Journal Homepage: -www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

ISSN NO. 2320-5407

Article DOI:10.21474/IJAR01/21366
DOI URL: http://dx.doi.org/10.21474/IJAR01/21366

RESEARCH ARTICLE

LABORATORY TECHNOLOGIES FOR CORROSION INHIBITOR RESIDUALS ANALYSIS

Nayif A. Al-Rasheedi
1. Research & Analytical Solution Department, Saudi Aramco, Dhahran/ Saudi Arabia.

……………………………………………………………………………………………………....

Manuscript Info

……………………….

Manuscript History
Received: 10 May 2025
Final Accepted: 13 June 2025
Published: July 2025

Abstract

……………………………………………………………

Corrosion inhibitors are vital in protecting metallic surfaces across various industrial applications, from oil and gas pipelines to water treatment systems. Accurate residual analysis of these inhibitors is essential to maintain their effectiveness, ensure economic efficiency, and minimize environmental impact. This paper explores various laboratory technologies for analyzing corrosion inhibitor residuals, including titration methods, chromatography, spectroscopy, and electrochemical techniques.By understanding these methodologies, industries can optimize corrosion management strategies, enhance equipment longevity, and comply with environmental regulations.

……………………………………………………………………………………………………....

Introduction:-

Corrosion significantly impacts industrial systems by deteriorating metallic components through electrochemical reactions with their surrounding environments. The use of corrosion inhibitors has become a standard practice to mitigate this issue. These substances, when added in low concentrations, reduce the corrosion rate by interacting with metal surfaces or the corrosive environment. However, to ensure their efficacy and cost-effectiveness, it is essential to monitor and quantify their residual concentrations accurately.Residual analysis of corrosion inhibitors involves various laboratory technologies, each with unique principles and applications.The current available technologies have the following limitations: Corrosion inhibitors have been detected in water systems using multiple different physicochemical techniques which are mostly instrumental ones. These techniques, involving chromatography and spectroscopy, are quite sophisticated in the sense of detection limits and accuracy of the measurement. However, the major drawbacks include their limited portability, and rather expensive instrumentation, which hinder their deployment and use in the field. In addition to this, the operational costs of the real time continuous measurements will be substantially high, which is against the demands of this project. Chromatographic techniques require extensive sample preparation while spectroscopy is considered non-specific and non-responsive towards compounds that are non-absorbing in certain wavelength ranges. Mass spectrometry can be an alternative to those techniques but with it comes with a huge cost burden.Corrosion inhibitors have been detected in water systems using multiple different physicochemical techniques which are mostly instrumental ones. These techniques, involving chromatography and spectroscopy, are quite sophisticated in the sense of detection limits and accuracy of the measurement. However, the major drawbacks include their limited portability, and rather expensive instrumentation, which hinder their deployment and use in the field. Chromatographic techniques require extensive sample preparation while spectroscopy is considered non-specific and non-responsive towards compounds that are non-absorbing in certain wavelength ranges. Mass spectrometry can be an alternative to those techniques but with it

Corresponding Author: Nayif A. Al-Rasheedi
Address**:** Research & Analytical Solution Department, Saudi Aramco, Dhahran/Saudi Arabia.

comes with a huge cost burden. Electrochemical sensors, on the other hand, are very inexpensive tools to continuously monitor redox species and furnish good selectivity for those species based on the selected oxidation-reduction potential. Moreover, the diversity in the selection and modification of electrode materials provides a quick adjustment, rather switching of the sensor functions against a certain analyte or a class of analytes.

The most common technique used is a so called "wet" method, which is essentially a series of manual extractions of corrosion inhibitors with chloroform or dichloromethane to partition the corrosion inhibitors and purify them in a stepwise fashion, followed by reacting corrosion inhibitors with a dye and measuring UV absorbance of this dye complex. This method has been used for decades and is still used daily by most oil and gas chemical service companies supplying producers with corrosion inhibition programs. This method is very laborious where maximum of around 35 samples per 8-hour shift is measured, it uses toxic chemicals, and is not very accurate.
Alternatives include use of expensive instruments, such as HPLC, HPLC/MS, LC, LC/MS, GC, NMR. fluorometers. While all these techniques are very feasible, the field samples cannot be measured directly. The samples must be first purified by use of expensive columns. The operation of such instruments requires highly trained operators with scientific background and are very expensive to maintain, not to mention their initial cost. It usually takes about 30 minutes to do a measurement and thus, these instruments are predominantly used as R&D tools.

