# Automated logical dilution for ion chromatographic determinations

S. Czyborra and N. Seifert

Metrohm Ion analysis

Ion Chromatography

## Summary

The combination of 850 Professional IC, 858 Professional Sample Processor, Dosino and MagIC Net™ software offers a variety of sophisticated ion chromatographic sample preparation techniques. One of these is the automated inline dilution of samples.

After the first sample injection, MagIC Net™ verifies if the area of the sample peak lies within the calibration range. If the measured peak area is outside these limits, the software calculates the appropriate dilution factor, dilutes and automatically re-injects the sample.

For all investigated ions ($Li^+$, $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $F^-$, $Cl^-$ , $NO_2^-$, $Br^-$, $NO_3^-$, $SO_4^{2-}$ ), automated logical dilution yielded coefficients of determination ($R^2$) better than 0.9999. Direct-injection recoveries for cations and anions were within 98.6…99.5% and 93.4…100.4%, respectively. In contrast, after logical dilution, recoveries for cations and anions were within 100.1…102.9% and 98.2…102.6%, respectively. The relative standard deviations for all determinations involving diluted sample solutions were smaller than 0.91%.

## Introduction

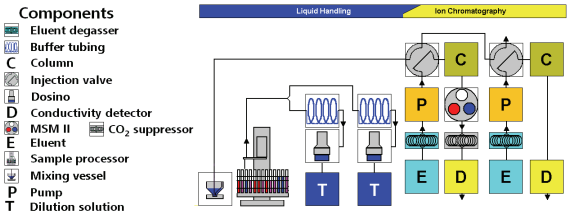
To get accurate results in chromatography, the determined sample peak areas need to be within the limits of calibration. Additionally, high ionic concentrations can overload the column and therefore adversely affect the accuracy of the measurement. Manual dilution, however, is error-prone and time-consuming.

This paper will give a description of the straightforward analytical setup and demonstrate the usefulness of the automated intelligent dilution applied to cation and anion determinations.

## Instrumentation

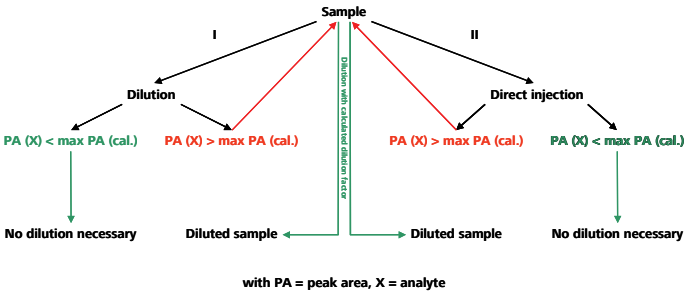
- 850 Professional IC AnCat – MCS
- 858 Professional Sample Processor – Pump
- Metrosep A Supp 5 – 150
- Metrosep C 4 – 150
- 800 Dosino(s)
- 801 Stirrer

## Analytical setup

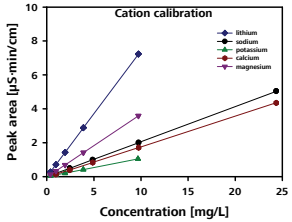



## Logical dilution

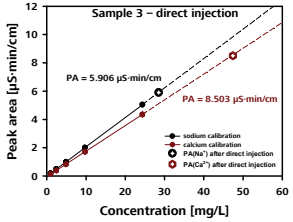
In order to perform automated dilutions, the 850 Professional IC, the 858 Professional Sample Processor and the MagIC Net™ software are additionally equipped with a magnetic stirrer and a 800 Dosino. The latter aspirates a defined volume of an undiluted sample and transfers it to the mixing vessel. Subsequently, the dilution medium, generally ultrapure water, is dosed into the mixing vessel (I). After intensive stirring, the peristaltic pump of the sample changer transfers the sample to the injection valve of the IC. Alternatively, the sample can be injected directly (II). After the quantitation of the sample's constituents, the software verifies if the peak areas (PAs) lie within the calibration range. If this is the case, the next sample will be analyzed. If not, the software, after calculating the dilution factor, re-analyzes the sample after applying the appropriate dilution.



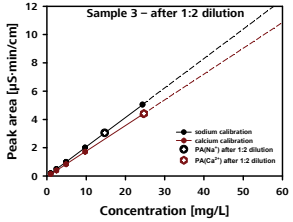

## Cations




| Analyte | Coefficient of determination |
|---|---|
| Lithium | 0.9999 |
| Sodium | 0.9999 |
| Potassium | 0.9999 |
| Calcium | 0.9999 |
| Magnesium | 0.9999 |



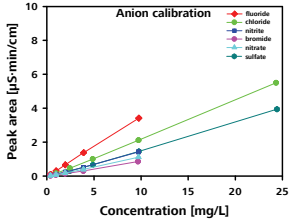

logical dilution



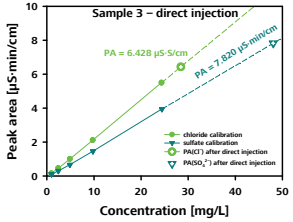

| | Dilution | $Li^+$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|
| Recovery [%] | none | 98.6 | 99.5 | 99.4 | 99.2 | 99.0 |
| | 1:2[a] | 100.1 | 100.7 | 100.4 | 101.4 | 101.8 |
| | 1:5[b] | 100.7 | 101.2 | 100.9 | 101.0 | 102.9 |
| Mean value[b] of peak area [µS·min/cm] | | 1.4481 | 1.2187 | 0.2101 | 1.7359 | 0.7095 |
| Standard deviation | 1:5[b] | 0.0038 | 0.0033 | 0.0019 | 0.0045 | 0.0041 |
| Relative standard deviation [%] | | 0.26 | 0.27 | 0.91 | 0.26 | 0.58 |

[a]one determination, [b]mean value of 10 determinations

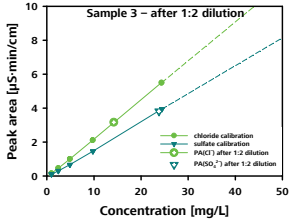
## Anions




| Analyte | Coefficient of determination |
|---|---|
| Fluoride | 0.9999 |
| Chloride | 0.9999 |
| Nitrite | 0.9999 |
| Bromide | 0.9999 |
| Nitrate | 0.9999 |
| Sulfate | 0.9999 |




logical dilution




| | Dilution | $F^-$ | $Cl^-$ | $NO_2^-$ | $Br^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| Recovery [%] | none | 99.4 | 99.2 | 100.1 | 99.4 | 100.4 | 93.4 |
| | 1:2[a] | 100.7 | 101.0 | 102.6 | 101.3 | 102.1 | 100.0 |
| | 1:5[b] | 99.5 | 100.6 | 98.7 | 98.2 | 98.5 | 100.2 |
| Mean value[b] of peak area [µS·min/cm] | | 0.6530 | 1.2017 | 0.2375 | 0.1382 | 0.1779 | 1.4047 |
| Standard deviation [µS·min/cm] | 1:5[b] | 0.0033 | 0.0051 | 0.0007 | 0.0004 | 0.0004 | 0.0018 |
| Relative standard deviation [%] | | 0.50 | 0.42 | 0.30 | 0.25 | 0.24 | 0.13 |

[a]one determination, [b]mean value of 10 determinations



Metrohm AG, CH-9101 Herisau/Switzerland, sc@metrohm.com, phone +41 71 353 86 63