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# Application Bulletin

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Of interest to:      General analytical laboratories

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## **Metrosep Anion Dual 2 IC column (6.1006.100)**

**for the determination of anions with and without chemical suppression**

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### **Summary**

This bulletin describes the determination by ion chromatography of anions, particularly fluoride, chloride, nitrite, bromide, nitrate, orthophosphate and sulfate using the Metrosep Anion Dual 2 IC column with and without chemical suppression.

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### **Instruments and accessories**

- 2.732.0010    IC Detector
- 2.733.0130    IC Separation Center with 1 loop injector and Metrohm Suppressor Module MSM
- 2.709.0010    IC Pump
- 2.752.0010    Pump Unit
- 2.714.0310    IC Metrodata for 1 chromatography system with a maximum of 2 detectors
- 6.1006.100    Metrosep Anion Dual 2 IC column
- 6.2620.150    Pulsation dampener

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### **Reagents**

- Anion standards:  
For the preparation of the standard solutions, commercial stock solutions containing  $\beta(\text{anion}) = 1000 \text{ mg/L}$  are used.
- Sodium carbonate, anhydrous, puriss. p.a.
- Sodium hydrogen carbonate (sodium bicarbonate), puriss. p.a.
- Sulfuric acid, puriss. p.a.
- Phthalic acid, puriss. p.a.
- Acetonitrile, HPLC quality
- Sodium hydroxide  $c(\text{NaOH}) = 2 \text{ mol/L}$

- Boric acid, puriss. p.a.
- Sodium tetraborate decahydrate, puriss. p.a.
- Potassium-D-gluconate, puriss. p.a.
- Glycerol, anhydrous, puriss. p.a.
- 1-Butanol, puriss. p.a.

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### **Column specifications**

- Column material: Polymethacrylate with quaternary ammonium groups
- Dimensions: 75 mm x 4.6 mm
- Precolumn: 6.1005.050 PRP-1 IC precolumn cartridge (RP phase on polystyrene/divinylbenzene; dimensions 4 mm x 20 mm); used together with the 6.2821.050 double cartridge holder.
- pH range: 1 ... 12
- Maximum flow: 1.2 mL/min (recommended flow 0.8 mL/min)
- Maximum pressure: 7 MPa (= 70 bar)
- Preparation: The column is delivered ex works filled with boric acid/gluconate eluent.
- Storage: The column is stored at room temperature in the eluent used.
- Regeneration: Rinse with 0.1 mol/L HNO<sub>3</sub> at 0.3 mL/min for approx. 2 h, then switch to the standard eluent.  
  
Rinse with eluent containing 100 mmol/L of the respective buffer salt.  
  
Organic impurities: Rinse the column with eluent containing an organic solvent (volume fraction <20%).

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### **General hints**

- Sample solutions must be microfiltered (0.45 µm).
- The determination of orthophosphate requires an IC system with alkaline eluent.
- Suitable for the determination of anions at the trace level.
- Eluents may contain up to 20% of organic solvents.
- **Tris(hydroxymethyl)-aminomethane (TRIS) must not be used** to adjust the pH value of the phthalic acid eluent.
- To increase the useful lifespan of the separation column, it is advisable to use the 6.2620.150 pulsation dampener to attenuate the pressure shocks caused by the injector.

