multiple shale plays within the United States. In order to verify that a high concentration of the Chloride analyte could be accurately measured with the ISE a spiking study was perfomed. A spiking study is a proven way to show that the procedure is producing the correct values by confirming that the addition of a known concentration of an analyte can be recovered.

The produced and flowback water samples were spiked with 7 g Cl^-/L, then a dilution factor of either 5 or 25 was applied to produce a concentration spike of 35 or 175 g Cl^-/L, respectively. As can be seen in Table 1 below, the spike recoveries were all above 90%. This shows that there were no interfering compounds encountered in the analysis of these fluids that would cause a negative response with the IntelliCAL™ Chloride ISE.

Table 1. Spike Recoveries in Flowback and Produced Waters

Sample ID	Unspiked conc (g/L)	Spiked conc (g/L)	% Recovery
1	345.0	547.5	108
2	243.3	420.0	101
3	26.9	62.5	102
4	81.5	110.0	92
5	20.5	56.5	105
4-A	169.8	330.0	91
11	213.5	375.0	94
20-13	60.0	92.5	96

The Goal: Accurate Chloride Measurement Made Easy

Understanding Chloride levels helps operators make important decisions that optimize hydraulic fracturing operations and help to avoid costly issues. The Hach IntelliCAL™ Chloride ISE allows for the fast and accurate determination of Chloride levels by any operator, regardless of experience level. The probe has been tested and performs well in hydraulic fracturing applications. Furthermore, its performance, portability, and virtually maintenance free operation allow Chloride measurement information to be produced in the field where it is needed most.

For more information on the Hach IntelliCAL™ Chloride ISE, as well as information on other Hach products suited for Oil and Gas applications, visit www.hach.com/fracwater and click on "On-site Testing."

Appendix—How to Calibrate the IntelliCAL™ Chloride ISE

Follow Hach Cl^- ISE Procedure for model ISECl18101 or ISECl18103, DOC022.53.80030

Calibration Standards Preparation

Step 1. Prepare Standard 3 – 35 g/L NaCl Solution

Weigh out 11.55 g of NaCl, transfer the NaCl into a 200-mL volumetric flask and bring to volume with DI water, then invert to mix.

Step 2. Prepare Standard 2 – 12.5 g/L

Transfer 71.43 mL (or g) of Standard 3 (35 g/L NaCl Solution) just preared into a 200 mL volumetric flask and bring to volume with DI water, then invert to mix.

Step 3. Prepare Standard 1 – 3.55 g/L

Transfer 56.8 mL (or g) of Standard 3 (35 g/L NaCl Solution) just prepared into a 200 mL volumetric flask and bring to volume with DI water, then invert to mix.

Setting up the HQ40d (portable) or HQ440d (bench top)

Changing the calibration setup (see "Change calibration options in the Cl^- ISE manual")

1. Press the setup key (wrench)
2. Select the ISECl181 settings, then change the current method from default to a difference method name, i.e. HR Cl
3. Select 'modify current settings', then select 'measurement options' and change the units to 'g/L'
4. Press exit
5. Go into the calibration options and select 'std set'
6. Choose 'custom standard set'
7. Set the 'calibration units' to g/L and press OK
8. Select 'std set values' and create a standard set of 3.55, 12.5 and 35 g/L
9. Scroll down to standard 3 and change the value to 'custom'
10. Once this has been selected, enter the standard concentration of 35 g/L
11. Press OK to confirm
12. Change std 2 to 12.5 g/L and std 1 to 3.55 g/L
13. Once the new calibration standards have been set, press 'exit' until you reach the main measurement screen
14. When you have returned to this screen, follow the calibration procedure listed in the Cl ISE manual.

For measurement, set up, interference, maintenance and troubleshooting information, refer to ISE manual DOC022.53.80030.

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