Ion chromatography – addressing the latest challenges in environmental analysis

Thomas Kolb, Product manager ion chromatography, Metrohm Germany

The analytical challenges of environmental analysis increase in difficulty from year to year. As well as analysis of particularly toxic types of metals such as chromium(VI), highly diverse and partially persistent organic fluorine compounds (e.g., trifluoroacetic acid) are presently in focus. The analysis of toxic oxohalides such as bromate and perchlorate is also a current subject of investigation.

Metrohm International Headquarters; Herisau, Switzerland

There are various means of achieving the lowest possible determination limits for the targeted trace parameters/analytes in the presence of high concentrations of chloride, nitrate, carbonate or sulfate often found in the complex environmental matrices. One approach is the coupling of chromatography systems with high-sensitivity, extremely specific mass detectors **[1]**, a long-established procedure in organic trace analysis.

Many trace analysis tasks in the ion chromatography field can also be performed with the far more robust and more affordable conductivity or UV/Vis detectors. In order to achieve the required determination limits, larger injection volumes are sometimes necessary, which can only be supplied by optimized and intelligent sample preparation techniques.

For many years now, numerous customers have experienced the value of Metrohm's Inline Sample Preparation for areas such as environmental analysis in their day-to-day work. Not least, Inline Dialysis, used by our customers for over 20 years, offers clear benefits compared to manual sample preparation techniques. Inline Ultra-Filtration and Inline Dilution have also long proved their worth in combination with Metrohm ion chromatographs.

These techniques are often capable of analyzing complex matrices, improving precision and accuracy of analysis results and minimizing time spent and cost of consumables.

Inline Dialysis	Fully automatic separation of high-molecular matrix components and particles for protecting the separating column using patented Metrohm Stopped Flow Dialysis.
Inline Ultra-Filtration	Fully automatic filtration (0.2 µm) of samples during sample introduction.
Inline Dilution	Fully automatic dilution system can be based on logical software decisions, combinable with Inline Dialysis an Inline Dilution.

Table 1. Summary of the three main Inline Sample Preparation Techniques

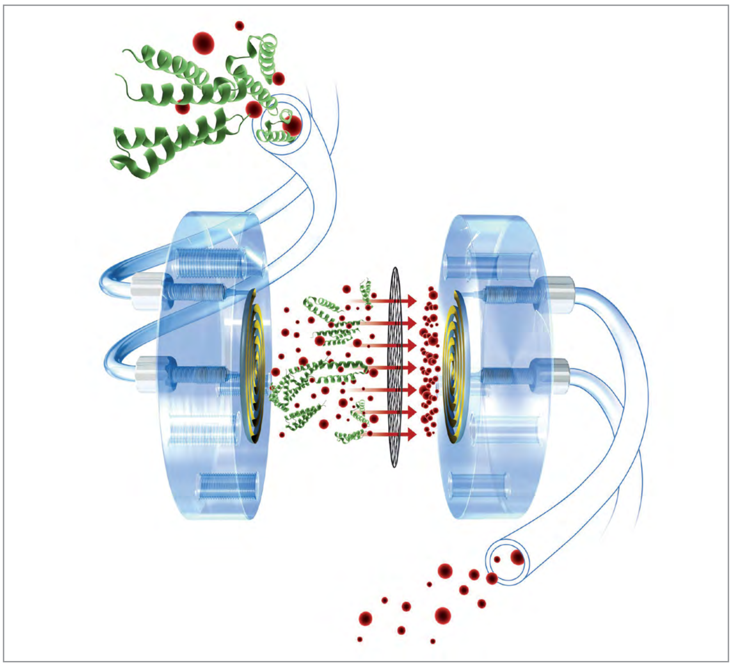

Figure 1. Working principle of patented Stopped Flow Dialysis:
During the whole sampling process, the charged sample is continiously passed through the sample side of the Dialysis Cell, to the left of the membrane. On the opposite side of the membrane, an acceptor solution is sitting idle in the dialysis cell and is being charged with the ions passing through the membrane due to the existing concentration gradient. This process is only stopped when an equilibrium is established, and thus the concentration of the acceptor solution matches that of the original sample. Finally the acceptor solution is injected directly and fully automatically into the IC.

