Cation suppression in ion chromatography

Straightforward cation analysis at trace levels

Metrohm

Suppression in cation analysis – benefits and applications

02

Trace analysis of cations, amines, and transition metals is possible with or without suppression. However, some applications require particularly high sensitivity of the analysis. This can only be achieved by sequential suppression, as suppression considerably lowers the detection limits for the analytes. Such analyses are common, for instance, in power plant applications or in pharmaceutical applications. Moreover, there are a number of norms and standards that request cation analysis with suppression.

In short, suppression reduces background conductivity to a minimum and decreases baseline noise. Both effects together improve the signal-to-noise ratio and increase the sensitivity of the measuring system. Thus, whenever the quantification of very low concentrations of cations is required, analysis with sequential suppression is the method of choice.

The Metrohm Suppressor Module

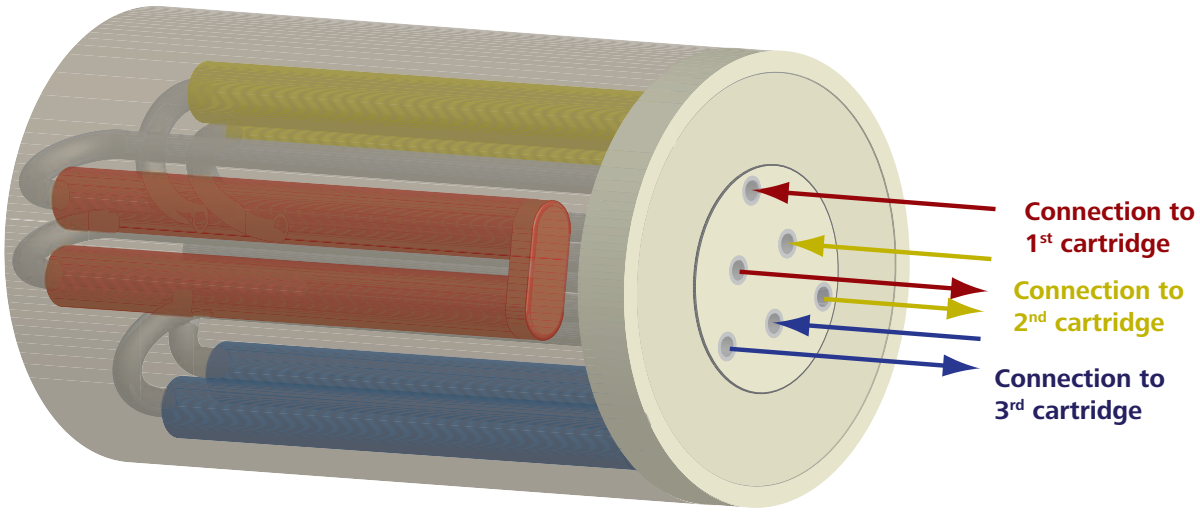
The patented Metrohm Suppressor Module (MSM) is a very effective and highly robust solution when suppression is needed. The heart of the MSM is a small rotor that contains three cartridges, filled with anion exchange resin. While the first cartridge is being used for suppression, the second one is regenerated. At the same time, the third cartridge is rinsed to remove any residual regenerant. As the cartridges are rotated one step before each new injection, there is always a freshly regenerated suppressor cartridge ready for the next injection.

STREAM – the green way of suppression

STREAM (Suppressor Treatment Re-using Eluent After Measurement) adds even more benefits to the suppression technique described. STREAM refers to a process whereby, instead of simply disposing of the suppressed eluent after detection, it is used to rinse the regenerated suppressor unit. Moreover, the use of the STREAM technique results in considerably lower consumption of regenerant.

The advantages of STREAM
• **Less waste**
• **Less use of consumables**
• **No additional rinsing solutions required**
• **Longer system run times due to lower regenerant consumption**

STREAM enables users to perform sustainable, «green chemistry» while saving on operating costs. Moreover, longer system run times frees up more time for the user to perform other tasks in the laboratory.



