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Modernizing Aqueous Fluid Analysis at the Rig: Introducing Chemical Analyzer as a Novel Mud Analysis Technology

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Abstract

Well-site methods of mud ion analysis, such as titrations, are time-consuming and can be prone to subjectivity and quantification interferences. For instance, amine-based shale inhibitors and amine-based corrosion inhibitors cannot be quantified separately using current titration methods. In this field context, we introduce a more accurate, repeatable and user friendly instrument dedicated to drilling fluid chemical analysis. Through extensive exploratory studies, we are proposing the use of the Chemical Analyzer (CA), as an innovative field method for identifying and quantifying various entities (ions and charged organics) directly in the drilling fluid. Furthermore, we designed and implemented first-of-its kind protocols for the application of drilling fluids analysis. Our methods quantified various ions in mud, including amine-based shale inhibitors, chloride, calcium, potassium, sulfate, formate, phosphate, and nitrate. In practice, the CA performances have been established by an extensive comparison between laboratory and field datasets (two wells), where a good agreement was found, validating the methodology for the calcium and chloride contents. By completing two field trials, the CA is robust and performs well in environments with power fluctuations and vibrations. This technology offers unprecedented opportunities for identifying correlations between rheological and physical properties (and fluid performance) with chemical measurements at high-frequency data collection. Moreover, CA not only provides our mud engineers with more reliable and previously inaccessible information, but also reduces their workload by several hours while increasing measurement frequency and allowing for more time devoted to fluid preparation and decision-making.

Introduction

Increasing adoption of water-based mud (WBM) necessitates the modernization of chemical mud checks at the rig site. This is due to several reasons. Firstly, WBM's chemical composition is more sensitive to environmental changes than that of oil-based mud (OBM), as most compounds in the earth's atmosphere have been exposed to water as a solvent throughout geological time. This sensitivity requires more frequent monitoring to maintain optimal fluid performance. Secondly, the digitization and automation of measurements can help reduce subjective bias, increase transparency, and shift the focus to informed decision-making. Lastly, by expanding the scope of chemical checks to measure ions not typically assessed before, this can provide great advantages during drilling operations by keeping customers fully aware about fluid composition changes and therefore optimize the drilling process through advanced and in-house models. In this publication, we demonstrate that CA can modernize chemical mud checks by measuring many ions in the drilling fluid and producing digital outputs.

Chemical Analyzer (CA)

CA is a laboratory chromatography technique used to separate and analyze different charged components within a mixture. It works by applying an electric field to a thin, fluid-filled tube, causing the various molecules to move at different speeds based on their size and charge. As the molecules travel through the tube, they are separated from one another, allowing scientists to identify and quantify each component. This method is particularly useful for tasks such as analyzing complex samples or identifying specific substances within a mixture.

Typical chromatography technology, particularly ion chromatography, is widely used for ion characterization. However, the high cost of columns has led our research team to explore CA as a cost-efficient and robust alternative. This paper describes the concept validation of using CA for WBM measurements in the lab and at the rig site. CA offers numerous advantages over traditional methods, such as the ability to measure various ions, both inorganic and organic components (e.g., amine inhibitors). The primary purpose of these improved checks is to equip drilling fluids engineers with more comprehensive information for a better fluid monitoring and decision-making process. Furthermore, this enhances transparency with clients by providing a higher data quality and potentially correlating previously unknown variables with mud performances.

Improvement and modernization of WBM monitoring at the rig site can enhance WBM preference over OBM, thus promoting sustainability. The ability to measure fluid properties at a fast pace is crucial for maintaining the quality of drilling fluid during operations. Currently, drilling fluids engineers spend more time conducting measurements for WBM compared to OBM, with some of the measurements being more tedious and less accurate. Bringing analytical laboratory-like approach to the field, CA offers faster and more reliable information for WBM chemical analysis and consequently improves WBM measurements by streamlining the monitoring process and enhancing overall performance.