Current applications in water and environment al analysis

In October 2017, the new ISO 19340:2017-10 for determining dissolved perchlorate in water samples by means of ion chromatography was published **[2]**. Perchlorate has come to public attention as an ionic contaminant of food which is also found in drinking water. By inhibiting iodine uptake in the thyroid gland, perchlorate can be harmful to health, especially in persons with iodine deficiency or thyroid disease and in newborns and children **[3]**. Unlike other countries, Germany currently has no threshold values for perchlorate in drinking water. Ion chromatography allows trace levels of perchlorate to be determined in drinking water next to higher concentrations of ions such as chloride, nitrate and sulfate. Apart from injecting the sample directly, detection sensitivity can be further improved by the use of a special re-injection technique, such as is described in ISO 19340:2017-10, Annex B. Unlike comparable procedures which use two coupled chromatographs, the technique described here merely requires an additional injection valve in addition to the classical ion chromatograph. This simplifies the used setup in many ways.

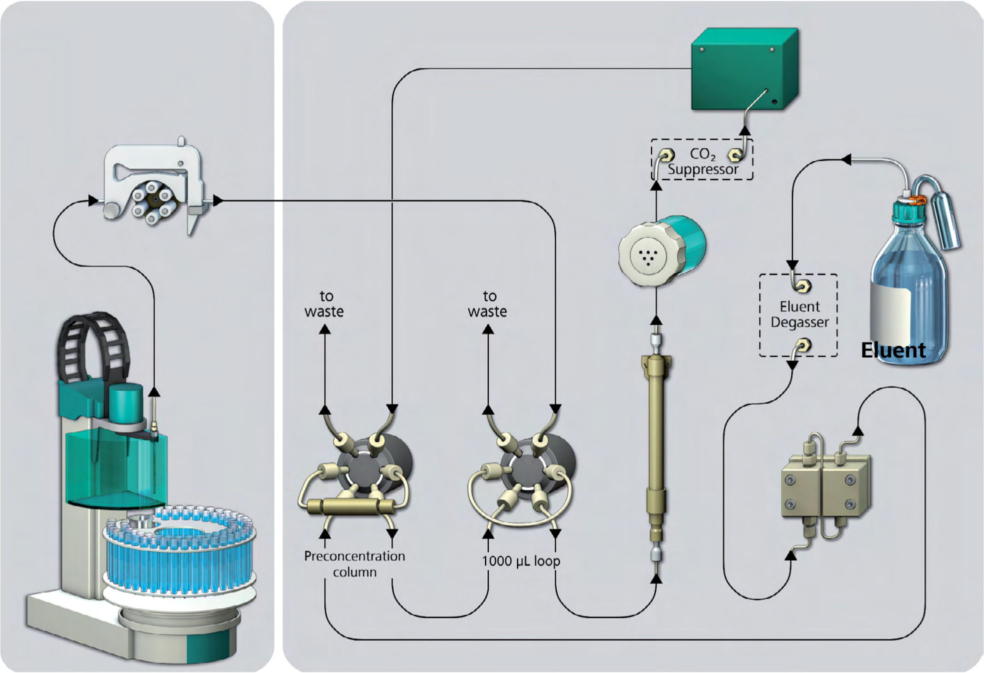

Figure 2. Set-up of an IC system for re-injection analysis

Re-injection analysis can also be used for determining traces of the environmental pollutant TFA (trifluoroacetic acid) **[4]**. TFA has hitherto been described as a non-relevant metabolite of the pesticide Flurtamone, for which the German Federal Environmental Agency has assigned a health protection benchmark (GOW) of 3 µg/L in drinking water **[5]**. It is important to monitor the quantity of TFA which could escape into the environment via the decomposition if coolants and other fluorine compounds. This important industrial solvent is highly water soluble, mobile and stable, properties which could lead to contamination of bank filtrates and aquifiers. The use of re-injection analysis allows the analysis of trifluoroacetic acid in different water samples in the lower µg/L range (e.g. for monitoring the GOW) with a simple IC system, merely extended with the use of an additional 6-port valve **[6]**. Alternative procedures for comparable trace analysis are often associated with a far greater use of apparatus (e.g. an IC-MS coupling).

