Application News

No. SCA-190-052

High Performance Liquid Chromatography

Ion-Chromatographic Determination of Seven Common Anions in Drinking and Surface Water according to the ISO 10304-1:2007 Standard

User Benefits

◆ Sensitive and reliable analysis of seven common anions in water
◆ Analysis of drinking water as well as surface water
◆ Optional UV detection for selective determination of nitrite

▪ **Introduction**

On 16 December 2020, the European Parliament formally adopted revised Drinking Water Directive[1]. The directive was initiated by the first-ever successful European citizens` initiative Right2Water[2] with the goals to improve the quality of drinking water and to guarantee safer access to water for all Europeans. It includes, i.a., specification of inorganic ions in drinking water.

The determination of seven common anions, namely fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate by ion chromatography (IC) in water is described in the ISO 10304-1:2007 standard. The method is based on the suppressed conductivity detection. The UV detection is not necessary, but it is suggested for more sensitive analysis of nitrite, bromide and nitrate or by interferences of the anions with matrix by use of conductivity detection.

In this article, a quantitative analysis of seven common inorganic anions in various types of water was performed according to the ISO 10304-1:2007 standard, using an HIC-ESP which is a new Shimadzu IC system equipped with an electrodialysis type suppressor (see Fig. 1), placed in the non-heated area of the column oven.

Figure 1: HIC-ESP Ion Chromatograph

▪ **Experimental**

The ion chromatograph applied for this article was a modular Shimadzu LC system equipped with a system controller CBM-40, an eluent degasser DGU-405, an inert eluent delivery pump LC-20Ai, an inert autosampler SIL-20A, a column oven CTO-40S and a conductivity detector CDD-10Avp. For optional detection, a UV detector SPD-40 with the inert cell was connected. The control of the instrument and data processing was performed by Shimadzu LabSolutions chromatography data system software. The analytical conditions are shown in Table 1.

Table 1: Analytical conditions

LC system	HIC-ESP Ion Chromatograph
Column	Shim-pack IC-SA2 (250 mm x 4.0 mm I.D., 9 µm; P/N 228-38983-91)
Guard column	Shim-pack IC-SA2 (G) (10 mm x 4.6 mm I.D., 9 µm; P/N 228-38983-92)
Column temperature	25 ºC
Eluent	1.8 mmol/L sodium carbonate / 1.7 mmol/L sodium bicarbonate
Flow rate	1 mL/min (isocratic)
Injection volume	20 µL
Rinse solution	DI water
Suppressor	ICDS-40A (P/N 228-74006-41)
Suppression mode	recovery (self-regenerating)
Detection	conductivity (28 ºC cell temperature)
Optional detection	UV (210 nm, inert cell)

Materials
The ultrapure water (ASTM Type 1) for preparation of the eluent and dilution of standards was prepared by arium® pro water purification system from Sartorius. Ion Chromatography Standards (1000 mg/L) of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate were purchased from Sigma Aldrich. Sodium carbonate (≥ 99.8 %) and sodium bicarbonate (≥ 99.7 %) for preparation of the eluent were purchased from Sigma Aldrich and Honeywell Fluka, respectively.

Sample collection and preparation

The samples were stored after collection in polyethylene containers at +4 ºC before analysis. For the analysis, the samples were filtered through 0.45 µm PET syringe filters. The dilution of samples 1/40 (v/v) was performed with DI water. The samples were placed in 1.5 mL PP screw vials (P/N 961-10020-16) and closed with UltraClean PP screw caps (P/N 961-10030-25) before the injection to IC.

Eluent preparation

For preparation of 100-fold stock solution: sodium carbonate (9.54 g) and sodium bicarbonate (7.14 g) were dissolved in a glass bottle with 500 mL DI water. For preparation of eluent: 20 mL of the stock solution were diluted in a glass bottle to 2 L with DI water.

