

Tips and tricks

Ion chromatography: suppression

Cation suppression for determinations in the trace range

For the determination of cations in the trace range, Metrohm offers new cation suppression. While suppression is a standard method of anion determination (see infobox below), cation suppression is used in particular when the application requires extremely high detection sensitivity, e.g., in the field of power station analytics, in the pharmaceutical industry, or if it is required by standards.

Like anion suppression, cation suppression also reduces background conductivity, whereby extremely sensitive conductivity detection is employed. In the first step, chemical suppression, background conductivity typically around 0.8 – 1.2 $\mu\text{S}/\text{cm}$ is produced by replacing the negatively charged counterions of the analyte and the eluent with hydrogen carbonate (HCO_3^-) by ion exchange. A dissociated acid (e.g., nitric acid, HNO_3) is used as an eluent; during suppression carbonic acid (H_2CO_3) is produced. The latter is in balance with the carbon dioxide:



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Because the dissociated part of the carbonic acid increases conductivity, a CO_2 suppression is then performed, producing a background conductivity of $< 0.2 \mu\text{S}$. The CO_2 produced during the chemical suppression is then removed using a negative pressure. The balance (1) is thereby shifted increasingly to the right so that the carbon dioxide can be almost completely removed. Eventually, water and analyte will remain.

To achieve a stable baseline, the eluent is dosed with traces of rubidium. This reacts with the hydrogen carbonate remaining in the suppressed eluate to form rubidium hydrogen carbonate. This provides stable background conductivity independent of whether analytes are present.

Cation suppression is typically used in the following:

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

Find more information on cation suppression in the free brochure with the document number 8.000.5163, available for download at www.metrohm.com.

Info

Suppression is used in ion chromatographical determinations to achieve a more sensitive conductivity detection. Following separation, it dramatically reduces the conductivity of the eluent. Its contribution to conductivity is therefore negligible compared with that of the analyte. Until recently, only Metrohm ion chromatography systems for anion determination were equipped with a suppressor, either for chemical suppression or for the more effective sequential suppression (chemical suppression followed by

CO_2 suppression). In chemical suppression, the eluent is converted by ion exchange to a poorly conductive to non-conductive compound, usually water or a non-dissociated acid. If carbonate or hydrogen carbonate eluents are used, carbonic acid will be produced during chemical suppression, which is in balance with the carbon dioxide dissolved in the water. During CO_2 suppression, CO_2 is removed using a negative pressure, therefore producing an extremely low background conductivity.



Conductivity detection of organic acids following ion-exclusion chromatography with inverse suppression

Organic acids and all other weak and medium-strength acids are either mostly or completely undissociated in the eluent (e.g., diluted sulfuric acid). Their detection by means of conductivity measurement therefore lacks sensitivity. Inverse suppression is a suitable remedy: it is a form of chemical suppression (see infobox on the previous page) that chemically modifies analyte and eluent in a way that allows the conductivity detection of weak acids to be much more sensitive.

During inverse suppression, the acids are converted to their lithium or sodium salts – unlike the acids, these are completely dissociated in the eluent. The anion suppressor (see Figure below), which is filled with cation exchanger, is charged with Li^+ or Na^+ instead of H^+ . When the suppressor is in operation, the analyte and eluent cations, i.e., protons, are replaced with Li^+ and Na^+ . Example: If the analyte is acetic acid (CH_3COOH), this is converted by ion exchange with lithium into lithium acetate (CH_3COOLi). Meanwhile, the eluent (normally diluted sulfuric acid – H_2SO_4) is converted to a lithium sulfate solution, which has a much lower conductivity than sulfuric acid. Together, both reactions increase the sensitivity of detection – in this case by a factor of 25. An example application is described in the Application Note AN-O-042 («Organic acids in organics with conductivity detection after inverse suppression»).

The Metrohm Suppressor Module houses three ion exchanger cartridges. After each suppression stage, they are regenerated and then rinsed – thanks to the three-cartridge system, a cartridge is available at all times for suppression operation.



All applications can be downloaded free of charge at:
www.metrohm.com/Applications