Types of Corrosion Inhibitors
Corrosion inhibitors can be classified into organic, inorganic, and mixed inhibitors, each with specific mechanisms and applications.

Organic Inhibitors
Organic inhibitors contain carbon-based compounds that protect metals primarily through adsorption, forming a protective layer on the surface. Common organic inhibitors include amines, carboxylates, and imidazolines. These inhibitors are particularly effective in oil and gas industries and are known for their versatility in various environmental conditions.

Inorganic Inhibitors
Inorganic inhibitors, such as chromates, phosphates, and silicates, function by forming passive films on the metal surfaces. These films prevent corrosive agents from initiating the corrosion process. Inorganic inhibitors are often used in cooling systems, boilers, and other high-temperature applications due to their stability under extreme conditions.

Mixed Inhibitors
Mixed inhibitors combine both organic and inorganic compounds, leveraging the benefits of each to provide enhanced protection. These inhibitors are used in environments where a single type of inhibitor might not suffice, offering a more comprehensive approach to corrosion control.

Importance of Residual Analysis
Accurate residual analysis is critical for several reasons:

Impact on Corrosion Control
Maintaining the correct inhibitor concentration ensures optimal protection. Insufficient levels can lead to increased corrosion rates, while excess inhibitors can be economically and environmentally detrimental.

Environmental Considerations
Many corrosion inhibitors are potentially harmful to the environment. Monitoring their residuals ensures that their use is minimized, preventing unnecessary environmental contamination and ensuring compliance with regulations.

Economic Implications
Proper dosage of inhibitors can lead to significant cost savings by preventing overuse and ensuring the longevity of industrial equipment, thus reducing maintenance and replacement costs.

Laboratory Technologies for Residual Analysis
Several laboratory techniques are employed to analyze corrosion inhibitor residuals. These techniques vary in complexity, accuracy, and suitability for different types of inhibitors.It is very challenging to detect corrosion inhibitors at low concentrations in water and oil systems considering the complexity of oilfield samples.

Furthermore, there is no international standardized analytical method available to monitor residual of these chemicals as a tool to validate their availabilities. Some oil companies developed custom-made analytical methods for their products and in-house use. The developed procedures were kept within the company either for technical advantage or proprietary reasons.

In recent years, new developments in the monitoring of residual corrosion inhibitors in oilfield fluids have been reported. The choice of analytical technique depends on many factors including total number of samples, technical experience of personnel and available equipment

Titration Methods

Titration is a classical analytical technique widely used for quantifying corrosion inhibitor residuals. It involves the gradual addition of a reagent to a solution until a reaction is complete, indicated by a color change or an electrical measurement.

Potentiometric Titration

This method uses an electrode to measure the potential change during the titration process. It is particularly useful for inhibitors that do not produce a visible color change. Potentiometric titration provides high precision and is suitable for various types of corrosion inhibitors.

Colorimetric Titration

Colorimetric titration involves the use of indicators that change color at the endpoint of the titration. This method is straightforward and cost-effective but may be less accurate than potentiometric titration, especially for inhibitors that do not produce a sharp color change.This method is more straightforward, inexpensive and can be run by personnel with minimal training. It is based on UV-Visible absorption in the 200-800 nm region, and involve the use of color-imparting reagents such as methyl orange, bromocresol purple and bromophenol blue.

Chromatography

Chromatography is a separation technique that can be used to analyze complex mixtures of corrosion inhibitors. It separates the components based on their interactions with a stationary phase and a mobile phase.

High-Performance Liquid Chromatography (HPLC)

HPLC is a powerful technique for analyzing organic inhibitors. It provides high resolution and sensitivity, making it ideal for detecting low concentrations of inhibitors in complex matrices.

Gas Chromatography (GC)

GC is used for volatile inhibitors or those that can be derivatized to form volatile compounds. It offers high sensitivity and specificity, making it suitable for analyzing trace levels of inhibitors.

Spectroscopy

Spectroscopic methods involve the interaction of light with the sample to measure the concentration of inhibitors. These techniques are highly sensitive and can provide qualitative and quantitative information.

UV-Visible Spectroscopy

UV-Visible spectroscopy is widely used for organic inhibitors that absorb light in the UV or visible range. It is a quick and non-destructive method that provides high sensitivity.The mainadvantageisrelatively simple, cost-effective, and rapid but it haslimited of selectivity for complex mixtures, susceptible to interferences from other UV-Vis absorbing compounds.