Laboratory Validation

Initial testing for the CA method was conducted to assess its viability for analyzing chemicals in water-based drilling fluids, with the main objective being analysis of amine shale inhibitors. Traditional titration methods for measuring inhibitors are time-consuming and cumbersome, involving multiple steps as shown in the example below:

1. Lowering the sample pH to 3
2. Boiling and cooling
3. Increasing the pH to 7
4. Titrating from pH 7 to 10.5

These steps require about 45 minutes, and the results may not accurately reflect individual amine inhibitor concentrations in the mud since other amine-based products, such as corrosion inhibitor, H_2S Scavenger, oxygen scavenger, are lumped together as a single pH-resistant value in this titration method's output. Additionally, pH readings from an electrode are dependent on the sample's salinity, making the titration method's variability reliant on electrode storage conditions. Therefore, resolving inhibitor quantification in a timely and accurate manner is a primary interest for maximizing WBM performance.

Initial work focused on determining CA's feasibility on drilling fluids measurements with considerations of (1) analyzing tube plugging and (2) output signal resolution. First, the analyzing tube is in micron size, therefore, the ability to flow solids-laden drilling fluids and its filtrate without plugging the tube is crucial to obtain measurements. Second, due to challenges from using titration techniques to identify and quantify amines as mentioned before, CA's potential capability in providing sufficient resolution to separate and analyze additives in the mud, amines in this particular interest, would be its key feature to prove its feasibility for WBM measurements. The functional range of the method with the ability to measure high salt content is also important as many WBM systems require the use of high salinity brines.

Feasibility Validation

Figure 1 presents an example of (a) cations and (b) anions outputs from CA measurements. High-performance water-based mud (HPWBM) with formulation shown in Table 1 was used in this study. By conducting measurements of each component in deionized water (DI) separately, sources of peaks in the drilling fluid can be identified. For example, barite weighting material contributes to the Na^+, Mg^{2+}, Ba^{2+}, Ca^{2+}, and SO_4^{2-} peaks. The components contribute to each peak signal in various intensities, leading to peak size corresponding to each ion concentration. The output data from this study with solid-laden HPWBM confirms the CA feasibility for measuring water-based drilling fluids containing solids without instrument plugging issues.

Table 1. High Performance Water-Based Mud Formulation

Component	Concentration (lb/bbl)
Water	291.6
Amine-based shale inhibitor	3.5
Encapsulator	1.0
Fluid loss control additive	1.0
Xanthan viscosifier	1.0
Lubrication agent	10.5
Weighting material	166.2

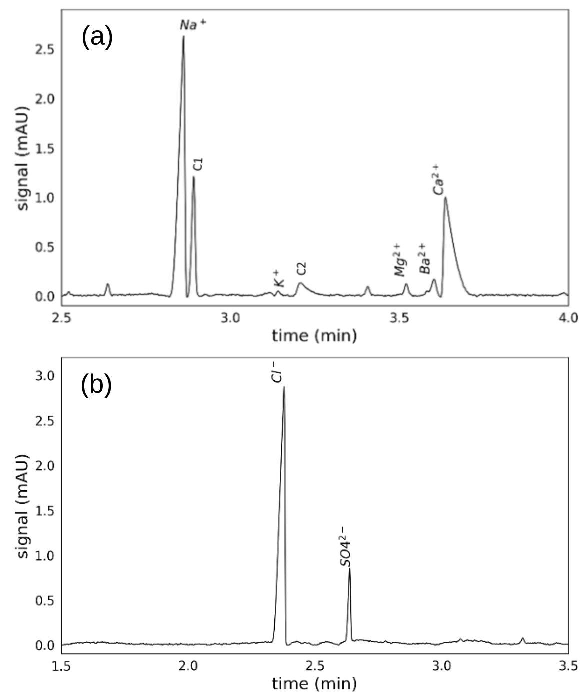
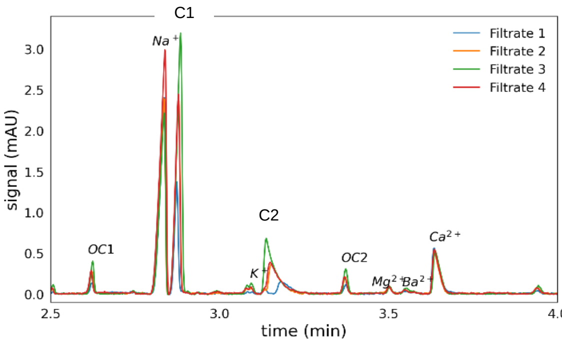


Figure 1. Signal output of (a) cations and (b) anions.