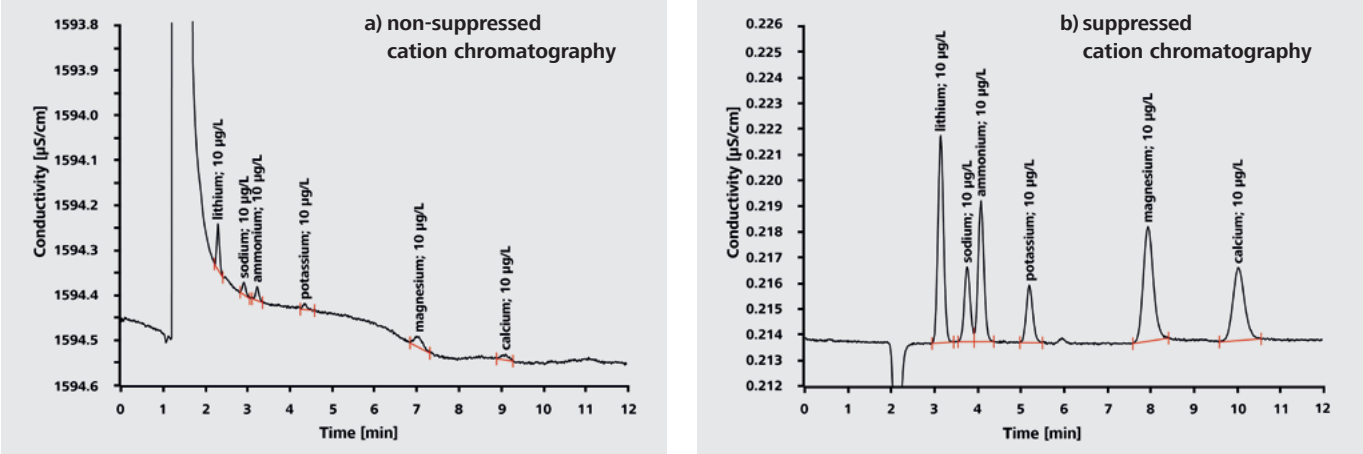
Determination of cations, amines, and transition metals after sequential suppression

Some typical examples are:

- Traces and ultratraces of sodium in the presence of monoethanolamine at high concentrations (typical of sample matrices in nuclear power plants).
- Trace and ultratrace concentrations of alkali and alkaline earth metals such as lithium, sodium, ammonium, potassium, magnesium or calcium in ultrapure water.
- Traces of transition metals, e.g., cobalt, nickel, zinc, manganese and cadmium in various types of water samples.
- Aliphatic and aromatic amines in pharmaceuticals, e.g., piperazine in cetirizine•HCl, tetrabutylammonium in atorvastatin, dimethylamine in meropenem, dimethylamine in imatinib mesylate, meglumine in meglumine salts.
- etc.

Advantages

- Ultratrace range can be quantified
- Lower detection limits
- Higher measurement sensitivity due to improved signal-to-noise ratios
- Stable baselines with minimal noise, < 0.1 nS/cm
- Rapidly eluting peaks are better evaluated
- Option of using gradients
- 100% pressure stability
- 100% resistance to solvents
- Short conditioning time
- STREAM – the green way of suppression
- Robust analyses



Lower limits of detection through improved signal-to-noise ratios

Differences between non-suppressed (a) and suppressed (b) cation chromatography. Sensitivity is increased by factor of 10 to 20. Determination of 10 µg/L standard cations in ultrapure water; column: Metrosep C Supp 1 - 150/4.0; eluent: 5 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression

How does cation suppression work?

Chemical Suppression

The Metrohm Suppressor Module (MSM) is regenerated using a carbonate buffer. All counterions are converted into hydrogen carbonate salts. Dissociated acids (e.g., nitric acid) are used as the eluent. In addition, trace amounts of rubidium are added to stabilize the baseline in trace analysis.