- **Results and Discussion**

Figure 2 shows an overlay of six chromatograms presenting the separation of seven common anions. Very low % RSD for retention time (≤ 0.040 %) and peak area (≤ 0.45 %) for all anions demonstrate high precision of the analysis system as shown in Table 2. The new low-void-volume ICDS-40A suppressor reduces peak dispersion improving the separation of fluoride from the water dip peak. The requirement of the ISO standard for the resolution R (1.3) calculated according to US Pharmacopeia (USP) was satisfied.
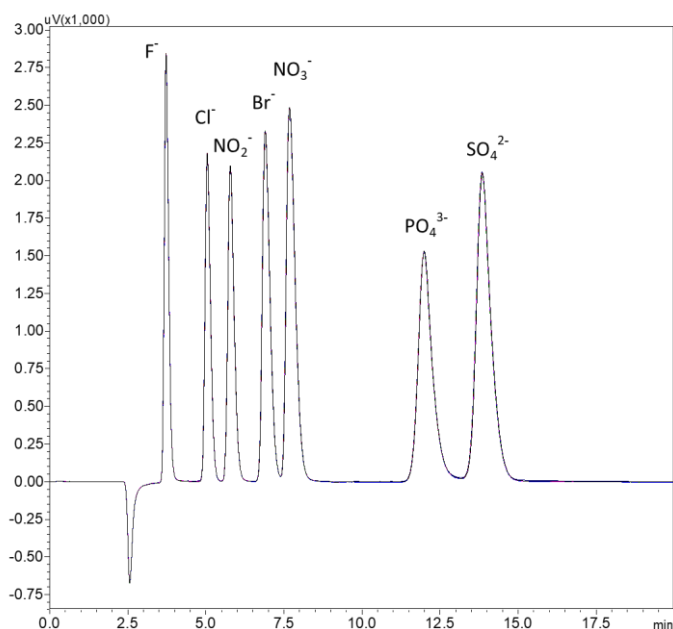

Figure 2: Separation of seven common anions (fluoride: 2 mg/L, chloride: 3 mg/L, nitrite: 5 mg/L, phosphate 20 mg/L, bromate, nitrate and sulfate: 10 mg/L

Table 2: % RSD (n=6) of retention time and peak area and resolution R

Compound	% RSD, t_R	% RSD, area	R
Fluoride	<0.010	0.45	--
Chloride	<0.010	0.12	4.5
Nitrite	0.035	0.12	2.1
Bromide	0.040	0.053	2.7
Nitrate	0.036	0.060	1.6
Phosphate	0.034	0.25	3.1
Sulfate	0.035	0.085	2.3

Linearity and signal to noise ratio

Figure 3 shows calibration curves of ions determined with external standard solutions. The working concentration range used by conductivity detection was from 0.1 to 5 mg/L with exception of bromide and nitrite measured from 0.05 to 5 mg/L. Due to higher sensitivity of nitrite detected by UV at 210 nm, the lowest concentration limit was lowered to 0.025 mg/L.
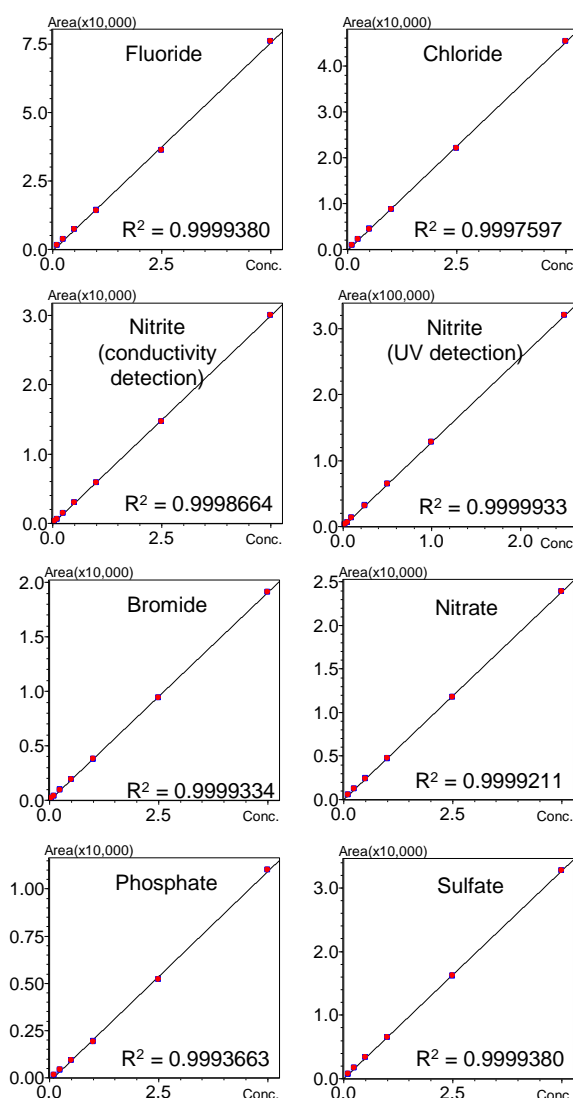

