

# Analysis of Food Samples with Ion Chromatography after Inline Dialysis


Alfred Steinbach, Metrohm

Andrea Wille, Metrohm

Silke Rick, Metrohm


**Ion chromatography (IC) as an analytical technique has experienced an impressive surge in popularity due to the simplicity and robustness of the method, the improved reliability and the great choice of columns, detectors and applications. For a sample in a homogeneous ionic form, very little sample preparation is required and results can be obtained within a matter of minutes. In complex matrices carrying high organic loads such as waste water, soil eluates or dairy products, a more extensive sample preparation is mandatory to prevent destruction of the column.**

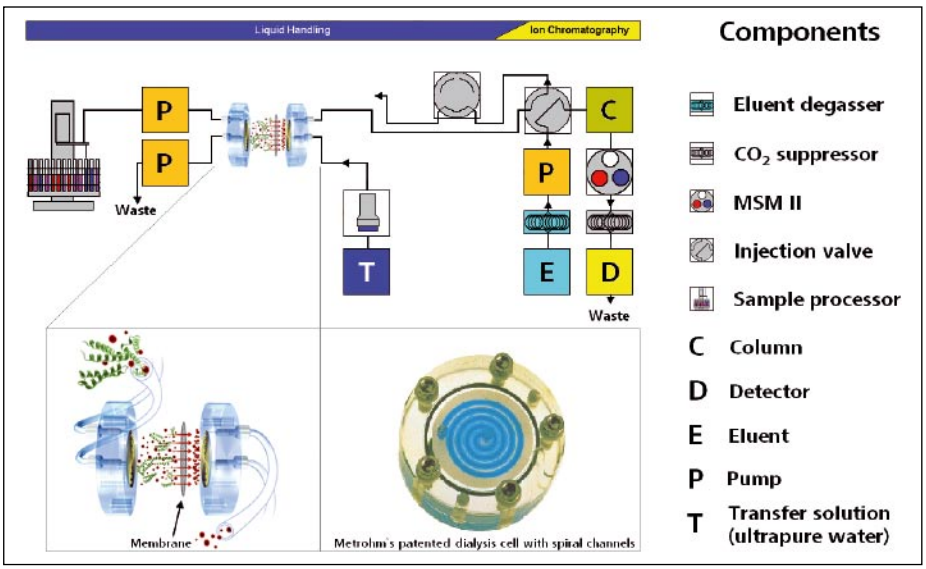


Fig. 1: Schematic diagram showing both the inline dialysis cell and its coupling to the compact IC. The diagram and photograph in the lower part of the figure show Metrohm's patented spiral-flow dialysis cell.

Although numerous sample preparation techniques have been developed, such as the Carrez precipitation for protein-containing samples, most of them are tedious and error-prone. To overcome these shortcomings, Metrohm launched the first coupling of IC with dialysis in 1997. Since then the procedure has been further improved and allows for an efficient inline elimination of undesired matrix components in a variety of demanding sample types.

Using as examples an ultra-high temperature (UHT) processed milk and a baby milk powder sample, this work presents a fully automated sample preparation setup coupled to the new ion chromatograph 881 Compact IC pro. Calibration parameters, carryover and recovery rates were tested with multi-anion standards.

## Materials and Methods

### a) Instrumentation

881 Compact IC pro
858 Professional IC Sample Processor
800 Dosino
Dialysis equipment

### b) Reagents and Eluents

All standard solutions and eluents were prepared with deionised water having a specific resistance higher than 18 MΩ·cm. Two standard solutions covering the concentration ranges 1.0…3.6 mg/L and 10…36 mg/L served to determine the system characteristics.

The ultra-high temperature (UHT) processed milk and the baby milk powder were purchased from Migros, Switzerland.

## Compact Stopped-flow Dialysis

Dialysis is based on the selective diffusion of molecules or ions from one liquid (donor or sample solution) to another (acceptor solution) via a membrane. The driving force for the transfer is the concentration gradient across the membrane. Contrary to dynamic dialysis, where two solutions continuously pass through the dialysis module, at least one solution is temporarily stopped until the concentration in the acceptor solution is the same as that in the donor solution. This patented stopped-flow procedure takes between 10 and 14 minutes and can be directly coupled to an IC setup. As the dialysis is performed during the recording of the previous sample`s chromatogram, the overall analysis time is not prolonged.

Whereas in the conventional setup 2 two-channel peristaltic pumps transport the sample and the acceptor solution to and from the dialysis cell, in compact dialysis a Dosino doses ultrapure water through the acceptor compartment of the cell. The stopped-flow status is achieved by stopping the Dosino and blocking the outlet capillary of the cell by feeding it through the valve of the sample processor. The latter, depending on its valve position, allows or blocks the acceptor solution flow.