A blind experiment was conducted to evaluate detection and quantification robustness of CA with filtrates. The results are presented in Figure 2. Mud filtrates were prepared by API filtration test with various concentrations of amine inhibitor and salt. Analysis was then conducted without compositional knowledge of the filtrates by the CA operator. The four filtrates were analyzed. Results show that Filtrate 1 had the lowest inhibitor concentration (peaks C1 and C2), Filtrates 2 and 4 had the same intermediate inhibitor concentration, and Filtrate 3 had the highest inhibitor concentration. Analysis also indicated that Filtrate 4 had a sodium concentration 15% larger than Filtrates 1, 2, and 3. Measurements were confirmed to match amine shale inhibitor and salt concentrations in each filtrate.



Sample Name	Inhibitor Concentration (%)	Sodium Concentration (%)
Filtrate 1	1	4.1
Filtrate 2	3	4.1
Filtrate 3	5	4.0
Filtrate 4	3	4.8

Figure 2. Blind test measuring cations in API filtrates with different compositions.

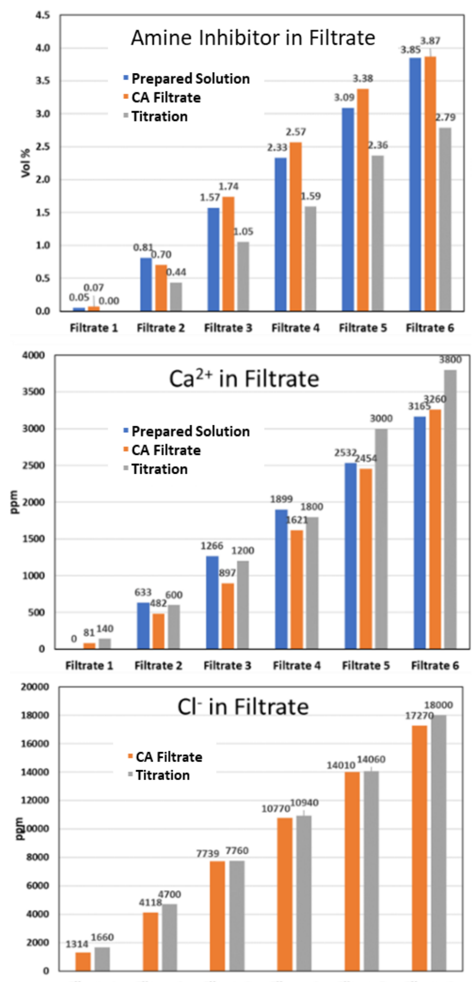


Figure 3. Comparison between conventional titrations and CA measurements for amine inhibitor, Ca^{2+}, and Cl^- in filtrates.

The first field target was a geothermal well drilled in US Land using a high salinity HPWBM system. Field readiness testing included laboratory validation of CA measurements against conventional titrations typically performed in the field. To execute these validation tests, filtrates from muds formulated with varying concentrations of $CaCl_2$ and amine inhibitor were collected. Samples were analyzed by both titrations and CA, enabling a comparison between the outputs of these two methods as shown in Figure 3.

The results demonstrate an exceptional correlation between CA outputs and titration measurements for chloride and calcium, though the same level was not demonstrated for amine inhibitor. Although the same trends were captured, CA provided a more accurate measurement of the inhibitor than titrations as the CA instrument's output more closely matched the prepared solution than did the titration. The titration of amines requires precise calibration and manipulation of pH meters. In particular, the calibration must be performed in brines with a salinity like that of the target solution. The discrepancies observed between the CA and the titrations for amine inhibitor measurements can be attributed to the lack of a salinity-matched calibration of the pH meter.