Figure 3: Calibration curves of analysed anions detected by suppressed conductivity detection and nitrite detected by UV detection (210 nm)

As shown in Table 3, the coefficient of determination R^2 was ≥ 0.9993 for all anions.

Table 3: Concentration of external standard solutions and related coefficients of determination

Compound	Concentration of external standards [mg/L]	Coefficient of determination R^2
Fluoride	0.1, 0.25, 0.5, 1, 2.5, 5	0.9999380
Chloride	0.1, 0.25, 0.5, 1, 2.5, 5	0.9997597
Nitrite (conductivity)	0.050, 0.1, 0.25, 0.5, 1, 2.5, 5	0.9998664
Nitrite (UV, 210 nm)	0.025, 0.050, 0.1, 0.25, 0.5, 1, 2.5	0.9999933
Bromide	0.050, 0.1, 0.25, 0.5, 1, 2.5, 5	0.9999334
Nitrate	0.1, 0.25, 0.5, 1, 2.5, 5	0.9999211
Phosphate	0.1, 0.25, 0.5, 1, 2.5, 5	0.9993663
Sulfate	0.1, 0.25, 0.5, 1, 2.5, 5	0.9999380

The signal to noise ratio (S/N) was calculated applying ASTM method for noise calculation in the range of 17-20 min for a 0.025 mg/L standard solution containing all seven analyzed anions. As expected, fluoride and chloride show the highest S/N ratio by using conductivity detection (Tab. 4). The S/N ratio for nitrite and nitrate is improved using UV detection at 210 nm.

Table 4: Concentration of external standard solutions and related coefficients of determination

Compound	S/N ratio (0.025 mg/L), conductivity detection	S/N ratio (0.025 mg/L), UV detection (210 nm)
Fluoride	68	--
Chloride	46	--
Nitrite	22	31
Bromide	12	7.8
Nitrate	13	28
Phosphate	3.5	--
Sulfate	14	--

Sample analysis
Figures 4 and 5 show analysis of drinking water and surface water (from two lake and one rivers near Duisburg), respectively. The concentration of analyzed anions varied in samples, but all of them showed high contrast in concentration between phosphate, sulfate and partly nitrate to other anions. Therefore, the samples were measured undiluted and diluted (1/40, v/v) to quantify all target compounds in the working concentration range shown in Table 3.

The content of highly concentrated phosphate, sulfate and partly nitrate was calculated from diluted samples. The concentration of residual anions was calculated from undiluted samples. Tables 5 and 6 present concentration of the anions in analyzed drinking water and surface water, respectively.

Table 5: Concentration of anions in drinking water determined by conductivity detection.

Compound	Lab tap water [mg/L]	Dispenser water [mg/L]	Bottle water [mg/L]
Fluoride	0.12	0.12	0.42
Chloride	36	36	96
Nitrite	--	--	--
Bromide	0.082	0.080	0.22
Nitrate	12	13	--
Phosphate	0.30	0.27	0.17
Sulfate	70	70	24

Table 6: Concentration of anions in surface water determined by conductivity detection with exception of nitrite quantified by UV detection

Compound	Rheinufer promenade [mg/L]	Wambach see [mg/L]	Masuren see [mg/L]
Fluoride	0.14	0.33	0.31
Chloride	45	20	19
Nitrite (UV detection)	0.097	0.012	0.030
Bromide	0.13	0.048	0.048
Nitrate	5.7	0.15	0.60
Phosphate	--	--	--
Sulfate	50	42	43

Method accuracy was estimated by fortifying blank DI water and surface water samples with 1 ppm concentration of each standard compound. Very good recoveries were obtained from different water matrices as shown in table 7.

