

Suppression in ion chromatography



More sensitive analysis of anions and organic acids

What is suppression?

02

Suppression plays a key role in the analysis of anions and organic acids using ion-exchange chromatography and conductivity detection.

Suppression

- decreases the background conductivity of the eluent
- minimizes baseline noise
- transforms analytes in free anions with protons as counterions (which involves a remarkable increase in the conductivity signal)
- optimizes the signal-to-noise ratio
- increases the detection sensitivity of the measurement system

The Metrohm Suppressor Module

The patented Metrohm Suppressor Module (MSM) is a suppression solution that is just as smart as it is reliable. It consists of a small rotor, containing three cartridges filled with cation exchanger resin. While one cartridge is used for suppression, a regeneration step is performed on the second one. The third cartridge is rinsed automatically during this time. Thus, a freshly regenerated suppressor cartridge is always available for every new sample.

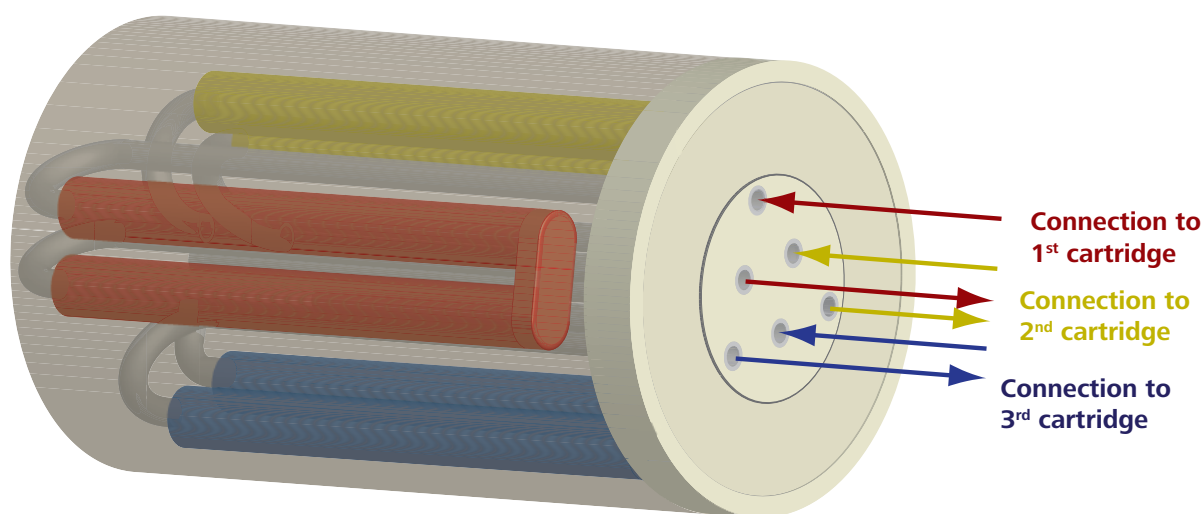
And now: STREAM – the green way of suppression

Suppression with the MSM is optimized and simplified even further thanks to STREAM (Suppressor Treatment Reusing Eluent After Measurement). STREAM refers to a process whereby, rather than simply disposing of the suppressed eluent after the detection, the eluate is used to rinse the regenerated suppressor unit. STREAM also leads to a significant reduction in regenerant consumption.

The advantages of STREAM at a glance

- No need for ultrapure water as a rinsing solution
- Less waste
- Regenerant consumption reduced by a factor of 3
- Significant reduction in demand for consumables

As a result, the system can be operated for much longer without requiring any intervention by the user.





The Metrohm Suppressor Module at a glance ...

