

Ion Chromatography

Theoretical basics

Chromatography is a physical-chemical procedure for material separation used for analysing purposes and for processing. In practice, it is often used for analysing water and waste-water samples. There are anionic and cationic chromatographs. In the BfS laboratory an ion chromatograph with an anion column is exclusively used for analysing purposes (see Figs. 1 - 4). After separation the individual substances are detected qualitatively and quantitatively using differing methods. Sample solutions must always be filtered through a 0.45 µm membrane filter before inducing them into the chromatograph (ISO Directive 2). In the chromatograph the sample solution will then seep through finely dispersed inorganic or organic material. Depending on their mobility the different components of the sample solution will move at different velocities and will thus separate. The difference in velocity is due to differing retention periods in the stationary phase, the flow rate of the mobile phase is constant. Chromatographic separation will be realised between two extreme cases:

- No interactions with the stationary phases, i.e. the components of the sample solution pass through the column at the same velocity as the fluid.
- Very strong interactions with the stationary phases, leading to a complete fixation and no transport.

All other evaluable chromatographic separations will be effected between these extremes.

The retention time of the components will be influenced by the size and charge of the sample ions as well as the pH value of the mobile phase. The separated ions will be detected by conductivity measurements.

For identifying the anions in the sample solution the output chromatogram has to be compared with standard solutions. Retention times (up to several 10 minutes) should agree up to the first decimal place in order to undoubtedly identify a peak. When comparing with literature values deviations of +/- 10% are tolerable depending on the used column, the eluent, and the flow rate.



Fig. 1: Anionic chromatograph composed of IC detector unit, IC separation center, IC pump unit and IC pump



Fig. 2: Column and suppressor unit of the anionic chromatograph



Fig. 3: Metrosep A Supp 4 column for the anionic chromatograph



Fig. 4: Compact autosampler

Establishing concentrates and eluents

All solutions are prepared with double deionized water (see Fig. 5; **attention - no distilled tap water may be used!**) and filtered by ultrafiltration which will take about 1 hour to 2 hours. Afterwards the eluent will be put into an ultrasonic bath for degassing. The ultrasonic bath should be limited to 20 minutes, thus avoiding an undesirable heat generation.

Before connecting the flask with the water suction pump the diaphragm of the connecting device has to be covered with a membrane filter (best accomplished using forceps) and then the feeding hopper has to be put on top of it and secured with the provided clamp. To ensure the quality of the measurements, the eluent must be exchanged every second week.



Fig. 5: Equipment for double deionized water

Establishing the anion multi-element-standard-solution

For measuring ions in the ion chromatograph usually only solutions with low concentrations are used (1 ppm – 10 ppm).

To calibrate the chromatography system at least 3-5 standard solutions of seven anions in different concentrations are used.

These anions are F^- , Cl^- , Br^- , SO_4^{2-} , NO_2^- , NO_3^- and PO_4^{3-} in concentrations ranging between 0.5 ppm and 10 ppm. They were diluted from a Roth anion-multi-element-standard solution (Fig. 6).