## Standard system

### 1. Ion chromatography with chemical suppression

#### Carbonate/hydrogen carbonate eluent

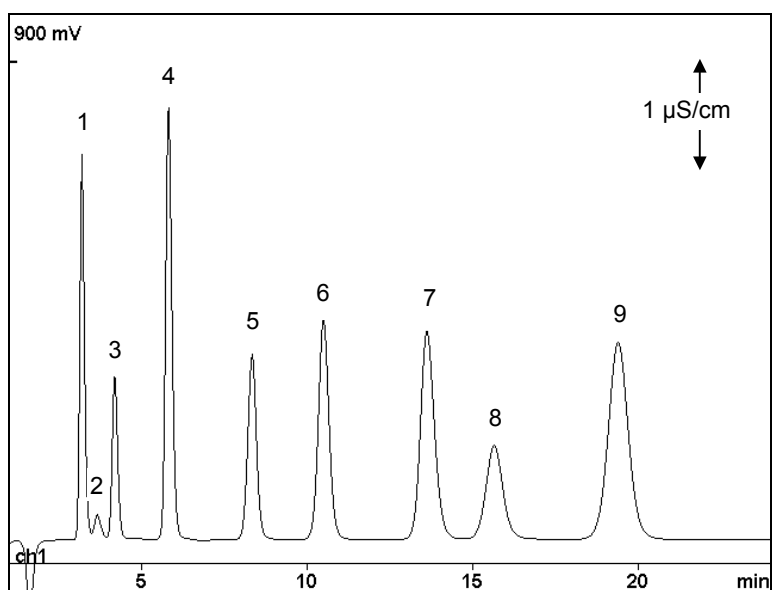
- **Composition:** 1.3 mmol/L sodium carbonate, 2.0 mmol/L sodium hydrogen carbonate (conductivity after chemical suppression approx. 14  $\mu\text{S}/\text{cm}$ )
- **Preparation:** Dissolve 275 mg sodium carbonate (anhydrous) and 336 mg sodium hydrogen carbonate in ultrapure water and then make up to 2 L with ultrapure water. Before use, degas the eluent applying vacuum.
- **Note:** Depending on the sample, organic acids can lead to interferences in the fluoride region (lactate, glycolate) and in the sulfate region (tartrate, malate, malonate).  
  
In contrast to most other anion columns the Metrosep Anion Dual 2 IC column allows a clear separation of fluoride, acetate and formate.
- **Standard:** For the preparation of the standard solutions, commercial stock solutions containing  $\beta(\text{anion}) = 1000 \text{ mg/L}$  are used.

As an alternative, the stock solutions containing  $\beta(\text{anion}) = 1000 \text{ mg/L}$  can also be prepared by dissolving the appropriate amount of a suitable salt (purity standard puriss. p.a.) in ultrapure water. The following table shows the sample weight required per liter ultrapure water:

Anion	Salt	Dry at	Sample weight [g]
Fluoride	NaF	105 °C	2.2100
Chloride	NaCl	105 °C	1.6484
Nitrite	NaNO <sub>2</sub>	105 °C	1.4998
Bromide	NaBr	105 °C	1.2877
Nitrate	NaNO <sub>3</sub>	105 °C	1.3707
Orthophosphate	KH <sub>2</sub> PO <sub>4</sub>	105 °C	1.4330
Sulfate	Na <sub>2</sub> SO <sub>4</sub>	105 °C	1.4790

To prepare the anion standard, these stock solutions are then diluted to the desired concentrations with ultrapure water.

- **Flow:** 0.8 mL/min
- **Injection volume:** 20  $\mu\text{L}$
- **Detection:** Conductivity after chemical suppression
- **Full Scale:** 5  $\mu\text{S}/\text{cm}$
- **Polarity:** +