- 10 year warranty
- 100% pressure stability
- 100% resistance to organic solvents
- Short conditioning time
- Minimum noise of < 0.2 nS/cm
- STREAM – the green way of suppression
- Cost-effective and robust

... and the advantages for the user

- The excellent signal-to-noise ratio enables anions and organic acids to be analyzed down to the ultratrace range.
- The IC system is only in operation when you really need it – saving eluent and consumables. Restarting after a pause is easy and convenient. Measurements can be started just half an hour after starting the system.
- The application can be changed at any time with no impact on system performance.
- If required by the application, an organic solvent can be added to the eluent.
- For even more sensitive quantitative analyses and additional qualitative results, the IC system can be coupled to an MS or ICP/MS at any time.

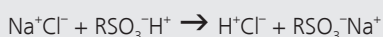


Chemical suppression

The MSM consists of three cartridges filled with cation exchanger material. The first cartridge is used for suppression. Simultaneously, the second cartridge is regenerated with diluted acid (e.g., sulfuric acid) and the third cartridge is rinsed with the eluate or water. Before each analysis, the suppressor is rotated 120° so that a freshly regenerated and rinsed cartridge is always available for suppression.

Reactions that take place during chemical suppression

Analyte:

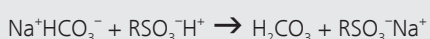


R = substrate

This example of an anion analysis includes a sodium analyte counterion. This ion is replaced with a proton with an equivalent conductivity that is five times higher. This significantly increases the conductivity of the sample solution and therefore also the signal strength.

Salts from weakly dissociated acids (e.g., sodium carbonate/sodium hydrogen carbonate) are used as eluent.

Eluent:



R = substrate

The eluent counterions are also replaced with protons. The carbonic acid that is produced in this way is unstable and only weakly dissociated, meaning that lower background conductivity is measured. Depending on the eluent composition, background conductivity values of 10 to 20 $\mu\text{S}/\text{cm}$ are typical for chemical suppression.

Sequential suppression

Sequential suppression combines chemical suppression and CO_2 suppression. For this, a Metrohm CO_2 Suppressor (MCS) is used in addition to the MSM.

Sequential suppression reduces the background conductivity further ($< 1.5 \mu\text{S}/\text{cm}$), minimizes the impact of carbonate in the sample matrix ($> 98\%$ of carbonate removed) and improves the separation of the injection peak from early eluting anions, such as fluoride. This also further increases the sensitivity of the analysis of anions and organic acids.

The MCS consists of a gas-permeable membrane, which is surrounded by a chamber and contains a vacuum. The carbonic acid produced during chemical suppression breaks down into carbon dioxide and water. The carbon dioxide diffuses through the gas-permeable membrane and is removed. This allows the chemical equilibrium to shift more and more towards carbon dioxide and water. As less and less carbonic acid and therefore less dissociated carbonic acid is present, background conductivity is reduced even further. This in turn improves the signal-to-noise ratio and allows lower detection limits than those that would be possible with chemical suppression alone.

The reaction that takes place in the Metrohm CO_2 Suppressor (MCS)