Table 7: % recovery in analysed surface water samples

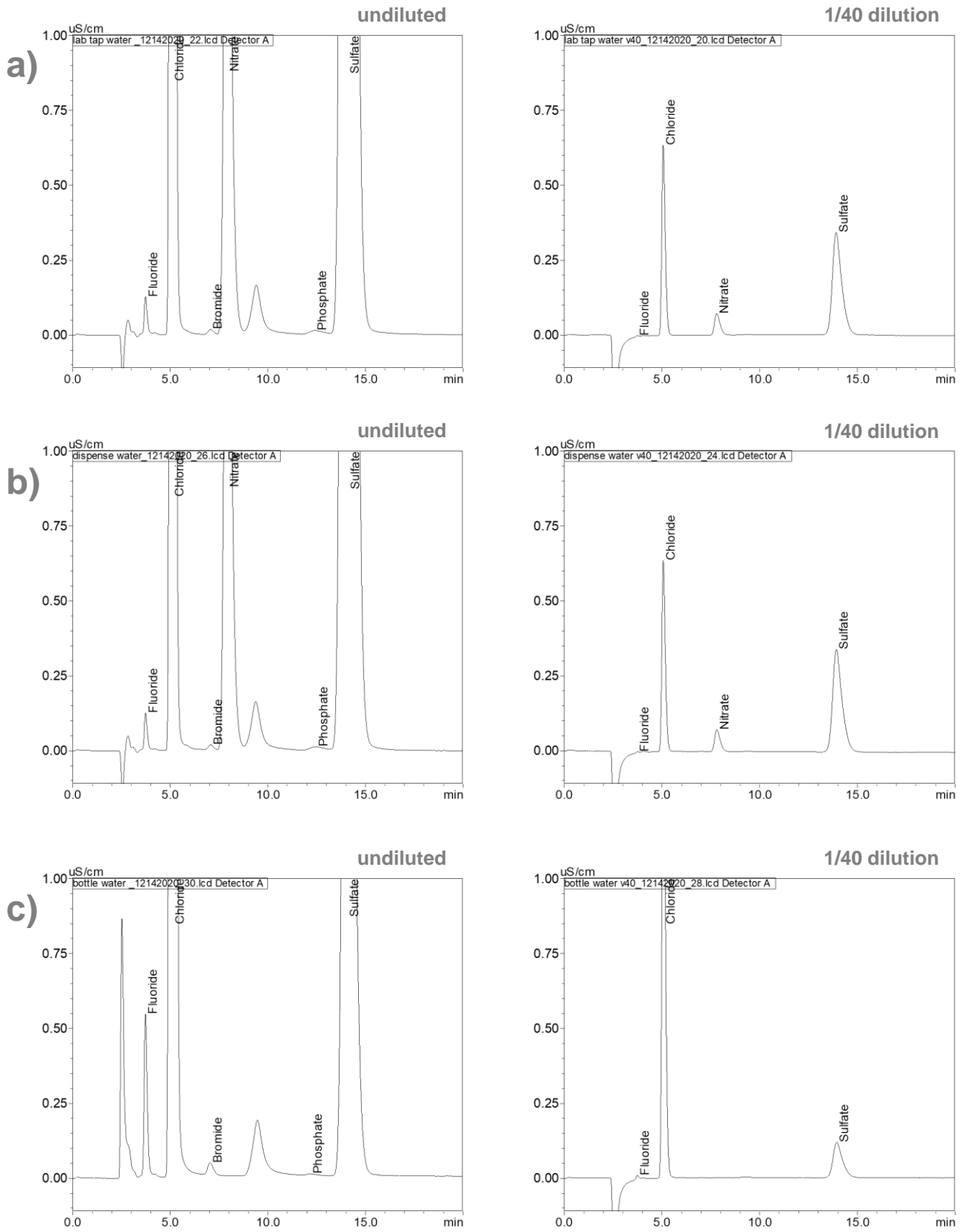| Compound	DI water [%]	Rheinufer promenade [%]	Wambach see [%]	Masuren see [%]
Fluoride	99	101	102	102
Chloride	99	100	102	102
Nitrite	98	98	99	100
Bromide	98	100	102	103
Nitrate (UV detection)	99	101	102	102
Phosphate	103	106	108	110
Sulfate	99	100	101	100