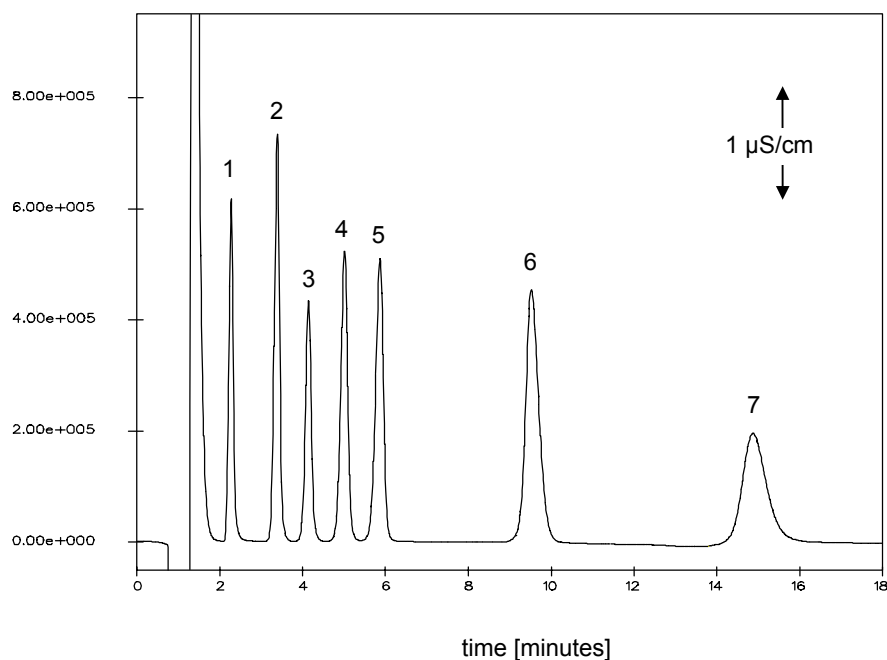


Peak no.	Retention time [min]	Ion	Concentration [mg/L]
1	3.2	Fluoride	2
2	3.6	Acetate	2
3	4.2	Formate	2
4	5.8	Chloride	5
	6.9	System peak	
5	8.3	Nitrite	5
6	10.5	Bromide	10
7	13.6	Nitrate	10
8	15.6	Orthophosphate	10
9	19.4	Sulfate	10

## 2. Ion chromatography without chemical suppression

### Phthalic acid eluent

- **Composition:** 5 mmol/L phthalic acid, 2% acetonitrile; pH = 4.6 (NaOH) (conductivity approx. 400  $\mu\text{S}/\text{cm}$ )
- **Preparation:** Dissolve 1.66 g phthalic acid in 40 mL acetonitrile with stirring, then make up to 2 L with ultrapure water and adjust the pH value to 4.6 with  $c(\text{NaOH}) = 2 \text{ mol/L}$ . Before use, microfilter the eluent (0.45  $\mu\text{m}$ ) and degas it applying vacuum.
- **Standard:** See under «1. Ion chromatography with chemical suppression». However, orthophosphate cannot be determined under these chromatographic conditions.
- **Flow:** 0.8 mL/min
- **Injection volume:** 100  $\mu\text{L}$
- **Detection:** Conductivity
- **Full Scale:** 5  $\mu\text{S}/\text{cm}$
- **Polarity:** +

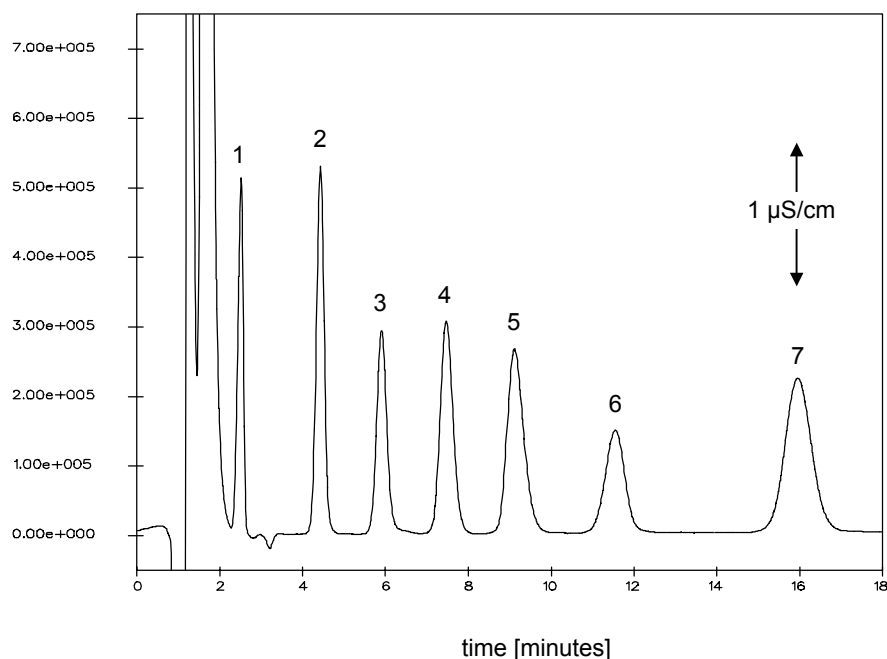


Peak no.	Retention time [min]	Ion	Concentration [mg/L]
1	2.3	Fluoride	5
2	3.4	Chloride	5
3	4.1	Nitrite	5
4	5.0	Bromide	10
5	5.9	Nitrate	10
6	9.5	Sulfate	10
7		System peak	