Reactions that take place during chemical cation suppression

Analyte:

$$Na^+ + NO_3^- + TNR_3^+HCO_3^- \rightarrow Na^+ + HCO_3^- + TNR_3^+NO_3^-$$

T = MSM substrate

Eluent:

MSM:

$$H^+ + NO_3^- \xrightarrow[-\,NO_3^-]{+\,HCO_3^-} H_2CO_3 \rightleftharpoons CO_2 + H_2O$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$Rb^+ + NO_3^- \xrightarrow[-\,NO_3^-]{+\,HCO_3^-} Rb^+ + HCO_3^-$$

The eluent counter ions are also replaced with hydrogen carbonate. The carbonic acid that is produced in this way is unstable and only weakly dissociated, meaning that a lower background conductivity is measured than would be found with the non-suppressed eluent. Depending on the eluent composition, background conductivity values of approximately 0.8–1.2 µS/cm are typical for chemical suppression.

Sequential Suppression

For sequential suppression, chemical suppression is combined with subsequent CO_2 suppression. This is accomplished with a Metrohm CO_2 Suppressor (MCS). In the MCS, the eluent is passed through a capillary made of a gas-permeable membrane which is surrounded by a vacuum. This serves to remove the carbon dioxide that is formed by the decomposition of carbonic acid into carbon dioxide and water. In this way, the carbonic acid equilibrium is constantly shifted in the direction of carbon dioxide and water. This results in the removal of nearly all the hydrogen carbonate from the flow path, so that what remains in addition to the analyte is mainly water.

The sequential suppression configuration described reduces background conductivity (< 0.2 µS/cm) and increases the detection sensitivity of the analysis. Suppression makes the injection peak very small. This means higher resolution between the injection peak and the early eluting cations, e.g., lithium, which makes the integration and quantification of these peaks easier.

Reactions that take place in the Metrohm CO_2 Suppressor (MCS)

$$CO_2(\uparrow) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

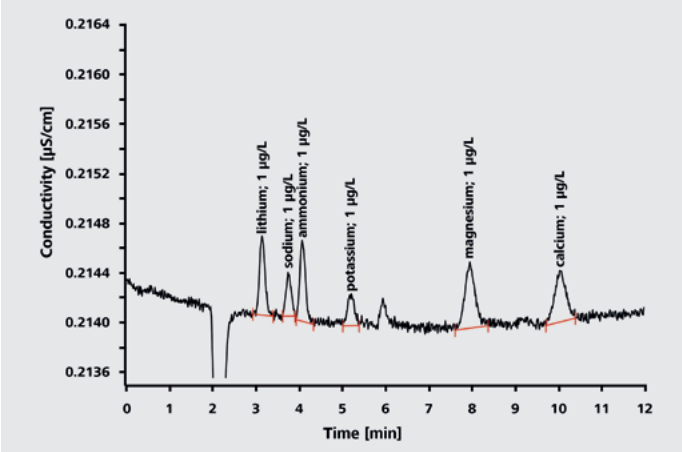
$$CO_2(\uparrow) + H_2O \rightleftharpoons H_2CO_3 \not\rightleftharpoons Rb^+ + HCO_3^-$$

The remaining hydrogen carbonate fraction is present as rubidium hydrogen carbonate in the suppressed eluate. This means that all of the hydrogen carbonate is bound as rubidium hydrogen carbonate. This provides stable background conductivity independent of whether analytes are present.

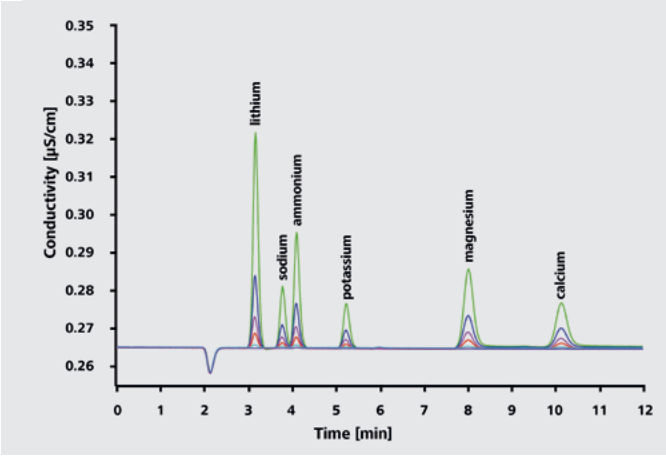
Trace analysis of cations with the new Metrosep C Supp 1 column