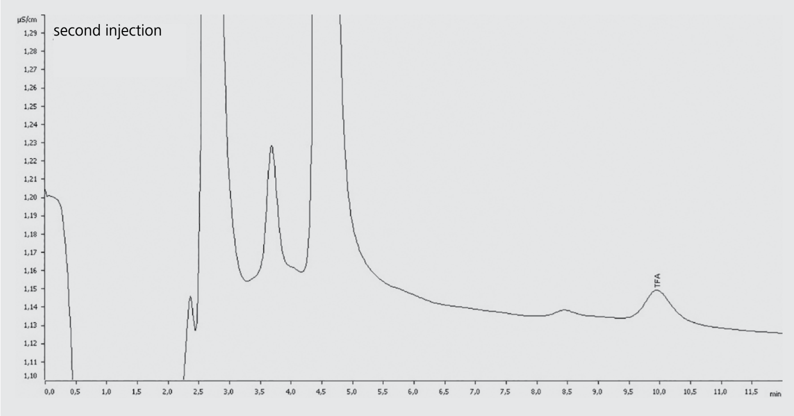

Figure 3. Chromatogram (re-injection) of a water sample prior to water treatment, result 4.8 µg/L TFA

Alongside TFA, more than 3 000 other per- and polyfluorinated substances may occur as contaminants in water and environmental samples **[7]**. As a project of the DIN Standards Committee NA 119-01-03, a standard for determining organically bound fluorine after adsorption to active charcoal via combustion ion chromatography (CIC) is currently being developed (Adsorbable organic fluorine compounds, AOF). This should provide a sum parameter permitting the estimation of the total contamination of water samples with organic fluorine compounds. The procedure has been developed in connection with AOX determination. It involves feeding a 100 mL of a water sample though columns packed with active charcoal. Following a subsequent flushing stage optimized to remove inorganic components, the active charcoal is transferred into a quartz or ceramic boat and combusted in an oxygen stream with addition of water (hydropyrolysis). The combustion gases are led through an adsorption solution, which is finally injected into an ion chromatography system. As well as the determination of organic fluorine compounds, this technique also allows the detection of adsorbable chlorine, bromine and iodine compounds. The Metrohm combustion ion chromatography system (CIC) used for combustion and analysis is a special fully-automated combination of inline sample preparation and ion chromatography, which is used in various fields for routine analysis of halogens and sulfur following combustion. The whole system is controlled by the Metrohm chromatography software MagIC Net. In order to guarantee complete combustion, a flame sensor is used which automatically controls and adjusts the passage of the sample boat through the combustion oven.

Figure 4. Metrohm Combustion IC system for determining adsorbable organic fluorine compounds (AOF)

One ionic trace parameter which has recently received increased attention in the drinking water analysis area is chromium(VI). Several years ago, the Federal Environmental Agency commissioned an opinion on the «Potential harmfulness of chromium» **[8]**. This led to discussions about a new threshold value for chromium(VI) of 0.3 µg/L. The current Drinking Water Ordinance for total chromium lays down a threshold value of 50 µg/L.

Anion exchange chromatography is excellently suited for distinguishing chromium(VI) from the less toxic chromium(III). In order to achieve a high detection sensitivity, after separation, detection is carried out by post-column derivatization with diphenyl carbazide, followed by VIS detection at 538 nm of the red color formed. This procedure, which has proved useful for many years for chromate determination in leather extracts **[9]** and for determining hexavalent chromium in migration specimens from toys **[10]**, permits detection thresholds in water sample analysis in the region of 0.02 µg/L chromium(VI). The method is described in EPA 218.7 **[11]** and elsewhere, and provides a good alternative to the far more cost-intensive IC-ICP-MS coupling.

The examples described show how ion chromatography methods with optimized inline sampling preparation (TFA, perchlorate, AOF), or with specialized detection techniques (chromium(VI)) can be used for modern trace analysis of ions in the environmental field. The procedures often represent a far cheaper alternative to the expensive coupling techniques. The robustness, high automation and low consumption costs of these systems makes them very well suited for routine analysis in connection with large sample volumes.

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