5. Detection Methods

5.6 Ion Chromatography

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5.6.1 What is ion chromatography?

Shortened taken from Schneider et al. (2016)
Chromatography is the general term for physical-chemical separation processes, which are based on the distribution of a substance between a mobile and a stationary phase. In ion chromatography, charged particles are being separated. It is based on three different separation mechanisms: ion exchange, ion pair production and ion exclusion. The ion exchange chromatography is simplified referred to as ion chromatography (IC); the ion pair chromatography (IPC) and the ion exclusion chromatography (IEC) are considered as more specific applications. Depending on the column, anions and cations may be separated in the IC.

An IC consists of a storage vessel with the eluents, a pump, the injector for the samples, the separation column, the suppressor system, the detector, the computer for data processing and a waste container (Fig. 5.6-1).

Structure
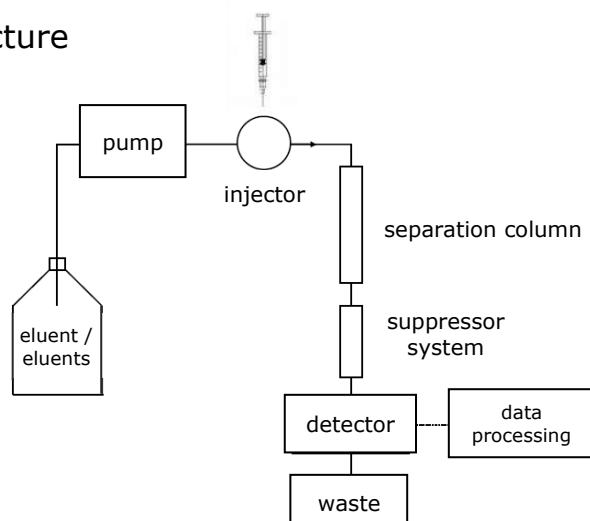
**Fig. 5.6-1** General structure of an IC, taken from Warnke (2006), p. 2

Shortened taken from Schneider et al. (2016)

The solid phase in the separation column normally consists of a polymer resin. Quaternary ammonium salt compounds, which are charged with the eluent (e.g. $NaHCO_3$ in the mobile phase), have been established for the separation of anions. The charging of the separation column before the injection of the sample is crucial, since the exchange of the ions from the sample are proceeded by stoichiometric amounts of the respective ions. In the course of the chromatography process the ions of the sample (e.g. Br^-, Cl^-) displace the counterion of the eluent (e.g. HCO_3^-). By the further adding of the eluent the ions of the sample are being replaced until they reach the detector and get detected. This is a reversible equilibrium process. As a result of the various affinity of the ions for the stationary phase a separation comes about. The constant, which characterizes the equilibrium process, is referred to as partition coefficient K and is defined as relation of the concentration of a substance A in the stationary and mobile phase.

$$K = \frac{[A^-]_{stationary}}{[A^-]_{mobile}}$$

Therefore, substances with a high partition coefficient K are held back stronger than those with a small K. The partition coefficient K is, on the one hand, proportional to the ionic charge (so for an anion Ax-: $K(A^{3-}) > K(A^{2-}) > K(A^-)$) and, on the other hand, proportional to 1 / ionic size (in solvated condition (dissolved ion + associated shell made of ionic solvent)).

Due to the different retention time of the anions at the column the anions are being released with time lag and thus detected (Fig. 5.6-2).
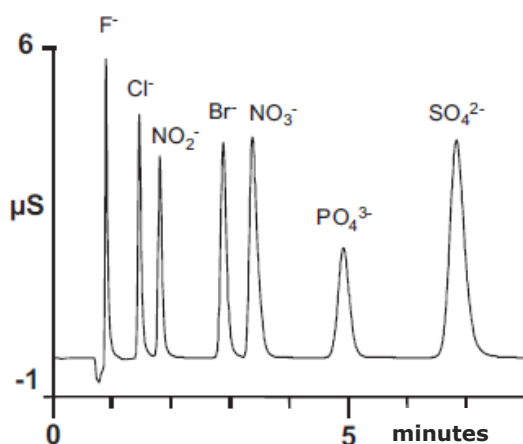
Fig. 5.6-2 Example of a chromatogram of a latex-anion exchanger, type Dionex IonPac AS4A-SC, taken from Jensen (2013), p. 13

With the appropriate sample preparation, the columns and device settings different phosphates can also be detected. In cheese for example, it was differentiated between open-chained condensed phosphates (P1 to P7) and cyclic phosphates (e.g. trimetaphosphate; P3m) (Jensen 2013, Fig. 5.6-3).
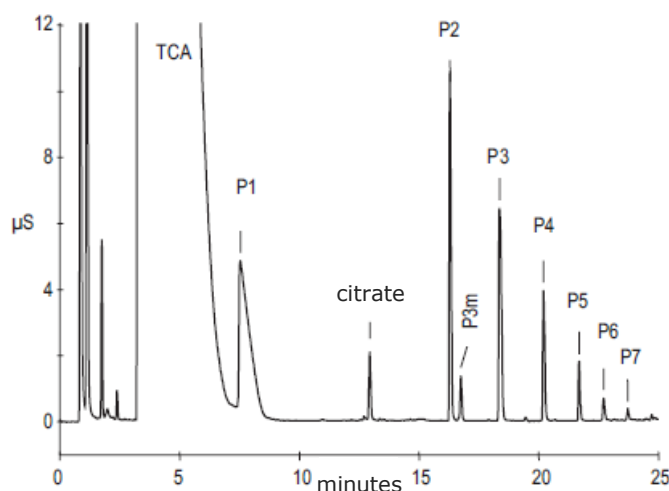

