Sequential suppression for conductivity detection in ion chromatography

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Summary

In ion chromatography (IC), suppression techniques are designed to improve the analytical performance where conductivity detection is normally used.

Depending on the application, electronic or chemical suppression techniques can be applied. While the first technique is appropriate for most cation analyses, the latter technique is preferentially used for anion analysis. Chemical suppressors utilize a cation exchange (Packed-Bed Suppressor, «MSM») to replace the metal cations accompanying the anions of interest by the more conductive hydronium ions. Moreover, the cation exchange transforms highly conductive eluents (hydroxide or carbonate/bicarbonate eluents) to non-dissociated and thus weakly conductive substances. The reduced baseline conductivity and the enhanced conductance of the analytes results in a significant improvement of the detection limits.

Yet another outstanding sensitivity enhancement in suppressed IC is achieved by the installation of the «MCS» CO $_2$ Suppressor between the «MSM» and the conductivity detector. The «MCS» removes any residual CO $_2$ and thus provides 20 to 50% larger peak areas, an extremely low background conductivity and an excellent linearity of calibration. Moreover the interfering injection and system peaks are largely eliminated.

Introduction

Chemical suppression exchanges the analyte and eluent counterions. In suppressed anion chromatography a cation exchanger is used and all cations are replaced by protons.

Analyte: Na⁺Cl⁻ + RSO₃⁻H⁺
$$\rightarrow$$
 H⁺Cl⁻ + RSO₃⁻Na⁺, R = resin

While the analyte in the sample flows through the suppressor the counterion sodium is replaced by the about 5 times more conductive hydrogen. This significantly improves the conductivity signal of the particular analyte.

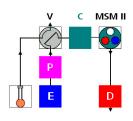
Eluent:
$$Na^+HCO_3^- + RSO_3^-H^+ \rightarrow H_2CO_3 + RSO_3^-Na^+$$
, R = resin

The cation of the ionized carbonate/bicarbonate eluent (highly conductive) is neutralized by H+ forming the only marginally dissociated carbonic acid (weakly conductive).

IC system with Suppressor Unit «MSM II»

E	Eluent
P	Pump
V	Valve
C	Column
"NASM II»	Metrohn

«MSM II» Metrohm Suppressor Module
Conductivity Detector



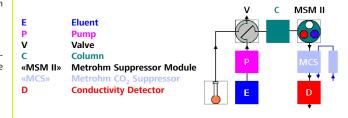
«MCS» CO₂ Suppressor

The carbonic acid formed during the chemical suppression is in equilibrium with the carbon dioxide dissolved in the water. Before CO_2 removal the background conductivity is in the range of 10 to 14 μ S/cm.

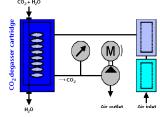
$$H^+ + HCO_3^- \hookrightarrow H_2CO_3 \longrightarrow H_2O + CO_2$$

The «MCS» CO_2 Suppressor, installed downstream of the chemical suppressor, removes the carbon dioxide from the eluent. As the CO_2 concentration decreases, the equilibrium shifts further to the right. This results in enhanced CO_2 removal and thus in decreasing carbonic acid concentration. Consequently, the value of the background conductivity is reduced to that of water.

IC system with «MSM II + MCS»







«MSM II»

Flow scheme of the «MCS»

After passing the «MSM», the CO_2 in the eluent is removed by vaccum in the CO_2 degasser cartridge of the «MCS». The CO_2 diffuses through the CO_2 -permeable membrane coil and is transferred to the vaccum pump by an additional small airflow.

«MSM» and «MSM + MCS»

Chromatogram with «MSM»

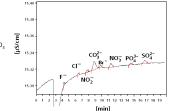
 Column:
 Metrosep A Supp 5 – 100

 Eluent:
 1 mmol/L NaHCO₃ and 3.2 mmol/L Na₂CO₃

 Flow:
 0.4 ml/min

 Suppression:
 «MSM»

 Loop:
 20 µL



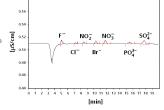
Chromatogram with «MSM + MCS»

 Column:
 Metrosep A Supp 5 – 100

 Eluent:
 1 mmol/L NaHCO₃ and 3.2 mmol/L Na₂CO₃

 Flow:
 0.4 ml/min

Suppression: «MSM + MCS



lon	Limit of detection [µg/L]	Concentration [µg/L]
Fluoride	0.7	2
Chloride	1.0	2
Nitrite	1.9	5
Bromide	1.0	10
Nitrate	1.5	10
Phosphate	1.9	10
Sulfate	1.5	10

Features of the «MCS» CO₂ Suppressor

- improves the detection limit (larger peak areas and extremely low background conductivity; noise is smaller than 0.2 nS/cm)
- \triangleright achieves LODs between 0.7 and 1.9 µg/L with only 20 µL injection volume
- > significantly reduces the injection peak and thus improves the determination of rapidly eluting anions such as fluoride
- eliminates the interfering system peak
- > quarantees baseline stability and enhances calibration linearity
- offers gradient capabilities.