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GETTING "PEAK" PERFORMANCE OUT OF YOUR ION CHROMATOGRAPH

As instrumentation users, we appreciate our instruments being up and running and have all felt the struggles of instrument downtime. It's no different for users of ion chromatography (IC).

IC is a method for separating and analyzing ions based on their interactions with an ion-selective resin and fluid flowing through it, called the eluent. IC is widely used to identify common anions and cations in applications such as the analysis of pharmaceuticals and water chemistry.

No matter the ion chromatograph being used or the user's level of experience, it is important to understand the basics of IC measurement, maintenance, and troubleshooting. Read on to travel the full path of an ion chromatograph, explore the function of its components, and learn best practices for maintenance and troubleshooting.

THE FLOW PATH

An ion chromatograph works by first taking a sample of the desired mixture and injecting it into the liquid eluent. A high-pressure pump then passes the mixture through a degasser and then through a column containing a fixed adsorbent material. Different analytes adhere to the adsorbent with different affinities—meaning that they move down the column at different speeds and separate. After leaving the column, analytes enter a detector that generates a signal correlating to the concentration of the analyte. The signals are plotted on a graph called a chromatogram, which shows signal intensity over time of an analysis. Retention time, or how long it takes for an analyte to leave the column under particular conditions, is a unique signature for individual components of a sample.

Along an ion chromatograph's flow path, several important components and considerations are critical to instrument reliability and accuracy (figure 1). For example, water is used in all aspects of IC, especially as a major component of

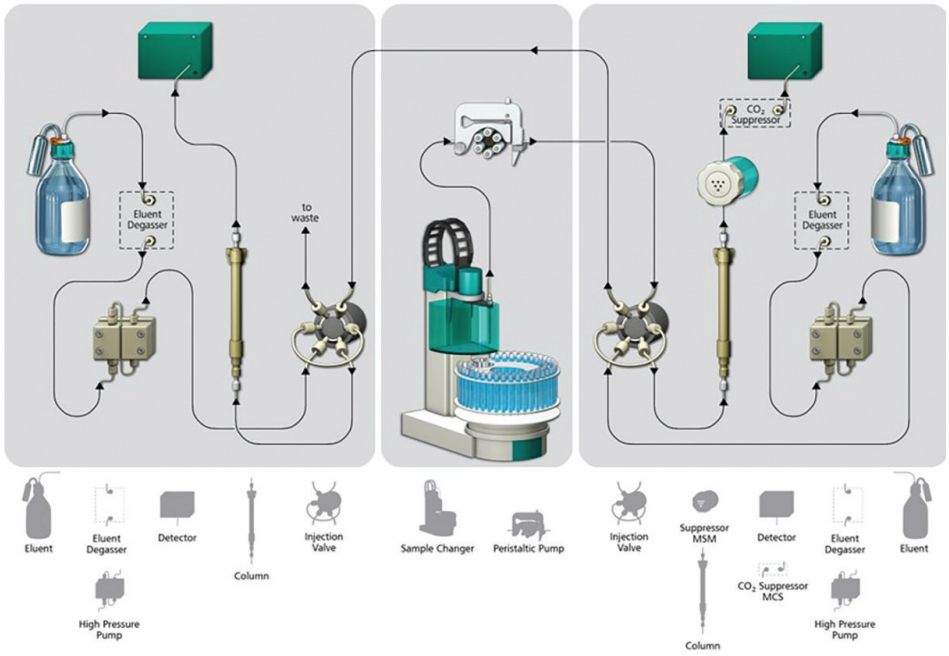

Figure 1: The connections and components of a standard ion chromatography flow path. The setup for anion analysis is on the right and cation analysis on the left. The center panel shows an autosampler and pump that directs analytes into the instrument's flow path. The suppressor MSM and MCS are described in the last section.

Credit: Metrohm USA

the eluent. Water quality is thus important to instrument maintenance, and features of water quality can be an area for troubleshooting.

The optimum purity of water for IC analysis is based on the American Society for Testing and Materials' type 1 water, which has a resistivity greater than 18.2 MΩ-cm. In addition, the water's total organic carbon content should be less than 10 parts per billion, to prevent sudden jumps in pressure during operation.

The other major component of the eluent is the salt-containing concentrate. This can be a solid to add to liquid or a stock solution ready for dilution. As with the water, it is important to ensure that the concentrate is free of particles, microbes, or growth that could contaminate the system. Generally, best practices are to use good-quality salts and commercially available concentrates for IC analysis, and to rinse eluent bottles before refilling.