Figure 4: Analysis of drinking water using conductivity detection. Panels for undiluted and diluted 1/40 (v/v) samples: a) lab tap water, b) dispenser water, c) bottle water
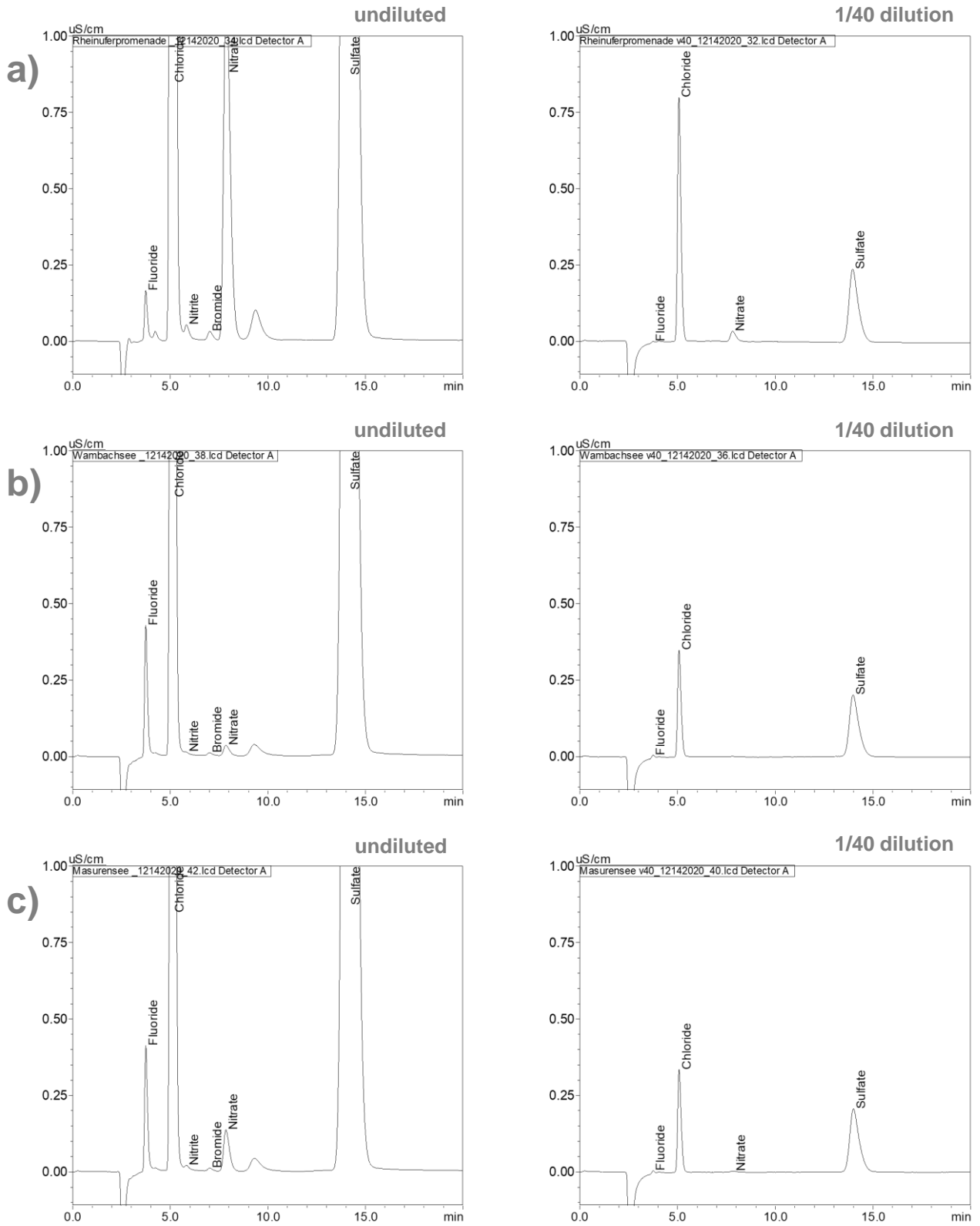
Figure 5: Analysis of surface water near Duisburg using conductivity detection. Panels for undiluted and diluted 1/40 (v/v) samples: a) Rheinuferpromenade, b) Wambachsee, c) Masurensee