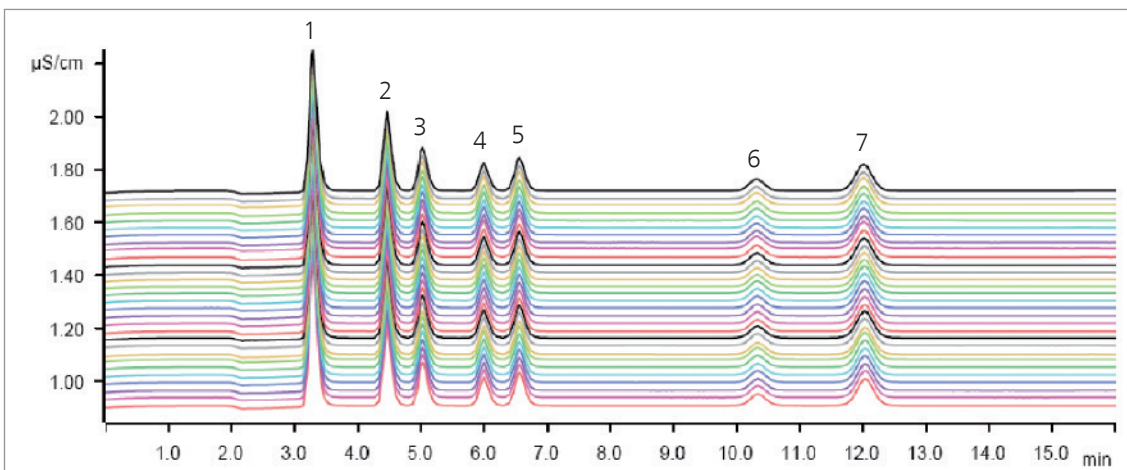


Precision with every analysis

A fresh suppressor cartridge is used for each measurement with the MSM. This means that users can be sure they are always working with a cation exchanger that is

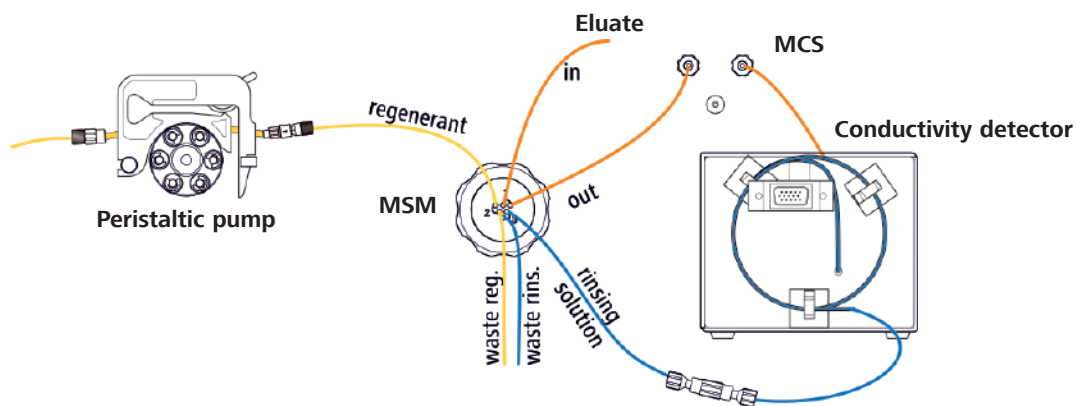
delivering its full performance: today, tomorrow, and for many years to come.

The chromatograms below demonstrate the outstanding reproducibility of measurements provided by the MSM – here with sequential suppression:



30 injections, separation of the standard anions on Metrosep A Supp 5 - 100/4.0, eluent 3.2 mmol/L Na_2CO_3 / 1.0 mmol/L NaHCO_3 , flow rate 0.7 mL/min, loop 20 μL , 45 °C, sequential suppression

Peak	1	2	3	4	5	6	7
Anions	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
Concentration in mg/L	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Relative standard deviation in % (n = 30)	0.26	0.06	0.42	0.17	0.30	0.46	0.25



Flow diagram for STREAM with peristaltic pump: the eluate is suppressed in the MSM and MCS before it is detected in the conductivity detector. The regenerant is supplied by a peristaltic pump.

Regeneration – two versions

Two options are available when it comes to regenerating the suppressor: the new STREAM process and the conventional version.

STREAM is the standard version that comes with every Metrohm IC. As described, STREAM reduces the consumption of chemicals and increases convenience for the user.

Conventional suppression is used if the eluent is coupled to another detector following conductivity detection (e.g., PCR-UV/VIS or amperometric detection but also IC-MS or IC-ICP/MS couplings). Thus, a second peristaltic channel is necessary to transfer the rinsing water through the suppressor.