To prevent acidic gases such as carbon dioxide from into an eluent, it is good practice to attach to the eluent bottle an adsorber tube containing soda lime. Diligence in replacing the material in the tube can help prevent dissolved gases from changing the eluent pH. Any changes to the eluent could cause a change in retention time for analyte ions.

Other important components at the eluent bottle may include the aspiration filter, which helps remove particles; the eluent degasser is a 660 µL chamber that removes bubbles from the eluent.

AUTOSAMPLER

Many scientists rely on autosamplers for proper automated sample handling. There are a few key elements in guaranteeing a high-functioning autosampler (figure 2).

A major component of an autosampler is the needle, which carries samples from the vials to the instrument. Check the needle frequently to ensure that it is clean outside and free of clogs inside.

After the needle, there is peristaltic tubing, which is a form of liquid handling on the autosampler. Check the tubing monthly to ensure that the specified flow is achieved according to the type of tubing and the rate at which the pump is moving. See that the tubing is not worn or flattened and that the polypropylene cartridge holds it taut.

Ultrafiltration can be used to automate the filtering of particles from the sample and reduce costly and time-consuming manual filtration. Change the membrane weekly and clean the ultrafiltration cells to prevent carryover. Note that the time between filter membrane changes can vary depending on the type of samples being analyzed.

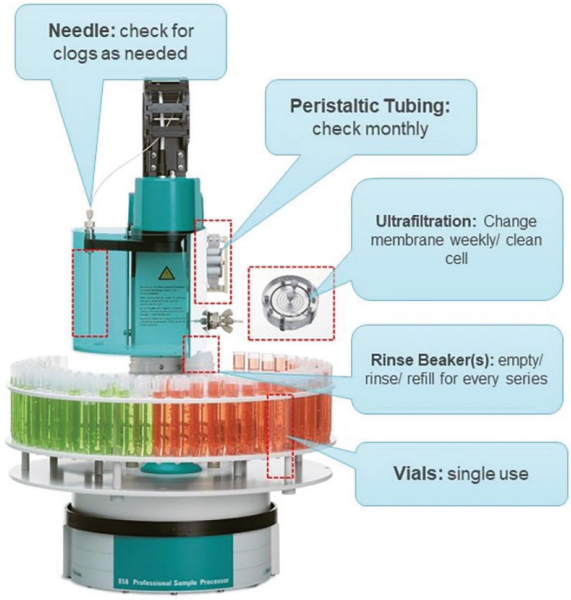

Figure 2: Recommendations for autosampler maintenance.

Credit: Metrohm USA

The rinse beakers rinse the outside and inside of the needle as well as the sample flow paths through the loop. It is important to empty, rinse, and clean the beakers with every sample series to prevent contamination. Be sure to label them appropriately and dispose of them correctly to prevent collecting incorrect data.

To simplify autosampler maintenance, ensure that the samples are soluble in aqueous media and free of particles. Further, take advantage of in-line sample preparation techniques such as ultrafiltration, matrix elimination, preconcentration, and cartridges.

HIGH-PRESSURE PUMP

The high-pressure pump head consists of four components: piston, seal, inlet valve, and outlet valve. Together, they maintain the flow of the eluent through the system and hence, the system's pressure.

Seals help bring the pump up to pressure. Watch for leaks or any crystallization damage to the pistons. It is typically a good practice to check behind the pump head for salt buildup, which indicates that it is time to change the seal.

Check valves maintain the directional flow of eluent and can relieve excessive pressure build-up. The inlet and outlet valves can be examined by squirting water through the valve both in and against the direction of flow to ensure flow is only in one direction. Reduced or absent flow or pressure suggests the inlet valve needs maintenance. Ideally, both the inlet and outlet valves should be replaced annually.

PURGE VALVE

The purge valve clears out the pump when it is time to change the eluent. When switching concentrations of eluent, or from anion to cation analysis, for example, it is a good idea to purge the system.

In addition, the pressure sensor is located at the purge valve. When the valve is closed, the sensor monitors the pressure in the system; when it opens, the system experiences a pressure drop.

There are several things to watch with the purge valve. Damage to the screw on the valve can lead to a pressure drop. If the valve is accidentally closed during the purge process, the increased eluent flow could damage the column. Finally, air bubbles retained in the system after purging could lead to vapor lock and, eventually, no eluent flow (figure 3).