The Metrosep C Supp 1 column is ideally suited for cation chromatography with suppression. The column excels by its outstanding separating efficiency, short retention times and high stability. Applications can be found in all major industries where cations, amines, and transition metals have to be determined at trace levels. Examples to be mentioned here include the pharmaceutical industry (e.g., piperazine in cetirizine•HCl) and the energy industry (e.g., sodium in the cooling water of nuclear power plants).

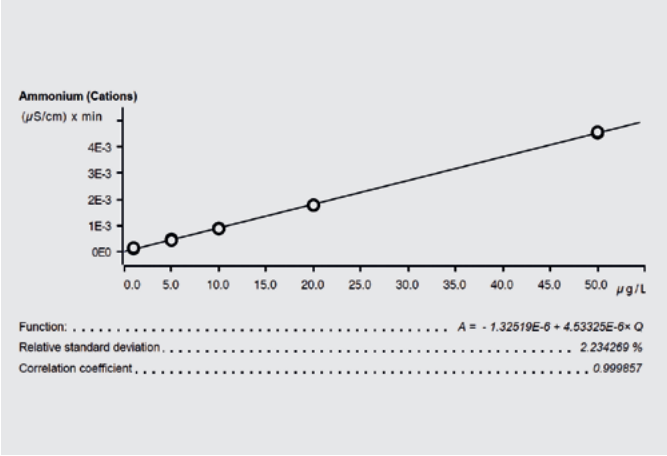
Alkali and alkaline earth metals can also be detected with small injection volumes (20 µL) down to the low µg/L concentration range. A linear calibration function can be applied over a wide concentration range.



Determination of 1 µg/L standard cations in ultrapure water
Column: Metrosep C Supp 1 - 150/4.0; eluent: 5 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression



Linear calibrations in the trace range 1–50 µg/L lithium, sodium, ammonium, potassium, magnesium, calcium
Column: Metrosep C Supp 1 - 150/4.0; eluent: 5 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression



Ammonium, linear calibration of 1–50 µg/L, 3 injections per level
Column: Metrosep C Supp 1 - 150/4.0; eluent: 5 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression

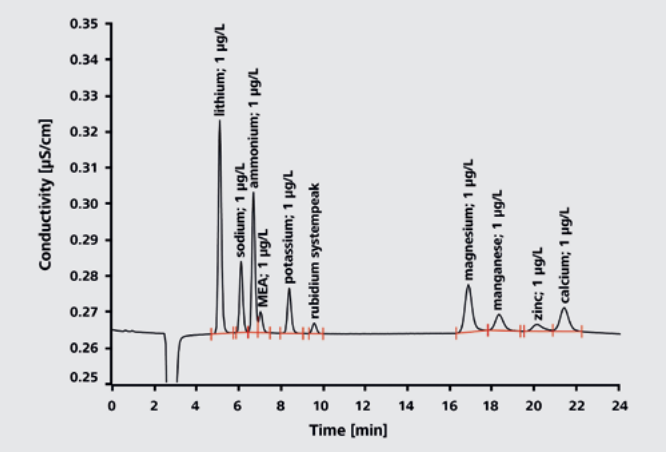
Applications

The Metrosep C Supp 1 column in combination with the IC cation suppressor is recommended, for routine analyses as well as for research applications. The free choice of column length ensures that the chromatography can be flexibly adapted to any application requirement.