Infrared Spectroscopy (IR)

IR spectroscopy measures the absorption of infrared light by the sample, providing information about the molecular structure of inhibitors. It is useful for identifying specific functional groups and analyzing complex mixtures.

Atomic Absorption Spectroscopy (AAS)

AAS is used for inorganic inhibitors that contain metal ions. It measures the absorption of light by free atoms, providing highly accurate quantification of metal-containing inhibitors.

Electrochemical Methods
Electrochemical techniques measure the electrical properties of the sample to analyze corrosion inhibitors. These methods are highly sensitive and can provide real-time monitoring.

Electrochemical Impedance Spectroscopy (EIS)
EIS measures the impedance of a system over a range of frequencies, providing information about the corrosion processes and inhibitor performance. It is a powerful technique for studying the effectiveness of inhibitors in real-time.

Emerged Detectiontechniques
There are several emerged technologies listed in the literature targeting field applications. Paper-Based Analytical Devices (PADs) have been emerged as a potential technology for replacing conventional ones for detection quaternary ammonium corrosion inhibitors using a portable 3D printed colorimetric sensor. The colorimetric reaction mechanism was based on dye reaction in an acidic medium. This technique was applied to analyze residual inhibitors produced water from pipelines. The advantages of these devices are simplicity of their use in field, portability, low cost, easy-to-use, and ability to integrate PADs with different analytical techniques. However, this approach may suffer from low reproducibility, poor selectivity and low sensitivity when compared to other methods.

A second technology example which is powered by a hand-held Raman spectrometer instrument to measure corrosion inhibitor residual at the ppm level as been claimed. The portable instrument allows field samples to be analyzed on-site. A calibration curve with a wide range of standard solutions of corrosion inhibitor shall be constructed based on the intensity of specific peaks in the spectrum. The next step is to stabilize the filtered sample by mixing it with a proprietary product and followed by the addition of a metal nanoparticle suspension solution. Finally, the obtained spectrum of the corrosion inhibitor residual of field samples will be compared with the calibration curve.

Fluorescence chemistry and tagged polymer technological approach has been adapted and protected by more than 27 patents to monitor and control the tendency of scale formation, corrosion rate, residual, and biological activity in the system. There are several challenges to applying fluorescence-based monitoring to water treatment. The molecule must be reasonably inert under the system's operating condition. In addition, various impurities in the water may fluoresce where others may absorb or scatter some of the light. This will distort product feed control accuracy. Another major disadvantage which is fluorescence will vary with temperature and so temperature compensation is needed for precise measurements. The main advantages of the developed technology are; fluorescence test does not require handling of test reagents, and the characteristic of fluorescence enables different types of molecules to be accurately measured at very low concentrations. Thus, the amount of fluorescent component in the product formula can be quite low and overall cost-effective.

Another portable optical measurement technology controlled for fluorescence was also introduced for quantification of corrosion inhibitor residuals in oilfield waters. It is suitable for inhibitor packages contain fluorescent products, such as quaternized alkyl pyridines. The fluorescence compounds are directly proportional to concentration only if they fall within the linear range of the calibration curve for the tested product. If the corrosion inhibitor residual concentration in the original water sample is unknown, then obtaining separate determinations on multiple dilutions is advisable. This technology is limited to selected fluorescence compounds and calibration curve must be developed for each individual corrosion inhibitor due to differences in formulations. Furthermore, the fluorescence signal is temperature dependent which mandates that the calibration and sample measurements must be done at the same temperature to obtain accurate concentration data.

TrueDetect™(TD)
This technology has developed to measure corrosion inhibitor at site which is based on a nanotechnology-enabled Raman spectroscopy (SERS) technique. TD is powered by a hand-held Raman spectrometer instrument to measure corrosion inhibitor residual at the ppm level as been claimed. The portable instrument allows field samples to be analyzed on-site. In comparison with traditional analytical laboratory techniques. Field trials were performed using inhibited water-based field brine and monoethylene glycol (MEG) samples.

Prior to TD analysis, a calibration curve with a wide range of standard solutions of corrosion inhibitor shall be constructed based on the intensity of specific peaks in the spectrum. The residual hydrocarbon that might present in field samples shall be removed by passing them through a cartridge. The next step is to stabilize the filtered sample by mixing it with a proprietary product and followed by the addition of a metal nanoparticle suspension solution. Finally, the complex mixture is ready for analysis using a handheld.