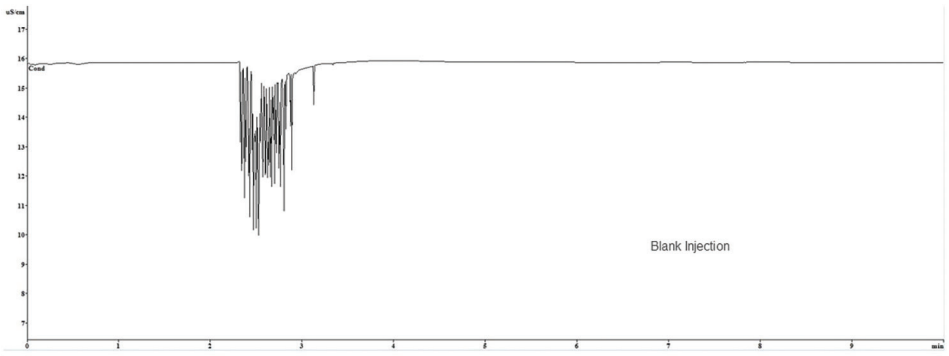

Figure 3: An air bubble in the system during ion chromatography analysis causes pressure ripples in the resulting data.

Credit: Metrohm USA

IN-LINE FILTER

Downstream from the high-pressure pump is the in-line filter, which helps protect the column from any contaminant that could come from the eluent. Blockage can lead to higher pressure on the system. In-line filters should be replaced quarterly or when issues such as increased pressure are observed.

PULSE ABSORBER

The pulse absorber, also known as the pulsation dampener, reduces pressure on

the column that can occur from the starting and stopping of the high-pressure pump. Changes in pressure from the pump can lead to noise in measurements or shorten a column's lifetime. Hence, the pulse absorber improves measurement reliability and prolongs the column's usability.

When troubleshooting on this component, look for damage to the packing material. For example, the presence of a blue liquid leaking from the pulsation dampener usually indicates such damage. If this is observed, good practice would be to shut down the instrument, remove the column from the flow path, and rinse the instrument clean of any packing material in the flow path.

Ideally, this component should be replaced only if damaged.

PERISTALTIC TUBING, INJECTION VALVE, AND SAMPLE LOOP

The peristaltic tubing is a three-stopper tubing used for sample handling. Some signs of trouble with this component include flattened tubes or reduced flow (figure 4). To ensure that the tubing is installed correctly, a good practice is to gradually increase pressure until the flow is visible. After this, check for the flow guidelines based on the instrument manual.

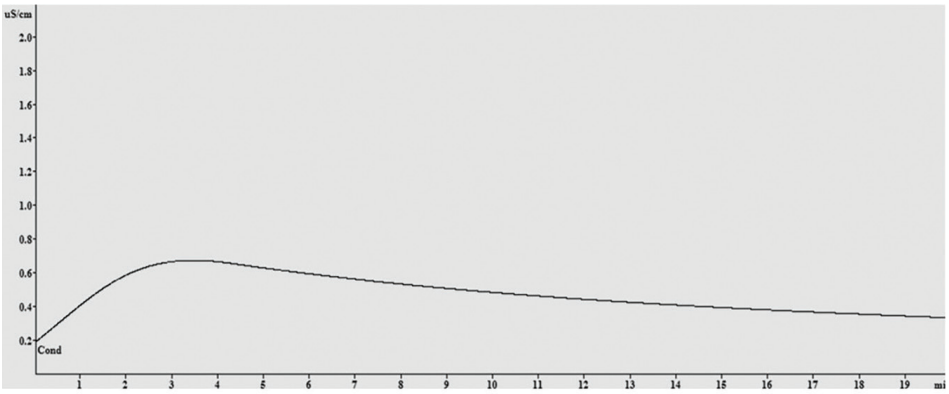

Figure 4: Overused and flattened peristaltic tubing can prevent a sample from filling the loop that leads to the flow path, resulting in no peaks appearing in a chromatogram.

Credit: Metrohm USA

Another important component is the injection valve, which meters the sample volume. Problems here can lead to peak broadening or low repeatability of measurements, so it is important that the valve is installed correctly, clean, and free of blockages. Injection valves are usually maintained by service providers, who should be contacted with any issues.

Finally, the sample loop is for loading samples. The first step in troubleshooting is to check for proper connections. In some instances, the polymer material in the tube can become activated, resulting in increased calcium and magnesium in the cation analysis. A good way to overcome this is to rinse the loop with concentrated nitric acid before use.

COLUMN

The analytical column houses the stationary phase of ion chromatography and is responsible for the separation of analytes. It is important to follow manufacturers' instructions (usually found in the column manual) on storage, monitoring, and regeneration for the particular column in use. Things that indicate when troubleshooting is needed include peak shifting and broadening, loss of analyte resolution, and overall poor performance.

Guard columns serve as an additional way of protecting the analytical column from contaminants in samples such as organics or small particles. The most popular type of guard column is the on column, which is attached directly to the column rather than connected with additional tubing.

