Water Lens, LLC
4265 San Felipe, Suite 1100
Houston, Texas 77027
Office: (844) 987-5367
www.waterlensusa.com

Pros and Cons of Water Analysis Methods

Prepared by:

Adam Garland, CTO

Water Lens, LLC

ICP-MS/OES

The most sensitive method for detecting ions in solution begins with an Inductively Coupled Plasma (ICP) generator. The operating principle of any ICP based technique is to heat the components of a sample to a sufficient temperature that they become ionized in a plasma. Once these ions are in the plasma, there are two common methods for detecting their presence.

If the plasma is hot enough, ions will begin to emit light in accordance with their atomic spectrum. Each ion's spectrum is specific to it, like a fingerprint. The spectrum can then be analyzed by sufficiently sensitive optical equipment. The intensity of the light being emitted by the plasma is directly proportional to the concentration of each of the ions in the plasma. This means that measuring the light patterns allow the concentrations of the ions to be calculated. This process is called Optical Emission Spectroscopy (OES). Using ICP in this way is known as ICP-OES. Even though the ions are emitting light in this way, the intensity of the emission is very low. The signal must be amplified using Photomultiplier Tubes (PMT) before being detected by the system's optics.

Instead of relying on their optical emission for detection, these ions can alternatively be injected into a Mass Spectrometer (MS). Here, the mass of an ion is directly calculated based on how the ion interacts with a magnetic field inside of the MS. The concentration of the ion is directly proportional to how often a species of that mass is detected. Each time an individual ion of a given mass is detected, the initial signal generated is very weak. The signal is typically amplified using a device called an Electron Multiplier Tube (EMT). This allows the concentrations of the ions to be quantified. When an ICP is used in this way, the combined technique is known as ICP-MS.

Both techniques have inherent advantages and disadvantages. These are summarized in **Figure 1**. Both PMTs and EMTs are very fragile and sensitive to their environment. Vibration or motion will cause these devices not to function appropriately, usually resulting in the machine rapidly losing its calibration. This restricts their application to laboratory environments with tightly controlled conditions. Both instruments will not tolerate high levels of salinity in the samples being run, like those found in the oil & gas industry. While the internal construction of an OES system lends to an increased tolerance of salinity versus MS based systems, both methods will require substantial dilution if the salinity of a sample is too high. This required dilution has a multiplicative effect on the Limit of Detection (LOD) of the instrument. The LOD as given in the specifications for the instrument only applies to an undiluted sample. If, for example, a sample must be diluted by a factor of 10,000:1 before it can be run, then the effective LOD on that sample will be 10,000 times higher than given in the instrument specifications. Although this principle applies to any analytical method when running diluted samples, ICP-MS/OES typically require the heaviest dilutions on a sample before it can be successfully analyzed.

The ICP generator must create large amounts of ions for the ions to be detected. Each element has an inherent amount of energy required to ionize it. This energy is called ionization potential. Elements

with high ionization potentials (such as non-metals) are much more difficult to detect in ICP based systems than elements with low ionization potentials (such as metals) because there are fewer of them reaching the detector.

The high thermal energy imparted by the ICP generator causes the complete breakdown of molecular bonds present in the system. Because of this, almost none of the material that reaches the detector will be involved in molecular bonding. Polyatomic ions such as sulfate (SO_4^{2-}) and ammonium (NH_4^+) are therefore undetectable by ICP based systems because they contain molecular bonds between their elements. In many cases, the presence of polyatomic ions can be calculated based on assumptions about the sample. For instance, while ICP based systems are insensitive to sulfate, they are still capable of quantifying sulfur which is formed whenever sulfate encounters the plasma. This sulfur value can be used to calculate the concentration of sulfate given the assumption that all the sulfur in the sample was originally in the form of sulfate before it was ionized. As with any assumption, this is not necessarily valid and tends to cause false positives in the quantification of species by this method, especially in the presence of sulfide and hydrogen sulfide.