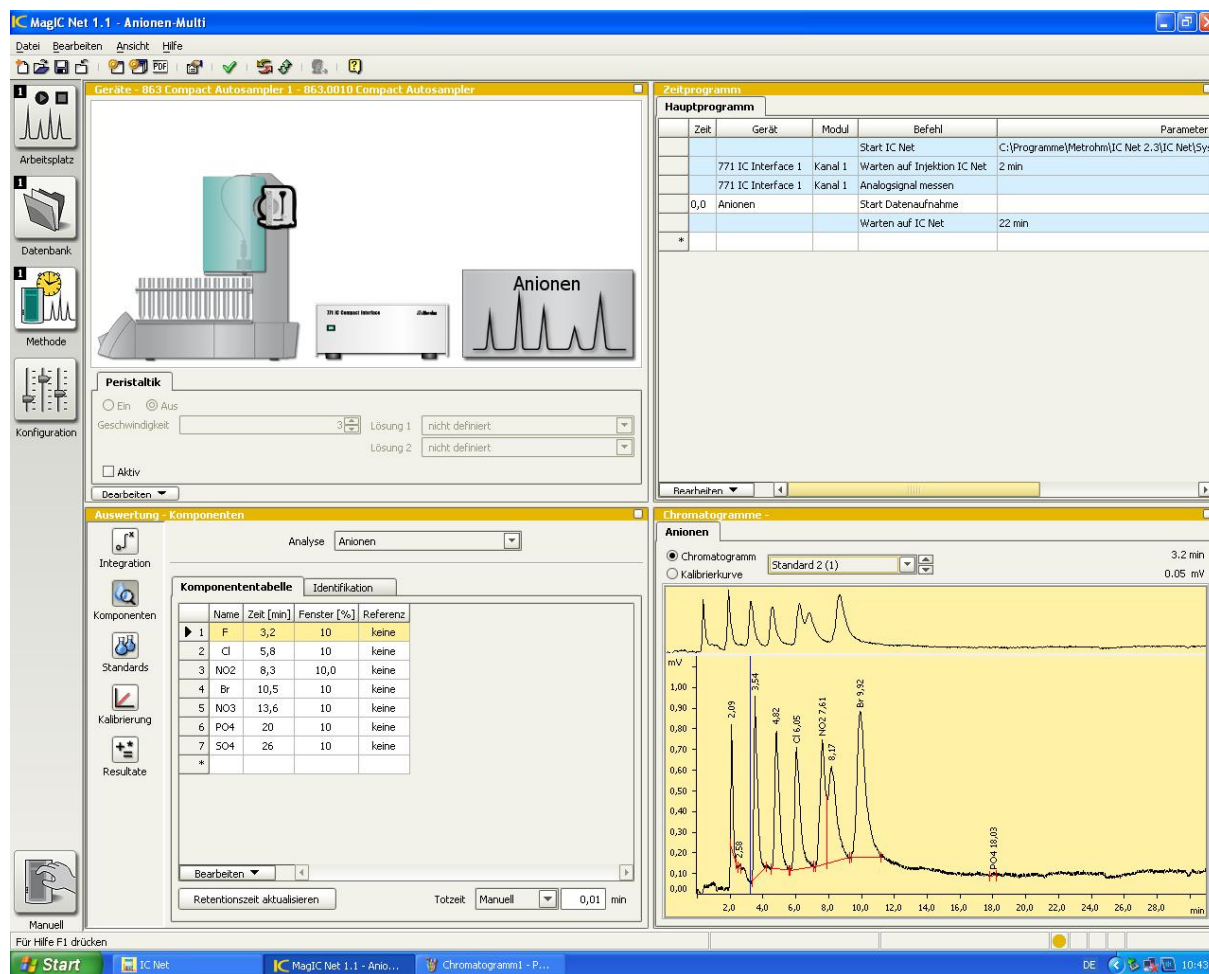


Fig. 6: Working window of the “MagIC Net” software showing an anion multi-element-standard

Preparing the measurement

Prior to sample measurements, several equilibration runs should be performed to warm up the chromatography system, depending on the age of the eluent.

If the base line of the measurement system shows no fluctuations, the actual measurement program (Anion-Multi) can be started (Fig. 7).