Blockage or damage to a guard column could present in the chromatograms as poor peak shape, decreased resolution, or unacceptable repeatability. High back pressure can be a sign of blockage or microbial growth in the column.

IN-LINE SUPPRESSION

Most anion analysis requires in-line suppression. Suppression reduces background conductivity of the eluent while increasing the conductivity of analytes, optimizing system sensitivity. During suppression, the positively charged ions of the eluent, along with positively charged counterions of the analyte anions, are replaced with protons via ion exchange.

Metrohm leverages a proprietary Metrohm Suppressor Module (MSM) in its IC systems. The MSM is a three-chamber system that performs suppression, regeneration, and rinsing simultaneously, so a freshly regenerated cartridge is always available for every new sample. The goal of the MSM is to increase signal conductivity and lower the chromatogram baseline, which raises the measurement's signal-to-noise ratio.

Metrohm also offers a Metrohm Carbonate Suppressor (MCS), which works together with the MSM to lower the chromatogram baseline via the removal of CO_2 from the system (figure 5). Carbonic acid eluent leaving the MSM separates into water and CO_2 gas, which is vented out of the system via the MCS. The

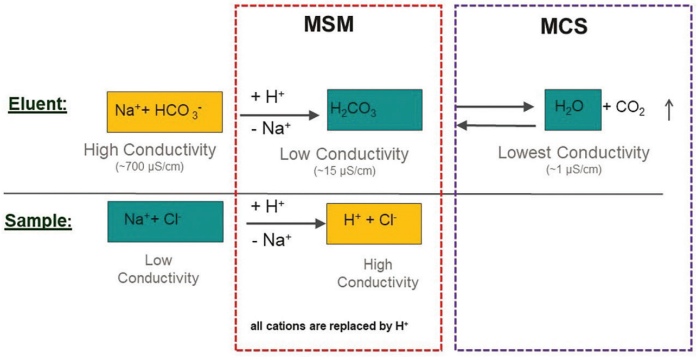

Figure 5: The Metrohm Suppressor Module (MSM) and Metrohm Carbonate Suppressor (MCS) exchange positively charged ions in the analyte and eluent to increase measurement sensitivity for ion chromatography.

Credit: Metrohm USA

result is a 30% increase in sensitivity due to enhanced overall peak response. Maintenance on the MCS is rare, and Metrohm should be contacted if needed.

Indications for suppressor maintenance include high conductivity, leaks from a chamber, contamination, and pressure changes. The MSM is generally very robust and will rarely need replaced, however, the cartridge can be easily replaced by the user if needed. Some areas to watch for on the MCS are back pressure, vacuum stability, and damage or clogging in the cartridge.

CONCLUSION

An ion chromatograph is a complex device with many different components, each with its own unique and important function. To achieve the best possible measurements and minimal instrument downtime, it is essential that users understand these components and their possible points of failure. With a deep understanding of the best practices for IC maintenance and troubleshooting, users can ensure proper measurement and device lifetime.

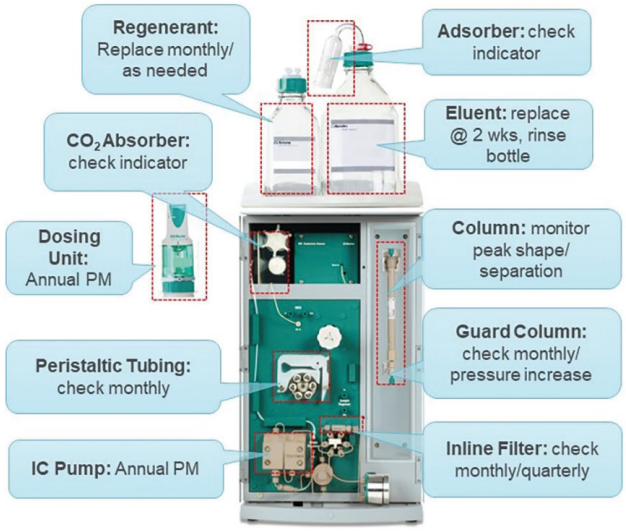

Figure 6: Recommended maintenance intervals on various components of ion chromatograph.
Credit: Metrohm USA

Figure 6 provides suggested maintenance intervals for the major components of an ion chromatograph. It is important to note that these are simply recommendations, and actual frequency of maintenance will depend on a number of factors, including type of sample and number of analyses. Each lab should establish a routine maintenance schedule to fit its needs and ensure optimal system performance.

REFERENCE:

1. C&EN webinars, Keep Your IC Running at "Peak" Performance, Metrohm USA, September 2022. https://connect.acspubs.org/CENWebinar_MetrohmUSA_9_27_22

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