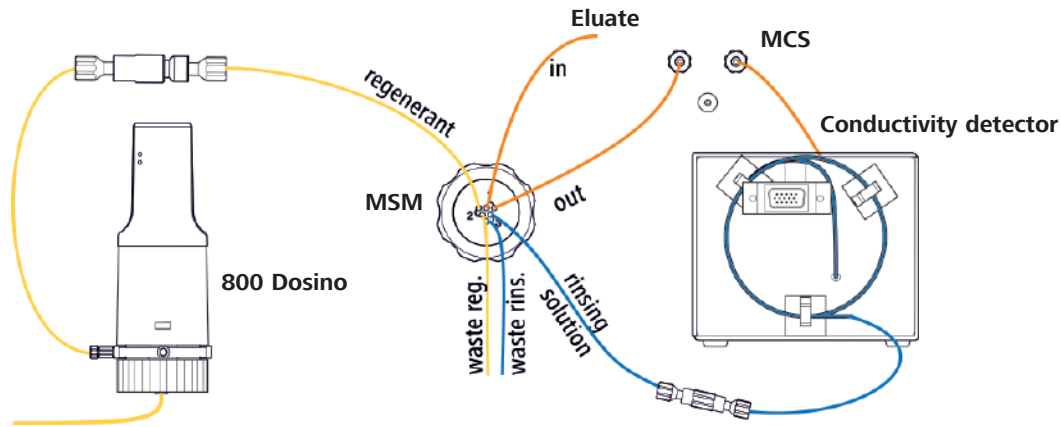
Free choice of suppressor

The suppressor rotor can be freely selected with ion chromatographs from the 940 Professional IC Vario and 930 Compact IC Flex series. Metrohm offers three chemical suppressors with different capacities (MSM, MSM-HC, MSM-LC).

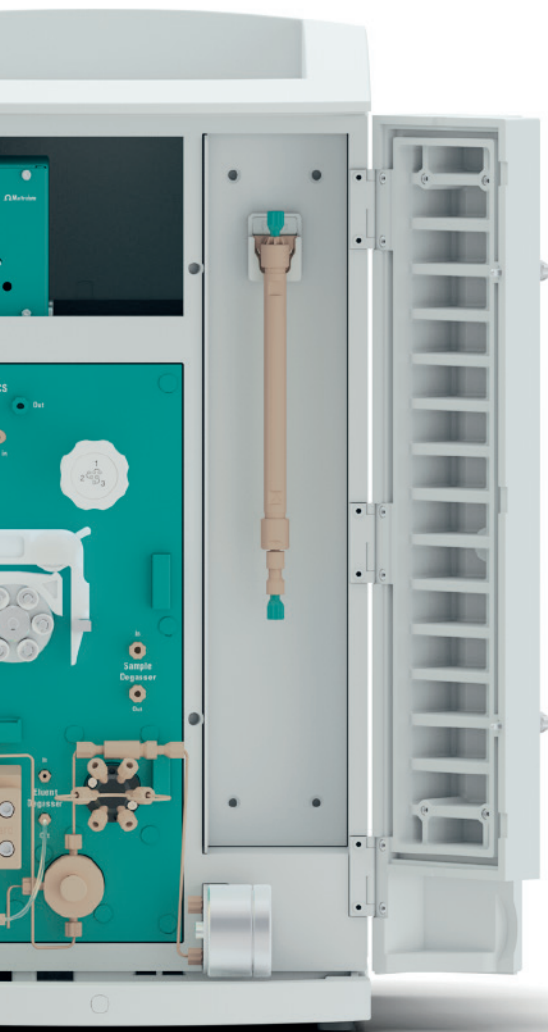
- The MSM is the suppressor rotor for universal use in routine applications
- The MSM-HC is the high-capacity suppressor rotor for gradient applications or isocratic applications with very strong eluents
- The MSM-LC is the low-capacity suppressor rotor with a minimum dead volume for applications with 2-mm columns



All three suppressor rotors – MSM-HC, MSM, and MSM-LC – have the same design and vary solely in terms of their capacity.



Flow diagram for STREAM with Dosino Regeneration: the eluate is suppressed in the MSM and MCS before it is detected in the conductivity detector. An 800 Dosino supplies the regenerant in this system.