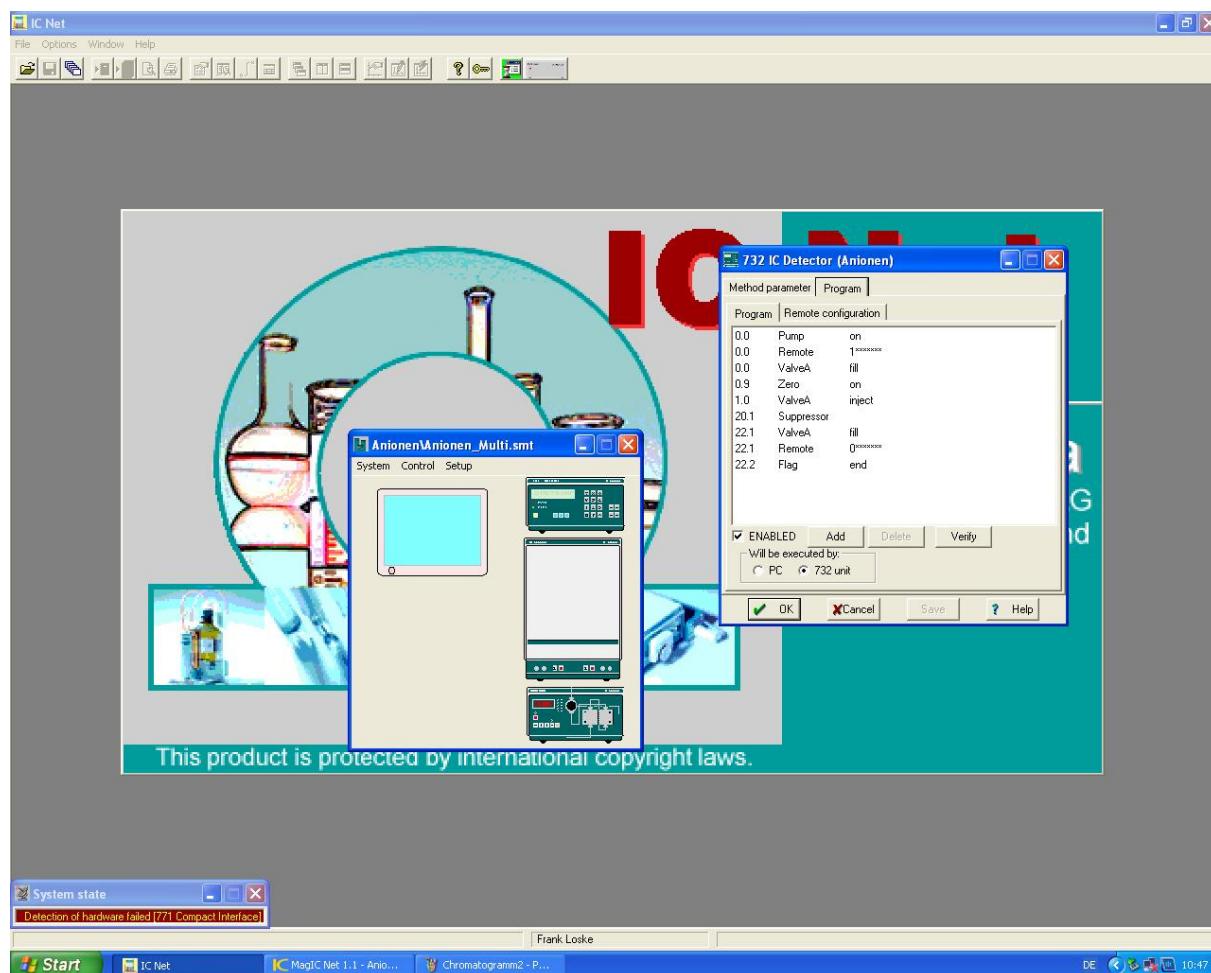


Fig. 7: Measurement programs are started via the "IC Net" software

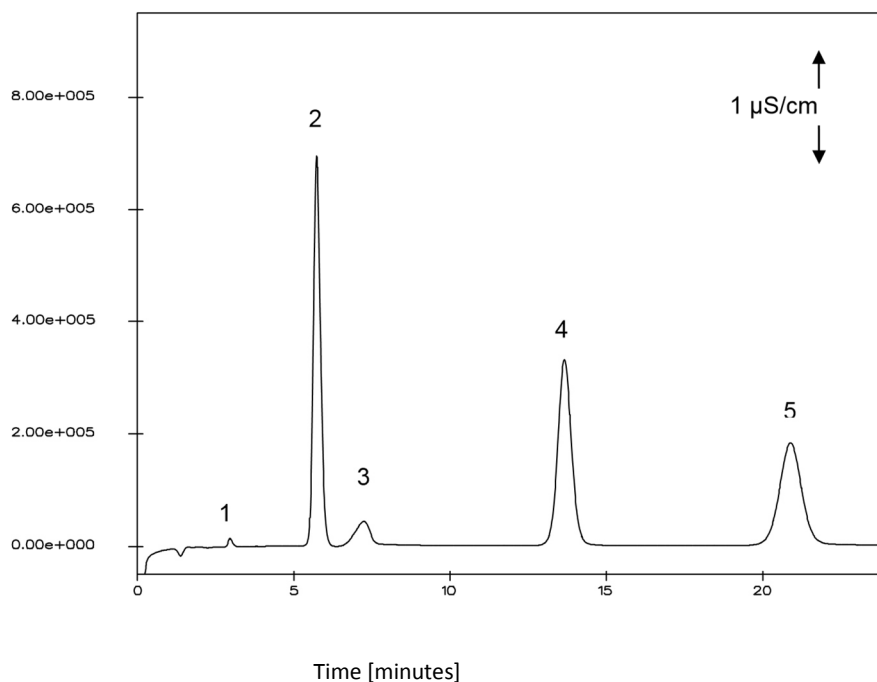
Applications with ion chromatography

Ion chromatography is used by BfS to analyze iodine in drinking water and to determine contaminations with anions and their concentration in aqueous solutions, e.g. condensate samples and saline solutions of the Asse mine (operated by BfS since 2009). It is also applied for the analysis of building materials arising from dismantling nuclear installations. It can also be used to determine the total loss factor in nuclear installations.

Fig. 8 shows a sample of drinking water with added iodine standard solution. For the detection of iodine in water this method can be used concurrently with a radiochemical analysis, thus determining even traces of long-lived iodine isotopes such as I-129.

Drinking water with added iodine standard solution

- Eluent: 1.8 mmol/L sodium carbonate, 1.6 mmol/L sodium hydrogen carbonate (conductivity after chemical suppression about 14 $\mu\text{S}/\text{cm}$)
- Flow: 0.8 mL/min
- Injection Volume: 20 μL
- Detection: Conductivity after chemical suppression
- Full Scale: 5 $\mu\text{S}/\text{cm}$



Peak Nr.	Retention time [min]	Ion	Concentration [mg/L]
1	3.0	Fluoride	0.05
2	5.7	Chloride	5.7
3	6.5	Nitrate	2.5
4	13.6	Sulfate	9.6
5	20.9	Iodine	6.9

Fig. 8: Example of a drinking water sample with added iodine standard solution

Problems encountered and troubleshooting

The main problem encountered when analyzing highly saline solutions is the overloading of the analytical column mainly with chloride. This problem can be resolved by highly diluting the sample, which in turn impedes the detection of other anions, or by purchasing a special analysis column for highly saline solutions.

Another problem is the outdated technique of chemical suppression. The suppressor used by BfS must be continuously regenerated with sulfuric acid. Recent suppressors are regenerated by the electrolysis of water thus saving chemicals. Due to the age of the ion chromatograph, replacement parts are partially no longer available and the service technicians are not trained for this equipment.