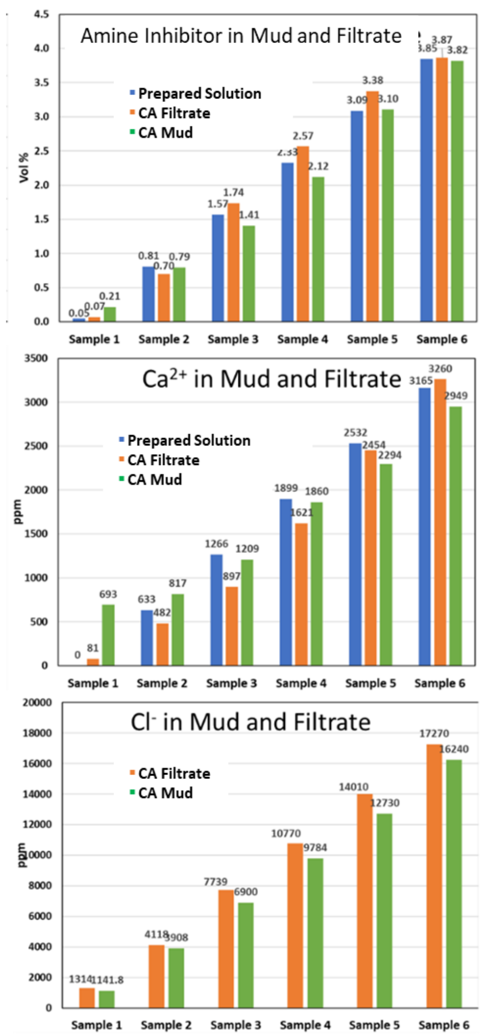


Figure 4. Comparison between mud and filtrate analysis for amine inhibitor, Ca^{2+}, and Cl^-.

CA measurements between mud and filtrate are shown in Figure 4. Except for calcium, which shows incorrectly large Ca^{2+} concentration for Sample 1 in the mud measured by CA, increases in amine inhibitor and Cl^- in the mud are well correlated by the CA. Capturing trends of compositional changes directly with mud is encouraging as it suggests that filtration is not necessary when measuring ionic content in drilling fluid by CA. This can translate to fewer steps in the field using CA method for chemical mud checks.

Case Histories

US Land Field Experiment

The operator drilled the well using the HPWBM to help researchers understand the geological conditions for future geothermal projects. The CA unit was used for daily chemical mud checks while drilling. The target ions for this extended lab test were amine inhibitor, chloride, and calcium.

Figure 5 shows the concentration measurements obtained by CA and titrations. The concentration of amine inhibitor from CA output (average 3.2% by volume in mud and 3.7% by volume in filtrate) matched closely with the volumetric addition (3% by volume). Measurements of Ca^{2+} showed a downward trend over the seven-day period of data collection. Soda ash was added daily to treat the mud for high Ca^{2+} content and to maintain a high pH. Additionally, the system was diluted with water during the first 4 days. The outcome of the treatment was observed in the measurements as concentration decreased from ~600 ppm to <100 ppm by the last few days. Cl^- measurements showed a nearly constant concentration with a slight downward trend. The largest decrease occurred during the first 4 days while the system was being diluted, otherwise, Cl^- concentration was nearly constant. The step-like increase in Cl^- concentration coincided with transferring 200 barrels of saturated NaCl mud to the active tank. Titration and CA measurements were again well correlated for Ca^{2+} and Cl^-.

Titration measurements were performed using the typical titration mud check kit. Cl^- was quantified using potassium chromate as color indicator, and silver nitrate as titrant. Ca^{2+} was quantified using a strong buffer, calmagite indicator, and titrated with EDTA. Amine inhibitors were quantified by pH titration. A typical chemical mud check consisted of measuring Ca^{2+} and Cl^-. Amine inhibitor was measured at most once per day due to titration complexity. On the other hand, CA measurements were performed every two hours and provided better continuous data trends compared to titrations, as shown in Figure 5.

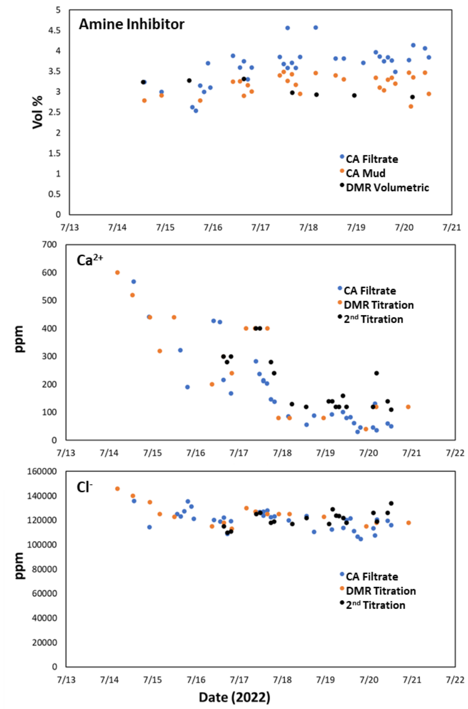


Figure 5. Measurements obtained for amine inhibitor, Ca^{2+}, and Cl^- by CA and titrations.