Fig. 5.6-3 Detection of different phosphates, taken from Jensen (2013), p. 124

5.6.2 Ion chromatography in the working group Soil Physics

In the working group Soil Physics (AUF, University of Rostock) a new IC, the 930 Compact IC Flex from Metrohm, is available since summer 2018. This instrument consists of two Compact IC Flex with column oven and Degasser (each for anions and cations), with separate auto samplers. That means that anions, cations and polar substances can be determined with and without sequential suppression. The background conductivity is reduced to a minimum by the sequential suppression (chemical suppressor and CO_2-suppressor), that means that especially anions can be detected better. Currently, the instrument has two columns Metrosep C4 - 150 (Metrohm 2015, p. 154) and Metrosep A Supp 5 - 150 (Metrohm 2015, p. 64), both including the precolumns. The Metrosep C4 – 150 is a universal standard column for analysis of cations of alkaline and alkaline earth metals (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, NH^{4+}) in aqueous solutions. The Metrosep A Supp 5 – 150 is an anions column, which can separate F^-, Cl^-, Br^-, I^-, ClO_2^-, ClO_3^-, ClO_4^-, BrO_3^-, und CrO_4^{2-} and phosphate ions (PO_4^{3-}) (Fig. 5.6-4). The instrument contains conductivity detectors for anions and cations and an UV/VIS detector for anions (to suppress high Cl concentrations). Additionally, for high ion concentrations an inline-dilution and inline-dialysis for anions is available.

chromatograms
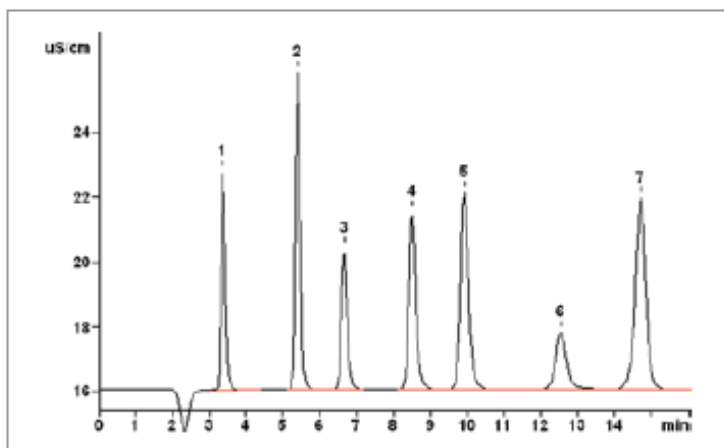
carbonate eluent, standard   conc. (mg/L)

1	fluoride	2.00	5	nitrate	10.00
2	chloride	5.00	6	phosphate	10.00
3	nitrite	5.00	7	sulfate	10.00
4	bromide	10.00			

Fig. 5.6-4 Detection of anions by using the column Metrosep A Supp 5 – 150, taken from Metrohm (2015), p. 65

5.6.3 Phosphate determination by ion chromatography – sample preparation and measurement in the working group Soil Physics

In the working group Soil Physics mainly water samples from a drain of an arable field are analysed currently. The following sample matrices can be analysed by this IC: fresh water, seawater, aqueous solutions of extracts from solid samples (has not been tested so far). Currently, samples of moor water of the projects WETSCAPES und BALTIC TRANSCOAST are analysed.

Sample preparation:
- ▶ Filtration of water samples with folded filters is only necessary if too much solids or larger particles are in the sample
- ▶ Setting of pH of the sample is only necessary if the pH value is outside the pH range of the column (A Supp 5-150: 3 bis 12); for this column that means pH values < 3
- ▶ Conductivity of the sample should be measured before to get an estimation of the concentration of anions in the sample

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► If enough sample is available, a minimum of 8 ml should be filled in the IC vials and placed in the fridge (if necessary) until measurement
► If there is too little sample material in the vial, it is diluted automatically in the instrument.

Measurement:

► It is calibrated once for a lot of measurements. The calibration is valid as longs as control standards do not exceed defined deviation. In this case the calibration has to be done again.
► Currently, the calibration range is between 0.2 bis 200 mg phosphate l^{-1} in 2 measurement ranges (0.2…20 mg l^{-1} and 20…200 mg l^{-1}). The samples are aromatically assigned to the range.

5.6.4 Limit of detection and quantification for phosphate in ion chromatography

The limit of detection is in the µg per litre range and could be lowered to ng per litre by previous enrichment process (Jensen 2013, p. 113). Until now, it has been calibrated to 0.2 mg phosphate per litre in the working group Soil Physics. Since the instrument is new, limits of detection and quantification are still in work for specific matrices. According to preliminary results, the limit of detection seems to be in the range of 5 µg phosphate per litre.

References

Jensen, D (2013) Grundlagen der Ionenchromatographie – modernste Trenntechnik. Thermo Fisher Scientific Inc. ISBN 978-3-00-044477-7, last accessed 28.05.2018

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Warnke, J (2006) Seminar zum Praktikum Analytische Chemie – Teil 2 Ionenchromatographie, AAS, Coulometrie, Aufschlussverfahren. University of Mainz, Institute of Inorganic and Analytical Chemistry, last accessed 29.05.2018

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