## System Characteristics

### Calibration

Five concentration levels (0.5, 1, 5, 10 and 20 mg/L) prepared from a multi-ion standard were used for external calibration.

**Table 1: Correlation coefficients and relative standard deviations of the five-point anion calibration**

| | Fluoride | Chloride | Nitrite | Bromide | Nitrate | Phosphate | Sulfate |
|---|---|---|---|---|---|---|---|
| Correlation coefficient | 0.99995 | 0.99996 | 0.99999 | 0.99996 | 0.99994 | 0.99990 | 0.99997 |
| RSD [%] | 1.516 | 1.242 | 0.834 | 1.169 | 1.479 | 2.491 | 1.176 |

### Carryover

Carryover was evaluated by injection of a blank (ultrapure water) immediately after injection of a standard.

**Table 2: Carryover in percent determined for the concentration ranges 1.0…3.6 mg/L and 10…36 mg/L**

| | Fluoride | Chloride | Nitrite | Bromide | Nitrate | Phosphate | Sulfate |
|---|---|---|---|---|---|---|---|
| Low standard conc. | 0.24 | 0.15 | 0.17 | 0.20 | 0.18 | 0.11 | 0.28 |
| High standard conc. | 0.49 | 0.12 | 0.13 | 0.22 | 0.11 | 0.00 | 0.38 |

### Recovery Rates

In order to determine recovery rates, results obtained by direct injection were compared to those obtained by injection of the dialysate.

**Table 3: Anion recovery rates**

| | Low standard concentration | | | | | High standard concentration | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Direct injection | | With dialysis | | Recovery | Direct injection | | With dialysis | | Recovery |
| | Mean [mg/L] | RSD [%] | Mean [mg/L] | RSD [%] | rate [%] | Mean [mg/L] | RSD [%] | Mean [mg/L] | RSD [%] | rate [%] |
| Fluoride | 1.06 | 0.12 | 1.03 | 0.24 | 97.2 | 10.81 | 0.09 | 10.57 | 0.06 | 97.8 |
| Chloride | 3.01 | 0.04 | 2.97 | 0.03 | 98.7 | 31.58 | 0.03 | 31.22 | 0.06 | 98.9 |
| Nitrite | 2.94 | 0.32 | 2.91 | 0.15 | 99.0 | 30.01 | 0.30 | 29.81 | 0.04 | 99.3 |
| Bromide | 1.02 | 0.08 | 1.01 | 0.00 | 99.0 | 10.50 | 0.04 | 10.38 | 0.17 | 98.9 |
| Nitrate | 3.02 | 0.07 | 2.97 | 0.00 | 98.3 | 30.80 | 0.03 | 30.40 | 0.03 | 98.7 |
| Phosphate | 3.81 | 0.17 | 3.47 | 0.10 | 91.1 | 33.74 | 0.02 | 31.83 | 0.03 | 94.3 |
| Sulfate | 3.52 | 0.09 | 3.35 | 0.07 | 95.2 | 35.57 | 0.04 | 34.17 | 0.07 | 96.1 |

## Dairy samples

### UHT Processed Milk

Prior to analysis, the UHT processed milk sample was diluted 1:100 with ultrapure water and placed in the sample vials upon the rack of the sample processor. The subsequent dialysis of the milk sample and the injection of the dialysate onto the separation column was fully automated. The calculation was carried out automatically using integration software MagIC Net 1.1 against the previously prepared calibration plots.