### Alternative eluents

#### Boric acid/gluconate eluent

- **Composition:** 5.8 mmol/L boric acid, 1.5 mmol/L sodium tetraborate, 1.5 mmol/L potassium gluconate, 5% glycerol, 4% acetonitrile, 3% 1-butanol (conductivity approx. 350  $\mu\text{S}/\text{cm}$ )
- **Preparation:** Dissolve 0.72 g boric acid, 1.15 g sodium tetraborate decahydrate and 0.70 g potassium gluconate in ultrapure water, add 100 mL glycerol, 80 mL acetonitrile and 60 mL 1-butanol, mix thoroughly and then make up to 2 L with ultrapure water. Before use, microfilter the eluent (0.45  $\mu\text{m}$ ) and degas it applying vacuum.
- **Note:** Injections of drinking water are possible only if  $\text{H}^+$  ion-exchanger cartridges (6.1012.110) are used as calcium gluconate interferes with the determination.
- **Flow:** 0.8 mL/min
- **Injection volume:** 100  $\mu\text{L}$
- **Detection:** Conductivity
- **Full Scale:** 5  $\mu\text{S}/\text{cm}$
- **Polarity:** +



Peak no.	Retention time [min]	Ion	Concentration [mg/L]
1	2.5	Fluoride	5
2	4.4	Chloride	5
3	5.9	Nitrite	5
4	7.5	Bromide	10
5	9.1	Nitrate	10
6	11.5	Orthophosphate	10
7	15.9	Sulfate	10

## Appendix 1

### Separation columns for ion chromatography

#### IC anion columns

Designation	Order no.	Chem. suppr. no	yes	Support material	pH range	Comments
Hamilton PRP-X100 IC anion column	6.1005.000	●		polystyrene/divinylbenzene	1 ... 13	rugged separation column for routine analysis; less well suited for fluoride determination
Super-Sep IC anion column	6.1009.000	●		polymethacrylate	1 ... 13	very good separation efficiency
Metrosep Anion Dual 1 IC glass cartridge	6.1006.020	●	●	hydroxylmethacrylate	2 ... 12	favorable price/performance ratio; for routine analysis; separation of fluoride, acetate, formate; not suitable for low fluoride concentrations with acidic eluents or for low nitrite concentrations with chemical suppression
Metrosep Anion Dual 2 IC column	6.1006.100	●	●	polymethacrylate	1 ... 12	better separation efficiency than 6.1006.020 IC column; suitable for low nitrite concentrations
Phenomenex Star Ion A300 IC anion column	6.1005.100		●	polystyrene/divinylbenzene	1 ... 12	short analysis times; carbonate interferes with chloride

#### IC cation columns

Designation	Order no.	Support material	pH range	Comments
Vydac 400 IC cation column	6.1008.000	silica gel	2 ... 7	for the separation of monovalent cations
Nucleosil 5SA IC cation column	6.1007.000	spherical silica gel	2 ... 7	for the separation of divalent cations
Metrosep Cation 1-2 IC column	6.1010.000	spherical silica gel	2 ... 7	suitable for the separation of monovalent and divalent cations as well as for amines

#### IC exclusion columns

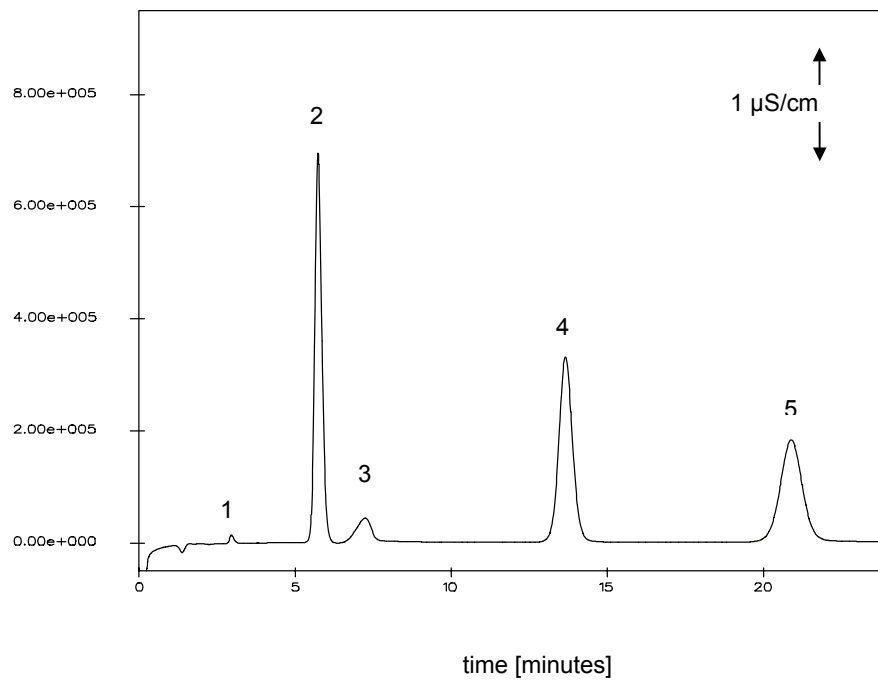
Designation	Order no.	Support material	pH range	Comments
Hamilton PRP-X300 IC exclusion column	6.1005.030	polystyrene/divinylbenzene	1 ... 13	determination of organic acids; sensitive formate determination