Regenerant supply

For STREAM, the regenerant can be supplied either by a peristaltic pump or an 800 Dosino. The latter of the two versions is known as «Dosino Regeneration» and offers the following advantages:

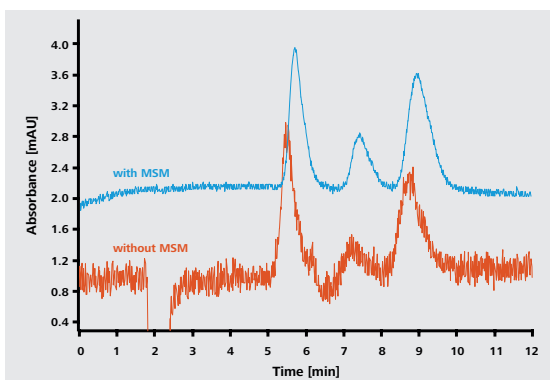
- The 800 Dosino requires less maintenance than the peristaltic pump
- MagIC Net can monitor the volume of regenerant consumed and informs the user if the regenerant needs to be refilled
- As the peristaltic pump is not required, it can be used for sample preparation techniques such as In-line Ultrafiltration and In-line Dialysis

Suppression from a different perspective

Until now, suppression has been considered in the context of determining anions and organic acids using ion-exchange chromatography and conductivity detection.

However, the use of a suppressor is recommended if anions are to be determined using UV/VIS detection (in particular between 190–230 nm) too. The suppression of the background signal decreases the noise in the UV/VIS detector. In addition, any interferences caused by carbonate in the sample matrix can be avoided; for example, when determining iodide in mineral water. Lower detection limits can be attained when the suppressor is combined with the 944 Professional UV/VIS Detector Vario.

An additional application for the suppressor is inverse suppression. This is used in the determination of organic acids with ion-exclusion chromatography and conductivity detection, for example. Producing lithium salts from the organic acids in the suppressor can significantly increase sensitivity (by a factor of 2-25 depending on the pK_s value of the acid). As a result, this type of ion chromatography can even be used to determine low concentrations.



UV/VIS detection at 218 nm with and without suppression: determination of nitrite, bromide, and nitrate

Technical information on the anion suppressor rotors

	MSM	MSM-HC	MSM-LC
Design	Robust and chemically resistant micro packed-bed suppressor		
Capacity	Approx. 90 min* (0.45 meq)	Approx. 350 min* (1.8 meq)	Approx. 45 min** (0.13 meq)
Dead volume	< 50 µL	< 250 µL	< 10 µL
Regeneration	Chemical regeneration with STREAM		
Maximum flow rate	No irreversible damage possible		
Backpressure limitations	No irreversible damage possible, no specific backpressure required for operation		
Solvent stability	100% solvent stability		
Temperature range	No limit		
Application	Universal use	High-capacity suppressor for gradient applications or isocratic applications with very strong eluents	Low-capacity suppressor with minimum dead volume for applications with 2-mm columns
Factory warranty	10 years		

*... Standard conditions for Metrosep A Supp 5 - 100/4.0: eluent 3.2 mmol/L Na₂CO₃ / 1.0 mmol/L NaHCO₃, flow rate 0.7 mL/min

**... Standard conditions for Metrosep A Supp 10 - 100/2.0: eluent 5.0 mmol/L Na₂CO₃ / 5.0 mmol/L NaHCO₃, flow rate 0.2 mL/min

Ordering information

Suppressor rotors

6.2832.000	MSM Rotor A
6.2842.000	MSM-HC Rotor A
6.2844.000	MSM-LC Rotor A

Accessories

6.2835.010	Connecting piece for MSM-HC and SPM
6.2842.020	Adapter for Suppressor Vario (always required if 6.2832.000 or 6.2844.000 is used in combination with 940 Professional IC Vario or 930 Compact IC Flex)

Dosino Regeneration

2.800.0010	800 Dosino
6.5330.190	IC equipment: Dosino Regeneration

www.metrohm.com