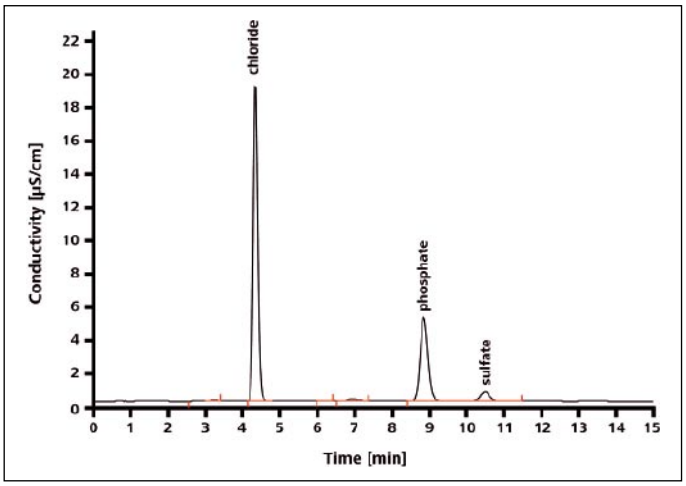


**Fig. 2: Anion chromatogram of a UHT milk dialysate containing 9.88 mg/L chloride, 17.40 mg/L phosphate and 1.09 mg/L sulfate (after dilution of the sample). Column: Metrosep A Supp 5–100, eluent: 3.2 mmol/L sodium carbonate and 1.0 mmol/L sodium hydrogen carbonate, flow: 0.7 ml/min, column temperature: 30 °C, injection volume: 20 µl, acceptor solution: ultrapure water, dialysis time: 14 min.**

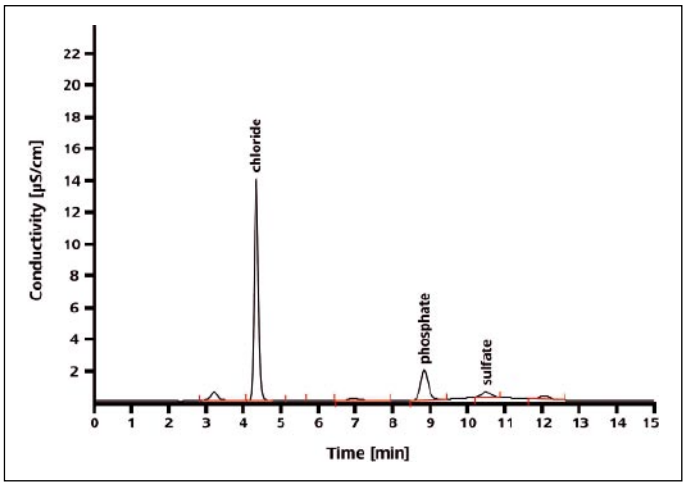


**Fig. 3: Anion chromatogram of a baby food milk sample containing 7.37 mg/L chloride, 7.41 mg/L phosphate and 0.76 mg/L sulfate (after dilution of the sample). Chromatographic conditions correspond to those indicated in figure 2.**

Under the conditions described in the caption of figure 2, excellent baseline separation of chloride, phosphate and sulfate is achieved within 12 min. Repetitive analyses showed no trending in peak areas or retention times, which suggests that sample proteins did not pass the membrane.

### Baby Food Milk Powder

Following the manufacturer's instructions, the baby food milk powder was replenished with water. Prior to analysis, the prepared milk sample was diluted 1:100.

As with the UHT milk sample, also here the chromatographic conditions applied provide an excellent baseline separation for chloride, phosphate and sulfate.

## Summary

The analytical challenge treated in the present work consists in the determination of chloride, phosphate and sulfate in the presence of difficult sample matrices that interact with the stationary column phase or even render it unusable. Metrohm's patented stopped-flow dialysis coupled to the new 881 Compact IC pro ion chromatograph overcomes these drawbacks.

Two standard solutions covering the concentration ranges 1.0…3.6 mg/L and 10…36 mg/L as well as two samples, an ultra-high temperature (UHT) processed milk and a baby milk powder, were characterised in terms of analyte concentration, relative standard deviation, calibration quality, carryover and recovery rates. While the five-point calibration curves yielded correlation coefficients (R) better than 0.9999, carryover between two subsequent injections of a concentrated sample and a blank was less than 0.49 %. Recoveries for the low (1.0…3.6 mg/L) and high standard concentrations (10…36 mg/L) were within 91…99 % and 94…100 %, respectively.

Automated compact stopped-flow dialysis is a highly efficient sample preparation technique that ensures optimum separation performance by protecting the column from detrimental matrix compounds.

**Fig. 4: The 881 Compact IC pro with the 858 Professional IC Sample Processor with dialysis cell and 800 Dosino. Instrument control, data acquisition and processing were performed by MagIC Net software.**

## References

[1] Metrohm Application Notes AN-S-044, AN-S-162, AN-N-018, AN-C-100 and AN-C-028, (downloadable under http://products.metrohm.com)

[2] Metrohm Monograph: Sample preparation techniques for ion chromatography, Metrohm AG, Herisau, Switzerland, 108 pages, 8.025.5003.

[3] Steinbach A. and Wille A.: Ion chromatographic analysis of carbohydrates in essential and non-essential foodstuffs, Food Engineering & Ingredients October, 33–36 (2008)

*Silke Rick*
*Alfred Steinbach*
*Andrea Wille*
*Metrohm AG*
*Herisau, Switzerland*
*ric@metrohm.com*