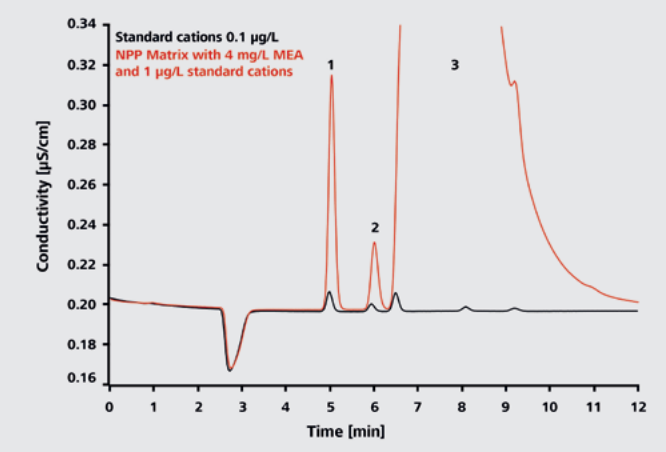
Typical applications

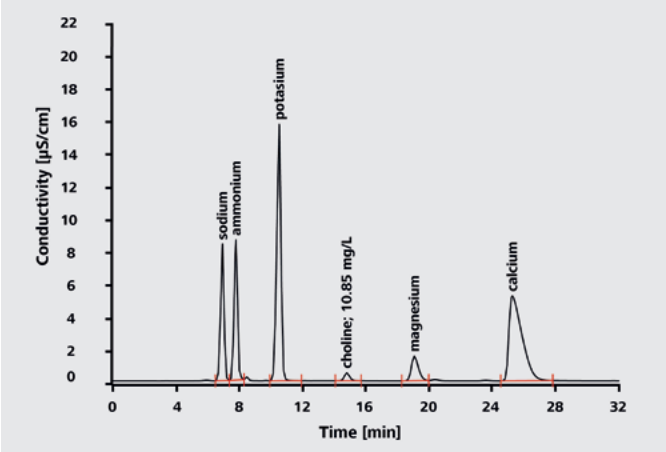
- Cations in the ultratrace range
- Aliphatic and aromatic amines in pharmaceuticals
- Ammonium determination in difficult matrices
- Transition metals in aqueous extracts

Determination of 1 µg/L alkali, alkaline earth, and transition metals in the cooling water of a nuclear reactor, with fully automatic removal of the matrix
Column: Metrosep C Supp 1 - 250/4.0; eluent: 4 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 100 µL; sample preparation: Inline Matrix Elimination and Inline Preconcentration with Metrosep C PCC 1 HC/4.0; flow rate: 1.0 mL/min, conductivity detection with sequential suppression



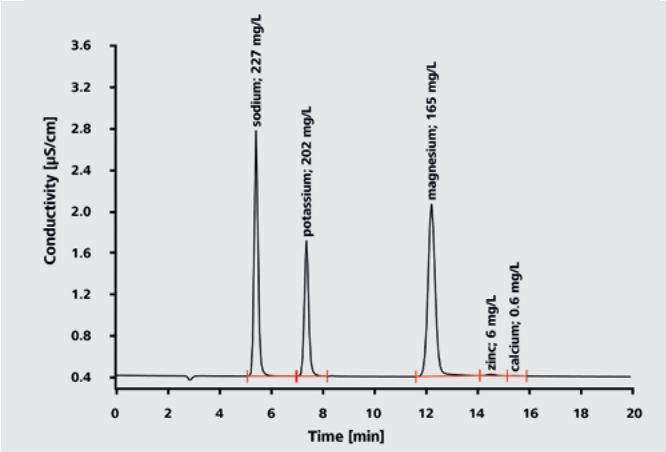
Determination of 1 µg/L lithium (1) and sodium (2) in a power plant sample with 4 mg/L monoethanolamine (3) (red). For comparison (black): Standard cations 0.1 µg/L
Column: Metrosep C Supp 1 - 250/4.0; eluent: 4 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 2000 µL; sample preparation: Inline Matrix Elimination and Inline Preconcentration with Metrosep C PCC 1 HC/4.0; flow rate: 1.0 mL/min, conductivity detection with sequential suppression