3D TRASAR™ (Ecolab)

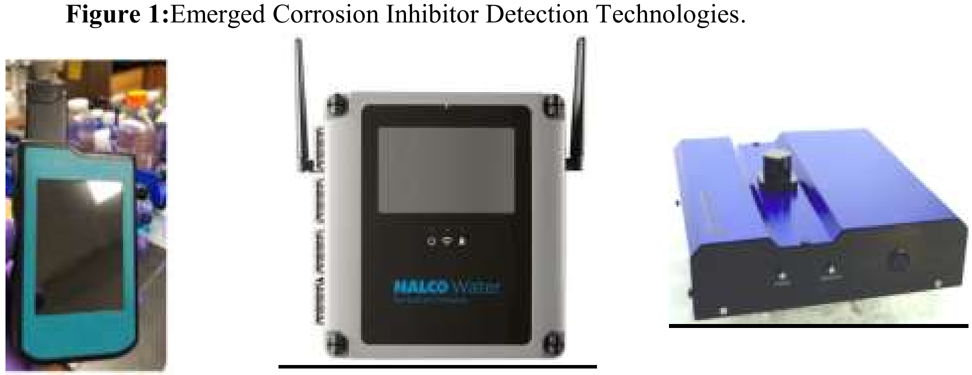
It is been developed by Ecolab for cooling water application, solid cooling water system and clean in place optimization program. It includes fluorescence chemistry and tagged polymer to monitor and control the tendency of scale formation, corrosion rate, residual, and biological activity in the system. Ecolab's claimed that 3D TRASAR is protected by more than 27 patents as shown in Figure 1-B.

There are several challenges to applying fluorescence-based monitoring to water treatment. The molecule must be reasonably inert under the system's operating condition. The main advantages of 3D TRASAR technology are; fluorescence test does not require handling of test reagents, and the characteristic of fluorescence enables different types of molecules to be accurately measured at very low concentrations. Thus, the amount of fluorescent component in the product formula can be quite low and overall cost-effective. In contrast, various impurities in the water may fluoresce where others may absorb or scatter some of the light. This will distort product feed control accuracy. Another major disadvantage which is fluorescence will vary with temperature and so temperature compensation is needed for precise measurements.

LabBoxTechnology™(Wilson Analytical)

It is an optical measurement system controlled for fluorescence using Wilson AnalyticalLightPilot software for quantification of corrosion inhibitor residuals in oilfield waters as shown in Figure 1-C. LabBox is suitable for inhibitor packages contain fluorescent products, such as quaternized alkyl pyridines. Alkyl pyridine quat intermediates are "quaternized" by heating under pressure with a quaternizing agent such as benzyl chloride. Typically, 30% or more of the starting material remains unquaternized. Fluorescence spectroscopy is a more selective and sensitive spectroscopic technique compared to UV-Vis absorption measurements. This is because not too many species fluoresce, although most substances absorb. So, the fluorescence method is much more sensitive than UV-Visible absorption methods. Quaternary amines are fluorescent and can be easily detected at low concentrations and imidazolines or amidoimidazolines may also be detected by fluorescence spectroscopy by complexing this analyte with fluorescamine. The inherent sensitivity of fluorescence spectroscopy means that much lower analyte concentration can be detected. While the fluorescence method is a suitable analytical technique for heterocyclic aromatic compounds, it has not been extensively used independently and specifically for CI detection. This lack of adoption may be due to the satisfactory attractive features of UV-Vis colorimetric methods such as low cost and simplicity. However, several chromatographic and capillary electrophoresis methods may use fluorescence machines as detectors. Regardless, a bioluminescence method has been previously used for the determination of minimal concentrations of biocorrosion inhibitors.

Figure 1: Emerged Corrosion Inhibitor Detection Technologies.



Case Studies and Applications

To illustrate the practical applications of these laboratory technologies, several case studies from various industries are presented.

Oil and Gas Industry

In the oil and gas industry, maintaining the integrity of pipelines and equipment is crucial. Residual analysis of corrosion inhibitors using HPLC and potentiometric titration has proven effective in ensuring optimal protection and preventing costly failures.

Water Treatment Plants

In water treatment plants, controlling corrosion is essential to maintain water quality and system efficiency. UV-Visible spectroscopy and AAS are commonly used to monitor inhibitor residuals, ensuring effective corrosion control while minimizing environmental impact.

Manufacturing Industry

In manufacturing, especially in high-temperature environments, inorganic inhibitors are widely used. Chromatography and electrochemical methods provide detailed analysis of inhibitor performance, helping to optimize usage and reduce operational costs.