Conclusions – US Land Field Experiment

This field test demonstrates the successful transportation and reliable performance of the CA unit under rig site conditions. This method is based on an analytical laboratory-like approach ensuring quantitative datasets at high frequency to enhance the drilling fluid maintenance in-real time. Ion concentrations are in strong agreement between CA measurements and those determined through titrations. Furthermore, a significant time advantage when using CA is validated. The CA unit provides the capability to measure several other ions in addition to the ones requested. A thorough analysis of the data collected during the field trial demonstrates that the instrument can also capture sodium, potassium, sulfate, and magnesium concentrations without additional effort (Figure 6) from the same measurement sequence for calcium, chloride, and amine inhibitor. In comparison to the approximately one hour required for titration to measure three ions, CA enables the analysis of seven ions in just around 30 minutes. These findings highlight the potential of CA technique as a valuable tool for ion analysis in water-based drilling fluids.

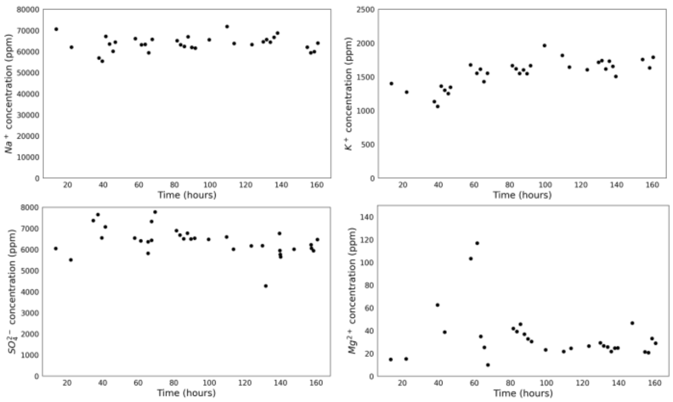


Figure 6. Measurements of Na$^+$, K$^+$, SO$_4^{2-}$, and Mg^{2+}.

South America Field Trial

After the first successful trial, a second field test took place in South America. There was an interest to test the CA unit at this location due to the complexity of the mud formulation. The HPWBM contained more than ten components and the mud had a dark color. These presented challenges to characterize mud components with titrations. Also, to enhance practicality of using the CA technique at any rig environment, both onshore and offshore, a compact prototype CA machine has been developed specifically for drilling fluids applications (Figure 7). The newly designed unit features a smaller footprint, lighter weight, and is equipped with a lithium battery that permits continuous operation for five hours without connecting to an electrical outlet. Besides ion analysis for WBM monitoring, another objective for this trial is to verify the robustness of the new CA unit operation.

Figure 7. CA unit.

The mud program utilized three systems: (1) a sacrificial mud using recycled water, (2) a sodium chloride HPWBM, and (3) a sodium formate HPWBM. Data obtained by CA and titrations are presented in Figure 8. The first two plots showing concentrations of Cl$^-$ and Ca^{2+} collected by CA and titrations demonstrate that the CA method captures the same trends as titrations. Notably, all the plots have discontinuities at 250 hours, when the operation drilled through the casing shoe and the mud system was switched from a sodium chloride HPWBM to a sodium formate HPWBM. Two orders of magnitude increase in Na$^+$ and formate (100s ppm to 10,000s ppm) are explained by the change in the mud system. Increases in the same order of magnitude of hardness (~50 ppm to ~200 ppm) and K$^+$ (~100 ppm to ~500 ppm) can be explained by cement leaching. Hardness ions and K$^+$ concentrations decrease readily in a few hours, indicating the influx was small and not sustained as the mud homogenized and soda lime was added. Sulfate increased from 50 hours to 200 hours as the operation added sulfonated fluid loss control additive into the system. Sulfate was removed from the active system as the operation switched from the used fluid to the fresh sodium formate HPWBM at 300 hours.