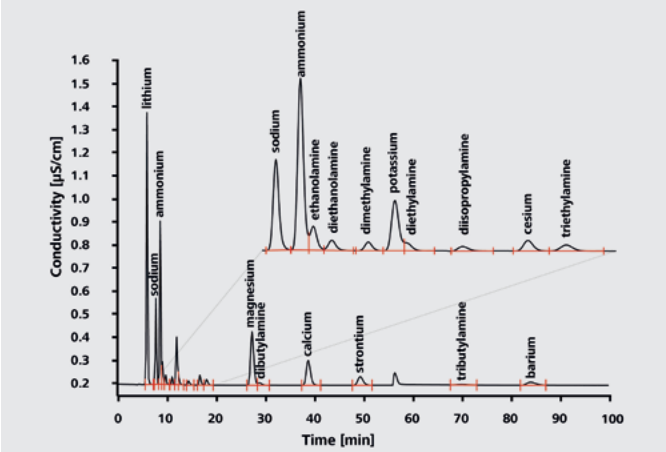
Determination of choline in baby food analogous to standard AOAC 2012.20

Calculated for the original sample weight, the chloline content is 82 mg/100 g of milk powder. Column: Metrosep C Supp 1 - 250/4.0; eluent: 4 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression



Analysis of zinc in a sports beverage

The relative standard deviation (n = 36) makes the precision of the measurement clear: Sodium 0.11%, potassium 1.60%, magnesium 0.31%, zinc 1.16% and calcium 2.01%. Column: Metrosep C Supp 1 - 250/4.0; eluent: 5 mmol/L HNO_3 + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression



Determination of aliphatic amines (1 mg/L each)

Column: Metrosep C Supp 1 - 250/4.0; eluent: 2.5 mmol/L HNO_3 + 7.5% (v/v) acetonitrile + 50 µg/L Rb^+; column temperature: 40 °C; sample volume: 20 µL; flow rate: 1.0 mL/min, conductivity detection with sequential suppression

Technical information

Rotor	MSM-HC C
Design	Micro packed-bed suppressor, robust, chemically resistant
Capacity	> 50 min* (0.25 meq)
Dead volume	< 250 µL
Regeneration	Chemical regeneration with STREAM
Maximum flow rate	Extremely robust: irreversible damage not possible
Backpressure limitations	Extremely robust: irreversible damage not possible, no specific backpressure required
Solvent stability	100% solvent stability
Temperature range	No limit

Separation column	Metrosep C Supp 1
Substrate	Polyvinyl alcohol with carboxyl groups
Particle size	5 µm
Standard eluent	5 mmol/L HNO_3 + 50 µg/L Rb^+
Standard flow rate	1.0 mL/min
Maximum flow rate	1.5 mL/min
Maximum pressure	15 MPa
Standard temperature	40 °C
Temperature range	20–40 °C
Capacity	30 µmol K^+ (250 mm column)
pH range	1–12
Organic modifier (in eluent)	0–30% (no methanol)
Organic modifier (in sample)	0–100% acetone, acetonitrile and methanol
Storage	At 2–4 °C rinsed with ultrapure water

*Standard conditions: Metrosep C Supp 1 - 250/4.0; eluent: 5 mmol/L HNO_3 + 50 µg/L Rb^+, flow rate: 1.0 mL/min

Ordering information

Suppressor rotor

6.2842.200 MSM-HC C

Accessories

6.2835.010 Connecting piece for MSM-HC and SPM

Dosino Regeneration

2.800.0010 800 Dosino
6.5330.190 IC equipment: Dosino Regeneration

Separation Columns

6.1052.410 Metrosep C Supp 1 - 100/4.0
6.1052.420 Metrosep C Supp 1 - 150/4.0
6.1052.430 Metrosep C Supp 1 - 250/4.0
6.1052.500 Metrosep C Supp 1 Guard/4.0
6.1052.510 Metrosep C Supp 1 S-Guard/4.0

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