Challenges and Future Directions:-

Residual Corrosion Inhibitors Determination Challenges:

Serious challenges are facing chemists who need to work on developing corrosion inhibitor residual methods including eliminating or minimizing interferences present in samples. Several limitations to the available procedures have become apparent. Some of the identified challenges in literature are:

1. There is no international or industrial recommended practice for detection corrosion inhibitor residuals.
2. Commercial corrosion inhibitors are complex mixtures and formulated with two or more components such as quaternary amines, imidazolines, amides, phosphate esters and surfactants.
3. Other oilfield chemicals might also be present in the fluid to be examined such as biocides.
4. Produced water chemistry represents a second dimension to the challenge. Produced waters are different in salinity, presence of hydrocarbons, and dissolved gases such as hydrogen sulfide and carbon dioxide.
5. Corrosion inhibitors dosage in produced fluids generally is very low which making the reproducibility of any developed laboratory analytical methods challengeable.
6. Difficulty in maintaining the sample integrity after collection specially in case of remote areas. (Adsorption of corrosion inhibitor in the sample bottle, precipitation, etc.).

The chemistry complexity of corrosion inhibitors presents a challenge in concentration determinations in oilfield waters. Also, many commercial CIs used in oil and gas industry are formulated with two or more components such as quaternary amines, imidazolines, amides, phosphate esters and surfactants. The quaternary ammonium compounds (usually referred to as quats) are particularly interesting because they can function as surfactants. Hence several detection methods developed for measuring residual corrosion inhibitors are solely based on quats. Ideally, any residual corrosion inhibitors monitoring method for a specific CI usually focuses on one of the major water-soluble/water-dispersible components. So, the aqueous phase is the one that is more commonly sampled for measurements. Furthermore, partitioning of different components of commercial CI formulations into different phases does occur and presents an added challenge since this may result in lower concentrations of the chemical species in the phase being measured. In addition, the sampling point can be crucial in establishing reliable corrosion inhibitor residual as a measure of corrosion protection, while maintaining sample integrity is equally important as it can make or break the accuracy of the measurements. Therefore, all these critical factors need to be carefully considered in developing a reliable analytical detection method.

Despite the advancements in laboratory technologies, challenges remain in the residual analysis of corrosion inhibitors. These include the need for more cost-effective methods, real-time monitoring capabilities, and improved sensitivity for detecting low inhibitor concentrations.

Future research is focused on developing advanced materials and techniques, such as nanotechnology-based sensors and automated analytical systems, to address these challenges. These innovations aim to provide more accurate, efficient, and sustainable solutions for corrosion inhibitor residual analysis.

Conclusion:-

Accurate residual analysis of corrosion inhibitors is vital for effective corrosion management, economic efficiency, and environmental protection. A variety of laboratory technologies, including titration methods, chromatography, spectroscopy, and electrochemical techniques, are available to meet the diverse needs of different industries. By understanding and applying these technologies, industries can optimize their corrosion control strategies, extend the lifespan of equipment, and ensure compliance with environmental regulations.The detection and monitoring of residual corrosion inhibitors can be challenging due to the complex nature of the matrix, the partitioning and solubility of the inhibitors and in some cases the remote locations where sampling must be done. Matrix interferences can be minimized by using standard addition approach and almost all the techniques can be tweaked to accommodate this procedure. If possible, the analyte corrosion inhibitor may be isolated from most components of the complex sample by means of solid-phase extraction (SPE) or solid-phase microextraction (SPME), although industrially this approach is not widely used. Partitioning and solubility problems may be minimized by use of partitioned standards while on-site sampling and analysis will alleviate difficulties due to remote sampling. When sampling at remote locations, transporting samples from field to the laboratory may also be problematic and can lead to loss of sample integrity. Also, necessary prompt action may be delayed if it takes a long time to get samples to the lab and perform analysis in order to decide how much corrosion inhibitor needs to be added. Catching a problem early on results in a quick and more effective solution. Aside from the automated fluorescence spectrometer successfully used in the field on-site detection of residual corrosion inhibitors is an advantage. However, simple, portable, fast and reliable detection platforms for such testing is still a big challenge. Such instruments must also meet the requirements of robustness, selectivity and low cost. Automation of such systems will also be an added advantage. Overall, the development of more sensitive, selective, and specific analytical methods for detecting corrosion inhibitors residuals in complex matrices, as well as real-time monitoring capabilities, would be beneficial for the prevention of corrosion in various industries.