## Appendix 2

### 1. Practical example with chemical suppression

#### Drinking water

- Eluent: 1.3 mmol/L sodium carbonate, 2.0 mmol/L sodium hydrogen carbonate (conductivity after chemical suppression approx. 14  $\mu\text{S}/\text{cm}$ )
- Flow: 0.8 mL/min
- Injection volume: 20  $\mu\text{L}$
- Detection: Conductivity after chemical suppression
- Full Scale: 5  $\mu\text{S}/\text{cm}$
- Polarity: +



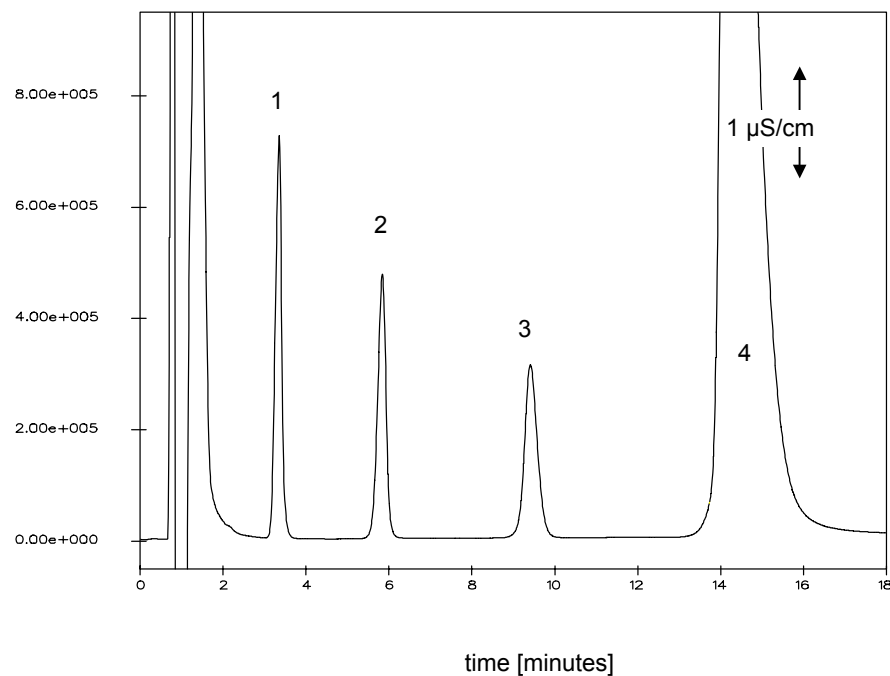
Peak no.	Retention time [min]	Ion	Concentration [mg/L]
1	3.0	Fluoride	0.05
2	5.7	Chloride	5.7
3		System peak	
4	13.6	Nitrate	9.6
5	20.9	Sulfate	6.9



## 2. Practical example without chemical suppression

### Drinking water

- Eluent: 5 mmol/L phthalic acid, 2% acetonitrile; pH = 4.6 (NaOH) (conductivity approx. 400  $\mu\text{S}/\text{cm}$ )
- Flow: 0.8 mL/min
- Injection volume: 100  $\mu\text{L}$
- Detection: Conductivity
- Full Scale: 5  $\mu\text{S}/\text{cm}$
- Polarity: +



Peak no.	Retention time [min]	Ion	Concentration [mg/L]
1	3.3	Chloride	6.0
2	5.8	Nitrate	10.0
3	9.4	Sulfate	6.6
4		System peak	