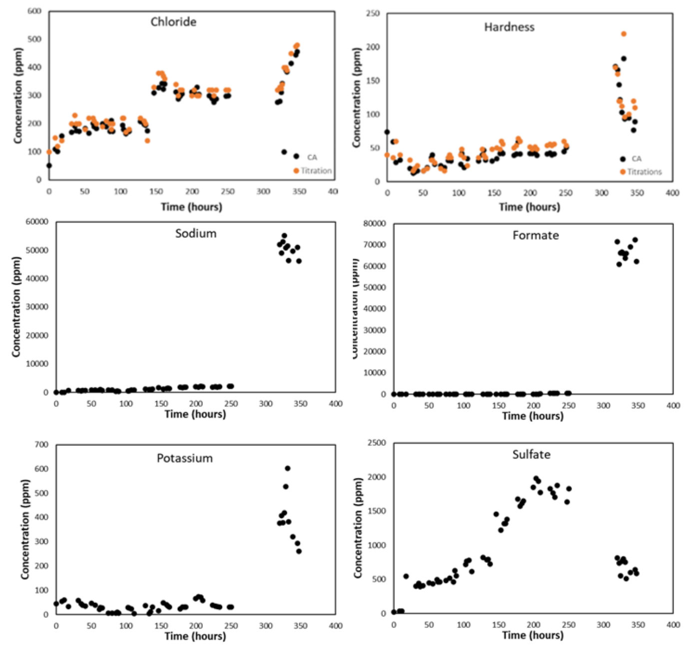


Figure 8. Ion measurements obtained by CA and titrations of filtrate.

Another objective of this field trial was to monitor the concentration of a different type of amine shale inhibitor. The polyamine inhibitor used in this job is different from the amine inhibitor used in the first field trial. The maximum concentration of amine inhibitor was ~0.3% by volume per the well's plan. Because the concentration of polyamine was very low, the ability to track its concentration while drilling was challenging. Figure 9 shows the detection of amine inhibitor at the suction pit when the material was added to the system (red curve). It seemed to be adsorbed within one circulation as no peak was found at 4.1 minutes while sampling from the shaker outflow (black curve). Tracing inhibitor concentrations while drilling did not produce a reliable data trend since the initial concentration was low and consumed quickly.

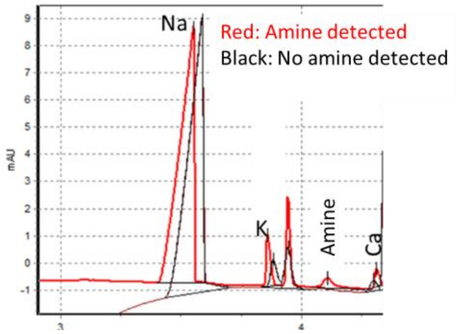


Figure 9. Electropherograms of mud sampling at the suction pit (red) and shaker (black).

Conclusions – South America Field Trial

In the second field trial, many ions in several mud systems including sacrificial mud, sodium chloride HPWBM, and sodium formate HPWBM. CA measurements were validated by comparing against titration values of calcium and chloride. The CA technique simplified the challenges of water-based muds analysis from titrating many components with dark-colored fluids. Operation of the CA unit was robust and sample preparation was straightforward as it included steps conducted in traditional mud checks such as filtration and dilution. The onsite drilling fluids engineer was also able to operate the equipment after only two days of observation and training.

Conclusions

- Chemical Analyzer (CA) is a viable technology for characterization of water-based drilling fluids in the field.
- Increased efficiency over conventional titrations is significant, reducing the time to analyze WBM by titrations from hours to minutes.
- Improvement in digital data output is significant as the CA test data is a two-column vector recorded and analyzed using a computer, not numbers written by hand in a lab notebook. This digital output can potentially be transmitted to drilling program to enhance fluids monitoring during operation.
- The scope of measurements is expanded as typical titrations can only track calcium and chloride, whereas the newly developed CA method measures potassium, sulfate, phosphate, nitrate, magnesium, lithium, amines, and others.

Acknowledgments

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