Pros	Cons
• Low LOD, when undiluted sample is capable of being analyzed, compared to alternative methods • High throughput • Increased resistance to interferences compared to alternative methods	• Not sensitive to most anions • Incapable of detecting polyatomic ions • Susceptible to loss of calibration from motion and vibration • Heavy dilution often required for sample analysis

Figure 1. Summary of the pros and cons of ICP based analysis.

Ion Chromatography

Ion Chromatography (IC) is a technique for quantifying dissolved ions in a solution. The critical component of an IC system is the separation column. Ions are separated from each other based on how strongly they interact with the inside of the separation column. As the sample is pumped into the separation column all the dissolved ions enter at the same time. However, some ions will interact with the inside of the column more strongly than others. This will cause some ions to be delayed in exiting the other end of the column more than others. The amount of time it takes for certain ions to make their way through the separation column is specific to each ion, allowing for classification of the ions based on their elution time. The ions pass through a detector as they come through the column which allows their concentration to be measured as well.

There are a number of inherent advantages and disadvantages to running an IC based system. These are summarized in **Figure 2**. The detector is inherently less sensitive than detectors used in ICP based systems, causing the LOD on IC systems to be significantly higher than in ICP based systems. Different separation columns can be used on the instrument based on what is desired to be quantified. This allows the system a very wide scope of detecting dissolved ions, albeit at the cost of maintaining a potentially large selection of separation columns. The detection mechanism does not involve breaking down molecular bonds, which allows an IC system to detect polyatomic ions as well unlike ICP based systems. While ICP based systems detect an entire emission spectrum from each ion present in the system, IC systems detect only an elution time. This makes the IC less specific in its detection than an ICP based system, allowing for comparatively more interferences and signal overlap from ions that come through the column at the same time. Reduction in signal overlap from co-eluting ions is the primary reason that samples on an IC system are often strongly diluted as in ICP based systems. The sample run time is also significantly longer on an IC system compared to an ICP based system. All ions in a sample must be removed from the separation column before a second sample can be run. This process can require up to 30 minutes to complete, resulting in significantly lower throughput than an ICP based system.

Pros	Cons
• Quantifies both anions and cations • Less sensitive to movement and vibration than other methods • Capable of quantifying polyatomic ions	• Large number of components required for wide scope of analysis • Susceptible to co-elution interferences • Lower throughput than alternative methods

Figure 2. Summary of the pros and cons of IC analysis.

X-Ray Fluorescence

X-ray Fluorescence (XRF) is considered the gold standard for analyzing solid samples. The operating principle of XRF involves bombarding a sample with x-rays. Each element will produce a unique spectrum of light when exposed to x-rays. This spectrum can be measured by an x-ray detector and used to determine which elements are present in a sample. The intensity of the spectrum can be used to determine the concentration of those elements.

The inherent advantages and disadvantages of XRF are summarized in **Figure 3**. XRF is unique compared to both ICP-OES/MS and IC in that it does not require a water based solution for analysis. Historically, XRF has been used as a qualitative or semi-quantitative technique compared to purely quantitative techniques like ICP-OES/MS and IC. It has seen extensive use in fields where the detection of small amounts of impurities in a sample is more crucial than determining exactly how much impurity is present. For example, the semiconductor industry requires their silicon samples to be as pure as possible before being transformed into microprocessors, so the ability to detect any impurity at all is more useful than quantifying them. The sample is characterized without having to move through the instrument or move through a column. This allows for very high throughput in gathering the characterization data. The signal from an XRF instrument is very sensitive to matrix effects from other components in the sample, and it is generally not reliable for a calibration curve generated on one sample to be used to quantify multiple samples. To achieve truly quantitative results from an XRF, matrix matched standards or reference materials are required to process each individual sample. Preparing these additional standards and analyzing the results can take considerable time and effort if matrix effects are to be properly accounted for. The intensity and uniqueness of an XRF spectrum is directly related to the number of electrons an element possesses. This means that XRF is much more sensitive to heavier elements than lighter ones. Most XRF instruments will struggle to quantify elements lighter than Sodium, such as Boron and Fluorine. There are also safety concerns associated with using x-rays for sample characterization. Proper standard operating procedures must be followed to ensure safe operation.