Depending on chromatographic conditions and composition of sample matrix, the determination of interfering anions at extremely different concentration level could be difficult applying only conductivity detection. Optional detection could provide accurate analysis of compounds. Following to the ISO standard, the UV detection at 210 nm is recommended for determination of nitrite in such samples, including wastewater, sea water etc. The UV detector could be connected in series after the conductivity flow cell in accordance with the ISO standard. Figure 6 shows the flow diagram of the system parts used in present work.
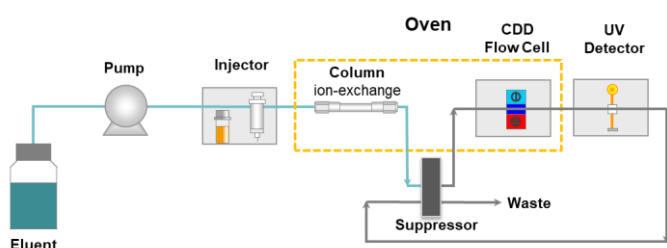

Figure 6: Flow diagram of IC system with conductivity and UV detectors connected in series in accordance to the ISO 10304-1:2007 standard

The analysis of nitrate by UV detection was demonstrated in analyzed surface water containing low-concentrated nitrite in presence of highly-concentrated chloride which elutes before nitrate (compare to Figure 5: undiluted). Figure 7 presents the analysis of a surface water applying UV detection. The concentration of nitrite in analyzed surface samples as well as recovery rate determination by UV is also shown in Tables 6 and 7, respectively. Beside nitrite also bromide and nitrate can be analyzed by UV detection.
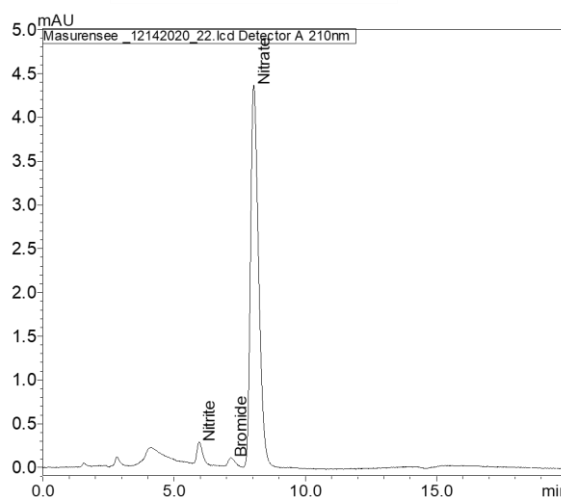

Figure 7: Analysis of an undiluted sample from Masurensee by UV detection

▪ Conclusion

The Shimadzu HIC-ESP ion chromatography system with electrolytic suppression provides sensitive and reliable analysis of seven common inorganic anions namely fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate listed in the ISO 10304-1:2007 standard in different types of water including drinking water and surface water. Optional UV detection for analysis of nitrite providing higher selectivity and sensitivity compared to conductivity detection is recommended for samples with complex matrix.

▪ References

[1]*Drinking Water*, European Commission, accessed 28 January 2021, <https://ec.europa.eu/environment/water/water-drink/index_en.html>
[2]*Rigth2Water,* European Citizens' Initiative (ECI), accessed 28 January 2021, <https://www.right2water.eu>
[3]*DIN EN ISO 10304-1:2009-07*, Beuth, accessed 6 December 2020, <https://www.beuth.de/en/standard/din-en-iso-10304-1/117316025>