Technological Gaps

The detection of corrosion inhibitor residuals can be challenging due to the complexity of the chemical matrices in which they are found. Some of the identified technological gaps are:

1. Lack of reliable and sensitive analytical methods to detect low concentrations of corrosion inhibitors. Corrosion inhibitors may be present in a variety of solutions, including water, oil, and gas. Furthermore, presence of other chemicals and impurities can interfere with their detection.
2. Need for real-time monitoring of corrosion inhibitor residuals in industrial processes. Currently, most analytical methods for detecting corrosion inhibitors require laboratory analysis, which can be time-consuming and expensive.
3. There is also a need for more selective and specific corrosion inhibitor detection methods. Many analytical methods used to detect corrosion inhibitors are not specific to a particular inhibitor, meaning that they cannot distinguish between different types of inhibitors. This can lead to false positives or false negatives in the detection of corrosion inhibitors

Acknowledgements:-

The authors would like to thank Saudi Aramco's management for their kind permission to publish this work.

References:-

1. Jones, D. A. (1996). Principles and Prevention of Corrosion. Prentice Hall.
2. Schmitt, G. (2009). Fundamentals and Applications of Corrosion Inhibition. Chemical Engineering and Materials Science.
3. Roberge, P. R. (2000). Handbook of Corrosion Engineering. McGraw-Hill.
4. Fontana, M. G. (1986). Corrosion Engineering. McGraw-Hill.
5. Uhlig, H. H., & Revie, R. W. (2008). Corrosion and Corrosion Control. Wiley.
6. Mansfeld, F. (1987). Electrochemical Impedance Spectroscopy (EIS) as a New Tool for Investigating Methods of Corrosion Protection. Electrochimica Acta, 32(6), 913-920.

7. Reda, S. M., & Gamal, A. (2009). Electrochemical Methods in Corrosion Research. Corrosion Science, 51(10), 2255-2263.
8. Pourbaix, M. (1974). Atlas of Electrochemical Equilibria in Aqueous Solutions. National Association of Corrosion Engineers.
9. ASTM International. (2017). Standard Guide for Electrochemical Measurements in Corrosion Testing. ASTM G5-94.
10. Zor, T., & Selinger, Z. (1996). Linearization of the Bradford Protein Assay Increases Its Sensitivity: Theoretical and Experimental Studies. Analytical Biochemistry, 236(2), 302-308.
11. Tracey Jackson, Jonathan Vargas, Derick Smith, and Brian Andrews "Corrosion Inhibitor Deliverability– A Corrosion Inhibitor Residual Success Story", 2020 NACE International Corrosion Conference & Expo, Paper No. 14998.
12. Peng Jin, Sankaran Murugesan, Zhengwei Liu, Haitao Fang, Shujun Gao, Lei Huang, Gilberto Guerrero, TraceyJackson, Sunder Ramachandran, and Johnathon Brooks" Prevent Failures and Extend Asset Life: A Reliable Onsite Corrosion Inhibitor Residuals Method Using SERS" SPE International Oilfield Corrosion Conference and Exhibition, 16 - 17 June 2021, Paper No. SPE-205048-MS.
13. Zhengwei Liu, Sankaran Murugesan, Sunder Ramachandran, and Peng Jin" Next Generation Oilfield On-Site Trace Chemicals Analysis by SERS" SPE International Conference on Oilfield Chemistry, Woodlands, Texas, USA, 6 – 7 December, 2021, Paper No. SPE-204369-MS.
14. Lucas R. Sousa, Habdias A. Silva-Neto, Pedro P.E. Campos, Gerson F. Duarte-Junior, Iris Medeiros Junior, Rogerio M. Carvalho, and Wendell K.T. Coltro" A portable tool for colorimetric detection of corrosion inhibitors using paper-based analytical devices" Microchemical Journal 183 (2022) 108024.
15. Resources – Wilson Analytical Services Inc. Wilson Analytical CI Determination Procedure, Corrosion Inhibitor Residual Measurements.
16. Nalco report "Nalco 3D TRASAR® Technology and Essential Expertise Improve Sustainability Performance at a Chemical Plant in Europe" https://ceowatermandate.org/wp-content/uploads/2018/07/CH-1502_-_Chemical_plant.pdf.
17. Abdulmajeed Saeed Al-Ghamdi "Performance Analysis of Automated Control System for Condenser Water Treatment Unit" Engineering, 2012, 4, 55-67.