Pros	Cons
• Capable of analyzing samples in any matrix • High throughput • Can detect any element of sufficient molecular weight	• Very sensitive to matrix interferences • Limited sensitivity with lighter elements • Considerable time/effort required to run complete sample analysis • Use of x-rays brings up safety concerns

Figure 3. Summary of the pros and cons of XRF analysis.

Legacy Colorimetric Tests

Analytical techniques based on colorimetry have become the go-to method for characterizing samples in the field. Colorimetric methods are based on molecular sensors that are sensitive to specific chemicals. The chemical that a sensor is designed to detect is called the analyte. When a sensor interacts with its intended analyte, it binds with the analyte in a specific way. When this happens, the color of the sensor changes in predictable way. The stronger the change in the color of the sensors, the higher the concentration of the analyte. This change in color is typically quantified by measuring the absorbance of a particular wavelength of light. This absorbance value can be fit to a calibration curve so that the analyte concentration can be quantified.

The advantages and disadvantages of legacy colorimetric tests are shown in **Figure 4**. Colorimetric tests do not commonly require large and expensive equipment, which allows them to be used in the field more effectively than competing methods. Often results are interpreted by eye, making the operation of such tests much cheaper than alternative methods. This of course opens the test to the subjectivity of human observation which leads to systematic errors and an inherently high LOD. The development times of colorimetric tests are very rapid, often a matter of seconds. This enables results to be obtained much more rapidly than competing methods. The binding of a sensor with its analyte is never perfectly specific. Colorimetric sensors are susceptible to interferences which can cause false positives or false negatives depending on the nature of the interaction. Accounting for these interferences can become time consuming and complicated with the number of tests required to measure the interfering species. Colorimetric tests are often single analyte, meaning that multiple different tests with their own respective procedures must be run to obtain data on multiple analytes in a sample.

Pros	Cons
• Quantifies both anions and cations • More portable and field friendly than competing methods • Results are obtained more rapidly than competing methods	• Several different procedures required to test multiple analytes • Human element causes systematic errors • More susceptible to interferences than competing methods • Higher LOD than competing methods

Figure 4. Summary of the pros and cons of legacy colorimetric analysis.

Water Lens™

The Water Lens method is an advanced colorimetric technique which works through all the shortcomings of legacy colorimetric tests. Raw data is generated by the same general principle as other colorimetric techniques. Each sensor as well as all supporting chemicals are preloaded into a 96-well plate. This format allows multiple analyses for multiple analytes to be run simultaneously. If the effects of Samples are directly loaded into each well of the 96-well plate. The colorimetric responses are read by a 96-well plate spectrometer. Once the initial data is imported, the effects of any interferences are processed. By running multiple analyses simultaneously, the Water Lens system can quantify the common interferences for a given sensor at the same time the primary analyte is quantified. This is what allows the system to remove the effects of interferences before reporting the results.

A general comparison of the Water Lens method with other analytical methods is shown in **Figure 5**. The ability of the system to remove the effects of interferences while running multiple samples simultaneously overcomes all the primary limitations of legacy colorimetric methods while maintaining their advantages. This creates a system which is ideal for applications both in the field and in the lab. The system is designed to be operated by a user of any skill level with minimal training. It is capable of characterizing water samples of any level of total dissolved solids due to simple and rapid serial dilution. The total time for sample analysis is approximately 10-12 minutes, including sample preparation. In this time, the primary components of most water samples can be quantified, including cations, anions, and organics as well as several calculated parameters.

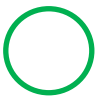
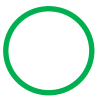
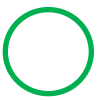
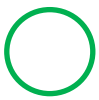
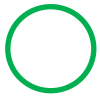
	ICP-MS/OES	Ion Chromatography	X-ray Fluorescence	Legacy Colorimetric Tests	Water Lens
Accurate and precise on real world samples					
Simple to operate at any skill level					
Tolerant of interferences and matrix effects					
Rapidly obtained results					
Cost of analysis equipment					
Deployable in field environment					
Wide variety of parameters per analysis					

Figure 5. Comparison of the Water Lens system to alternative analytical methods.